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OPTIMIZATION OF RAWHIDE COLLAGEN DEFIBRILLIZATION PROCESS

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ABSTRACT

The paper features the rawhide collagen defibrillization process in the elastic leather materials manufacturing. Optimal colloid-chemical properties of semi-processed products were defined by way of using mathematical optimization of rowhide liming process. It was found that during the alkaline treatment of raw material (in the operating temperature range) the degree of defibrillation of raw material raises (in proportion to the derm collagen swelling) with increase in the ratio of process solution to the mass of raw material, and the extremum of hydrothermal stability and leather yield can be estimated. It was also shown that the degree of swelling decreases with a decreasing ratio of sodium sulphide and sodium hydrosulphide, and the leather area yield reaches the maximum value at the equal proportion of these reagents. Multicriteria optimization of rawhide liming process using the Harrington’s desirability function was carried out. The developed technology of soaking and liming was tested under production conditions. The above-mentioned low-waste technology provides elastic leather materials with a yield increase by 3.5%, which meet the industry standards requirements.

KEYWORDS

Defibrillization; Derm collagen; Rawhide; Liming; Swelling; Multicriteria optimization; Desirability function.

INTRODUCTION

The collagen is a widespread biopolymer, which is part of the animal skins, and is part of their internal organs. Collagen and collagen-derived products are widely used in different industries such as light and food industries, medicine, etc. [1, 2]. The fibrillar collagen of animal skin is 90% of the dry weight of the dermis, and under the action of chemical reagents changes the structure and properties in the process of forming the finished material. Thus, it is important to remove unstructured components of the dermis, that is various cells [3], surrounded by plasma membranes consisting of lipids up to 45% of their mass and more than 50% of proteins that mainly have globular structure. In the processes of soaking, liming, alkaline treatment (unhairing), reliming, enzyme treatment (softening) and acid-salt treatment (pickling) unstructured components are replaced by technological solutions. It is especially important to investigate such a substitution in the case of soaking and liming processes, in which soluble proteins, mucopolysaccharides, some lipid inclusions, and preservative chemicals are removed. Conversely, the derm collagen restores the water balance of raw materials and under the action of alkaline reagents the mass of raw materials increases, collagen is defibrillazed. Further, amide intermolecular bonds are destroyed with the formation of ionized amine and carboxyl side chain groups that increases the chemical activity of collagen for the efficient subsequent technological processes’ implementation.

Leather and fur materials quality depends on the rawhide type and processing technique. Given the rawhide quality [4], the multi-stage colloid-chemical and mechanical working operations, there is a necessity for effective use of a wide range of chemical reagents at all technological stages and especially in soaking and liming processes of collagen-derived raw materials. However, considering the significant cost of environmentally hazardous reagents at soaking and liming stages [5], it is reasonably required to minimize reagent costs with the most efficient use of raw materials.

Due to the amphoteric nature, the derm collagen changes its properties in the technological processes depending on the pH of working solution [6]. According to the impact on the swelling of the derm

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collagen spatial structure, the alkaline reagents form a row KOH> NaOH> $Ba(OH)_2$> $Ca(OH)_2$. However, according to the chemical interaction degree with collagen, chemical reagents can be arranged in the following sequence: $Ca(OH)_2$> $Ba(OH)_2$> KOH> NaOH> Na_2S> NH_4OH, and according to the unstructured components removal degree, the above mentioned reagents have the reverse sequence. It should be noted that strong base solutions can cause significant collagen destruction. In particular, a 10% NaOH solution at a temperature of 18-20°C causes the collagen destruction, which reaches 24%, in two days [7]. Moreover, even in weak alkali solutions, telopeptides with amino acid residues of tyrosine are cleaved, which indicates the collagen destruction. In contrast to strong base, the use of calcium hydroxide hydrolysis collagen destruction is significantly reduced. Thus, in a saturated 0.13% calcium hydroxide solution, the collagen destruction is only 12% upon contact of the components for 120 days [8]. Notably, in an alkaline condition, there is ammonia cleavage from aspartic and glutamic acid residues observed, as well as ionic and hydrogen bonds rupture, destruction of cross-molecular and intra-molecular bonds, that leads to the release of blocked amino, carboxyl and hydro groups. In addition, the formation of free amino and carboxyl groups can occur due to the covalent bonds' breakdown in the collagen molecule main chains, along with the removal of guanidine group of arginine. The course of these side reactions is much slower than the interaction of alkalis with carboxyl groups in the side radicals of collagen macromolecules.

The authors of [9] assumed that using saturated solutions of calcium hydroxide only provides a more pronounced effect of fibrillar separation of the derm collagen structure if alkali solutions with a significant solids content (4.0-4.5% of calcium hydroxide by rawhide weight) are used. This effect can be explained by action of the dispersed calcium hydroxide particles on the collagen structure and other proteins. It can be considered that smaller amount of dispersed alkali in liming processes [10] maintains not only to obtain high-quality leather, but also reduces wastewater pollution.

The saline agents adding in the alkaline working solution reduce the hydrolyzing effect on collagen, while swelling decreases it, depending on the type of salt alkaline-salt treatment [7]. Reich [11] showed that the active groups of collagen also adsorb neutral salts while changing its swelling degree. There are three groups of salts according to the watering degree. Strong swelling of the derm collagen is caused by rhodanates, iodides, chlorates, salts of barium, calcium, magnesium and lithium, which is expressed in a significant fibril thickening and reducing, and decreasing their denaturation temperature. The impact of the second group salts is determined by their concentration in solution: low concentrations of sodium chloride cause significant swelling whereas large concentrations cause collagen dehydration. Salts of the third group - sulfates, thiosulfates and carbonates have a dehydrating ability and do not show increased adsorption.

Over sodium hydroxide, the calcium hydroxide solubility decreases and the working solution reduces the chemical activity. This also occurs when calcium hydroxide is used in combination with one of the exacerbating salts: potassium or sodium, which form insoluble calcium salts. When insoluble salt ($CaCO_3$, CaC_2O_4) sets up, there is a direct dependence between the salt concentration and the liming solution properties. If salt is sparingly soluble, for example $CaSO_4$, CaS_2O_3 or $Ca(C_2H_3O_2)_2$, or salt ($CaCl_2$) soluble in the sodium chloride presence in the skin, then with increasing the salt amount, the maximum alkalinity is quickly reached. In this case, the double salts ($CaCO_4 \cdot Na_2SO_4$) formation is possible [8]. The use of sodium hyposulfite in the liming solution is advantageous because it eliminates the insoluble compounds formation and leads to a controlled increase in the liming solution alkalinity.

The globular protein body is removed at the soaking stage because it is contained in a tissue saline solution. This process can be intensified by the surfactants use. Fibrils dispersion depends on the removal completeness of globular proteins and polysaccharides as they contribute to cell adhesion [12]. Surfactants used in soaking and liming processes are multifunctional. They promote diffusion of electrolytes into the dermis by reducing the surface tension at the interface, increasing the water content in the dermis, and have a dispersing effect on the substances removed and plasticizing effect on the derm collagen fibrillar structure. When using sulfonol in a soaking solution with a concentration of more than 2 g/dm^3, the hexoses yield increased by almost 8 times in the treatment solution, and proteins increased by 4 times. A similar effect on polysaccharides is achieved at the liming stage with the non-ionic surfactants use along with a slight yield of soluble proteins and oxyproline.

The interfibrillar matter removal from the dermis structure enables to separate its fibrils and increase the collagen reactivity. At the same time partial disorientation of fibrillar structure elements with decrease in its durability is reached. Further, the hydration and swelling degree of the neutralized dermis increases, the collagen destruction degree caused by enzymes increases [13]. It is important to consider that an effective removal of unstructured derm components, in particular polysaccharides and proteoglycans, is observed at the rawhide alkaline treatment stage due to enzymatic rawhide rehydration when used of sodium sulphide and calcium hydroxide in existing technologies [14]. The study of the collagen structure at eight stages of fresh ovine skins processing into dry crust leather using small-angle X-ray scattering is devoted to paper [15].

The authors defined a dependence between the structure stability and the collagen fibrils orientation index from its hydration degree. In the liming process, the cross-links are destroyed, which destabilizes the collagen structure [16], its fibrils are stretched and slightly straightened by reducing the collagen D-gap [17].

Thus, despite the significant number of works devoted to the influence of different chemical reagents and collagen structure on the rawhide liming process as well as on the semi-finished product properties obtained, there is virtually no scientific justification for effective soaking and liming processes. This is especially true to minimize the cost of environmentally hazardous reagents.

RESEARCH PROBLEM

The aim of the work was to establish the dependence between the effective rawhide use with a set of colloidal chemical properties of the semi-finished product at the soaking-liming stage. The following tasks were solved:

- colloid-chemical properties determination of alkaline treated semi-finished product;
- rawhide liming technology optimization;
- testing of the developed rawhide soaking-liming process.

MATERIALS AND METHODS

The cattle hide sulphide liming process and effective rawhide use were studied. The wet salted extreme light steer hides, fleshed until complete subcutaneous tissue removal, weighing 19-21 kg were used for the study. Rawhide samples with an area of 5 dm^2 taken from the central (butt) and peripheral (belly) areas were soaked in a wooden drum with a volume of 18 dm^3 at a working solution ratio to semi-finished product equal to 1.3:1 with float ratio (FR) 1.3 at a temperature of 27-29°C with the addition of 0.5% Na_2CO_3 by rawhides weight for 6 hours. Drum rotation speed during soaking-liming processes was 3-4 min^{-1} for 50% of the total time with a frequency of 0.5 h of rotation and rest. After soaking, the rawhide was washed twice at FR 2.0 with a water change after 0.5 h.

Natural water ISO 5667-11-2013, sodium sulphide GOST 596-89, sodium hydrosulphide TU 2153-541-05763441-2012 and calcium hydroxide VP-K-G DSTU B B.2.7-90:2011 were used for liming. Note: The names of state and industrial standards, which guide research and industrial production, are given for reference.

The influence of the liming process factors on the semi-finished product formation was determined by liming process physico-chemical and technological properties. Elastoplastic properties of the semi-finished product in compression strain were measured by an indicator gauge with a division value of 0.01 mm according to the standard method described in [18]. Swelling of the limed semi-finished product was expressed as an increased percentage in thickness after washing to the soaked rawhide thickness. Residual engineering strain was measured after unloading the sample after 0.5 hours. Hydrothermal stability was determined by the sample initial length reduction when semi-finished product heated in water or a glycerine and water mixture by weighting ratio 4:1 with a speed of 2-3 ºC/min according to DSTU 2726-94. The porosity of rawhides, limed semi-finished product after alcohol-ether dehydration, and the leather after conditioning at a temperature of 20 ± 2°C and humidity of 65 ± 5% was set by the ratio of pore volumes and sample elongation at rapture of 9.81 MPa on the rupture machine RT- 250M (belt A) and at a deformation rate of 80 mm/min according to the methods indicated in [18, 19]. To render gelatin, limed samples were used from the rump washed for 24 h under flowing water. The rendered gelatin amount obtained from the semi-finished product was set at a temperature of (65±0.1) ºC for 1.5 h on a photoelectrocalorimeter "FEK-56M" according to the calibration graph "Optical density of gelatin solution - the percentage of semi-finished product dry residue" at a 520 nm wavelength and the standard distilled water. The yield area was set by the leather area elongation after drying and moisturizing processes to the soaked rawhide area.

PRELIMINARY STUDIES OF LIMING PROCESS

The soaked samples of raw materials were subjected to liming for 12 hours at the temperature of the process suspension 27-29 °C [20], at the float ratio 0.5-3, at a concentration of sodium sulphide and calcium hydroxide of 8 g/dm^3 and 7 g/dm^3, respectively.

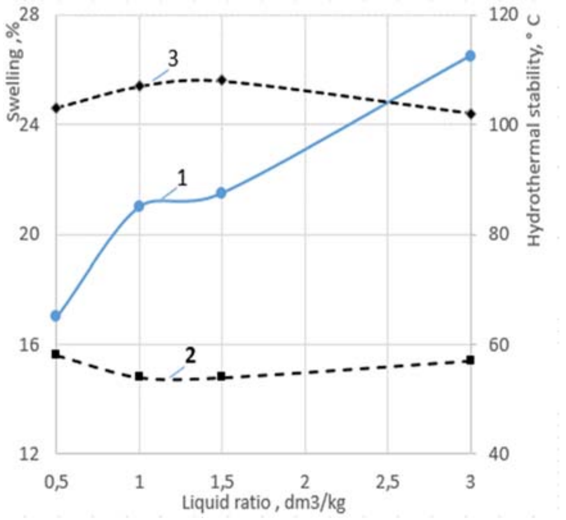
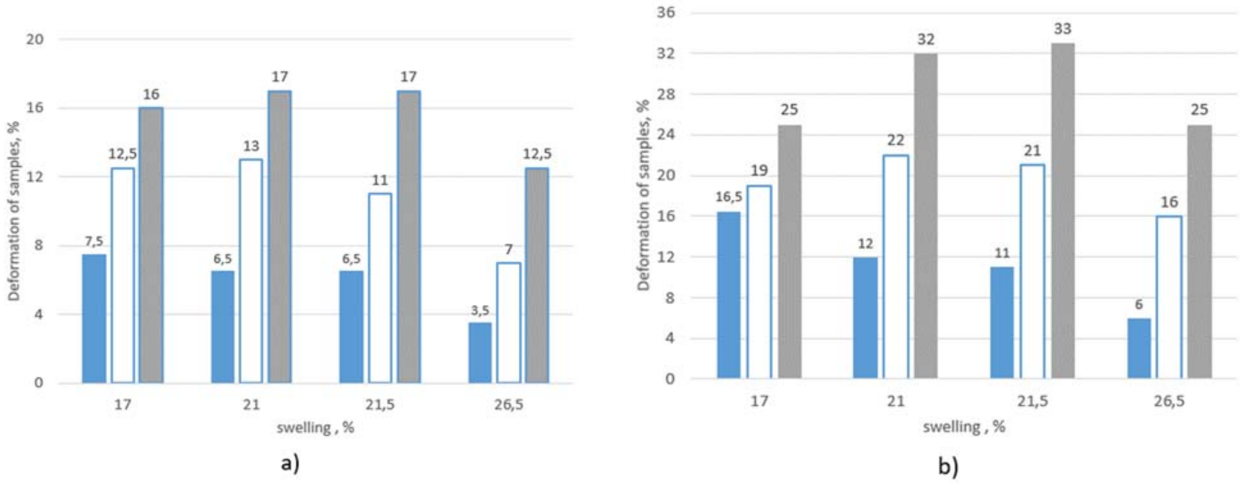


Figure 1. Change in swelling and temperature of hydrothermal stability depending on the values of the float ratio. **Note.** Curve 1 corresponds to the swelling process, curve 2 describes the change in the hydrothermal stability of the limed semi-finished product, curve 3 describes the change in the hydrothermal stability of the tanned semi-finished product.



a)

b)

Figure 2. Dependence of deformation of limed semi-finished product on swelling. **Note 1.** Visualization is presented for different topographic areas of the the semi-finished product: (a) corresponds to the butt, (b) corresponds to the belly; **Note 2.** Stress values (kPa) are color marked: 1 is blue, 3 is white, 5 is gray.

The subsequent washing with a water change lasted 40 minutes. To determine the yield of the area, the resulting semi-finished product was subjected to reliming with ammonium sulfate at a temperature of 28-30 °C followed by washing, pickling and tanning with basic chromium sulfate with a basicity of 38-42% and a consumption of 1.6% by weight of limed sheared skin. The following drying and wetting processes and operations were performed according to the current technology [21].

The studies of the deformation properties of the limed semi-finished product under compression showed the following results (see Figure 1) depending on water consumption. The decrease in float ratio was followed by the reduction of the limed hide collagen swelling. The hydrothermal stability of the tanned semi-finished product acquires the maximum value at the minimum value of the hydrothermal stability of the limed semi-finished product.

When compressing the limed semi-finished product, there was an increase in its deformation capacity at low pressure (Figure 2). With increasing compression stress at higher values of the float ratio, the deformation of the semi-finished product increases even more. The described phenomenon is especially characteristic of areas with a loose structure (Figure 2(b)). With increasing compression stress, the samples obtained at the values of the float ratio 1.0-1.5 have the maximum deformation.

The behaviour of the conditional permanent deformation of the samples of the limed semi-finished product depending on the values of the float ratio (Figure 3) is similar to that described above. The yield of the hide area increases therewith. Reducing the float ratio when liming to a value of 0.5 leads to the limed semi-finished product with lower swelling and lower area yield. This can be explained by insufficient defibrillation of the middle of corium, i.e., a lower degree of fibrillar dispersion of collagen.

Therefore, to obtain a semi-finished product with the maximum yield of the area, the float ratio must be in the range of 1-1.5; this contributes to the optimal swelling of the limed semi-finished product.

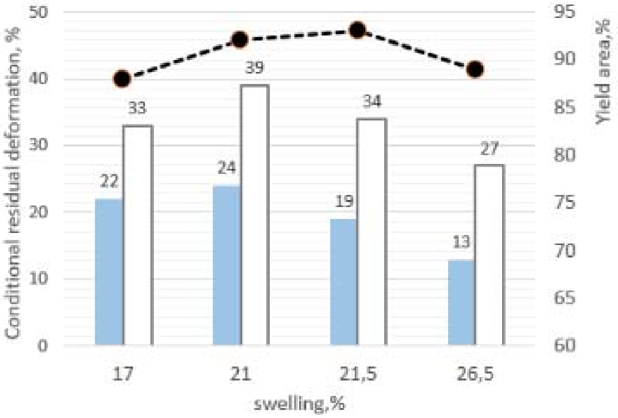


Figure 3. The dependence of the conditional permanent deformation of the limed semi-finished product and the yield of the hide area on the degree of swelling of the semi-finished product. **Note.** Topographic areas of hide correspond to the color of the columns: the butt – blue columns, the belly – white columns; the dotted curve describes the change in area yield.

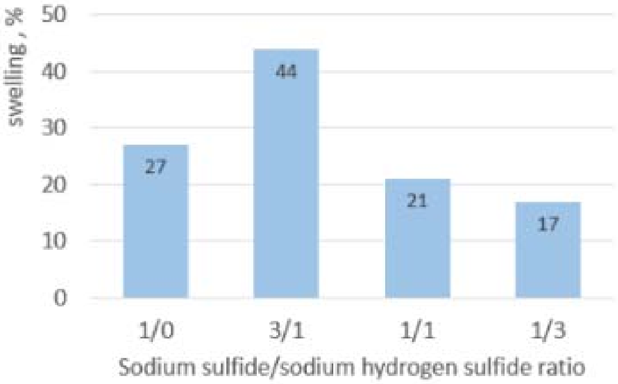


Figure 4. Dependence of the degree of swelling on the sodium sulphide to sodium hydrosulphide ratio.

Table 1. Characteristics of process factors.

Description	**Value of factors**		
	X_1	X_2	X_3
Middle level	1.16	1.00	12.0
Variability interval	0.2	0.22	4.0

To reduce the consumption of environmentally hazardous sodium sulphide during liming, the effect of the ratio of sodium sulphide and sodium hydrosulphide on the swelling of dermal collagen was studied (Figure 4). The increased consumption of sodium hydrosulphide contributes to reducing the degree of swelling. When the value of the ratio of sodium sulphide to sodium hydrosulphide equaled 1/3, incomplete dehumidification of hide was observed. Therefore, the optimal content of sodium hydrosulphide in the liming solution to obtain the maximum yield of the hide area should be at least 50%.

Thus, the limed semi-finished product with optimal elastic-plastic properties and moderate swelling can be obtained by carrying out soaking and liming processes at a stable temperature of 27-29 °C and at a reduced consumption of chemical reagents in accordance with current technologies, with water consumption ratio 1.0-1.5 relative to the weight of raw materials. This creates the conditions for more uniform swelling of individual topographic areas of the corium collagen, which facilitates the action of chemical reagents on the structure of the corium. The result was a more uniform defibrillation of elementary fibers and fibrils of the corium collagen.

OPTIMIZATION OF THE RAW HIDES LIMING PROCESS

Obtaining the mathematical model

Optimization of the raw hides liming process requires the development of the properly specified model based on the principles of an active experiment design. As a result of the preliminary analysis of the object of research, the factors influencing the liming process and the quality characteristics of the liming process were selected. The following parameters were chosen as factors: X_1 (% by weight of raw materials) – the total consumption of alkaline reagents (the alkaline reagents Na_2S and NaHS were dosed in equal proportions 1/1), X_2 (% by weight of raw materials) – consumption of calcium hydroxide, and X_3 (hours) – liming process duration. The response values were: the consumption of raw materials per 1 m^2 of product – y_1, kg/m^2; swelling of the semi-finished product – y_2, % by weight of soaked raw materials; stretch elongation at 9.81 MPa – y_3, %.

For the experiment, 20 trial amounts of 8 samples, measuring 150 by 160 mm and 3.0–3.5 mm thick, were used. The samples were obtained from the butt topographic area of two wet salted extreme light steer hides. The samples were completed in batches by the method of asymmetric fringe [18]. The hypodermis tissue of the hides was removed using a shaving machine. Processing of each batch of samples was completed by chrome tanning. After aging and squeezing, the samples were subjected to splitting to a thickness of 1.5 mm and brought to the finished form by the technology of production of elastic leather [20].

The experiments were performed according to a pre-built experimental design. The zero level of the factors of the studied process and their interval of variation are given in Table 1.

The specificity of the experimental studies was that at the beginning a 23 full factorial design was implemented. Since the first-order mathematical models and incomplete quadratic models based on the results of a full factorial design turned out to be inadequate, it was decided to switch to second-order experimental designs. To make optimum use of the results of the experiments already performed, the classic central composite rotatable plan [22] with six experimental points in the center of the domain under study and with axial "star value" of 1.682 was chosen from the second-order plans (Table 2). The selected plan has a significant advantage over the central orthogonal plan: the information surface of the rotatable plan is close to spherical, as a result of which the accuracy of the output variable in all directions at the same distance from the center of the domain under study is almost the same. Therefore, the compositional plan makes it possible to minimize errors in the definition of the response variable associated with the inadequacy of the presentation of the results of the study of the process using the model in the form of a second-order polynomial.

After processing the response values, the coefficients of regression mathematical models (polynomials of the second degree $\boldsymbol{\hat{y}_j = f(x_i)}$ were obtained:

$$\begin{cases} \hat{y}_1 = 6.5509 - 0.0673x_1 - 0.1053x_2 - 0.1163x_3 + 0.0538x_1x_2 - 0.0062x_1x_3 + \\ +0.0438x_2x_3 + 0.1148{x_1}^2 + 0.0353{x_2}^2 + 0.0883{x_3}^2; \\ \hat{y}_2 = 20.3670 + 2.6459x_1 + 1.7140x_2 + 2.8156x_3 + 0.1250x_1x_2 - 0.1250x_1x_3 + \\ +0.0438x_2x_3 + 0.1148{x_1}^2 + 0.0353{x_2}^2 + 0.0883{x_3}^2; \\ \hat{y}_3 = 34.7190 + 3.8241x_1 + 5.0721x_2 + 5.1487x_3 + 0.3750x_1x_2 + 0.3750x_1x_3 + \\ +0.375x_2x_3 + 3.6488{x_1}^2 - 2.4117{x_2}^2 - 3.2954{x_3}^2, \end{cases} \tag{1}$$

s.t. $\hat{y}_j$are predicted response values for the j-th model.

Table 2. Experimental design and the obtained response values.

#	Factor Values						Response Values		
	Coded			Uncoded (natural)					
	x_1	x_2	x_3	X_1	X_2	X_3	y_1	y_2	y_3
1	–	–	–	0.96	0.78	8.00	7.21	14.0	12.0
2	+	–	–	1.36	0.78	8.00	6.93	19.0	18.0
3	–	+	–	0.96	1.22	8.00	6.78	17.0	21.0
4	+	+	–	1.36	1.22	8.00	6.71	23.0	27.0
5	–	–	+	0.96	0.78	16.00	6.98	20.0	20.0
6	+	–	+	1.36	0.78	16.00	6.67	25.0	26.0
7	–	+	+	0.96	1.22	16.00	6.72	24.0	29.0
8	+	+	+	1.36	1.22	16.00	6.63	29.0	38.0
9	$-\alpha$	0	0	0.8236	1.00	12.00	6.87	17.0	19.0
10	$+\alpha$	0	0	1.4964	1.00	12.00	6.77	26.0	34.0
11	0	$-\alpha$	0	1.16	0.63	12.00	6.74	19.0	21.0
12	0	$+\alpha$	0	1.16	1.37	12.00	6.45	24.0	39.0
13	0	0	$-\alpha$	1.16	1.00	5.27	7.03	15.0	17.0
14	0	0	$+\alpha$	1.16	1.00	18.73	6.46	23.0	38.0
15	0	0	0	1.16	1.00	12.00	6.57	20.5	34.0
16	0	0	0	1.16	1.00	12.00	6.44	21.5	35.0
17	0	0	0	1.16	1.00	12.00	6.5	21.0	37.0
18	0	0	0	1.16	1.00	12.00	6.45	20.0	35.0
19	0	0	0	1.16	1.00	12.00	6.55	21.5	32.0
20	0	0	0	1.16	1.00	12.00	6.59	21.0	33.0

Note 1. # is number of experimental run. **Note 2.** The signs "+" and "-" indicate the corresponding levels of change of technological factors: the upper +1 and lower -1; α indicates the special “axial” value of distance from the center of the domain under study.

The statistical study of the obtained models showed that they adequately describe the process of liming of raw hides and therefore can be used to further search for optimal parameters of the liming process.

Multi-objective optimization of liming technology using Harrington's desirability function

Multi-objective optimization is the search for solutions that in the multidimensional space of objective functions are acceptable and close to the optimum of all criteria simultaneously [23]. In contrast to the single-objective optimization problems [24], multicriteria optimization solves the issues related to the contradiction of individual optimality criteria.

In the study presented the optimization strategy on the basis of the generalized criterion of desirability was applied. This strategy is to reduce the multi-objective problem to a certain generalized criterion (i.e., to the single-objective problem) with its subsequent optimization. The generalized desirability criterion is a weighted product of partial desirability criteria, which, in their turn, are normalized estimates of the state of the studied system, presented in fractions of a scale unit (from 0.0 to 1.0) and obtained from target functions by encoding these functions based on a special “scale of preferences”.

Harrington's desirability function was used in this study, which showed sufficient efficiency compared to other desirability functions [25]. The effectiveness of the desirability-based approach compared to other multi-purpose optimization strategies has been confirmed by numerous studies [26–29]. It should be noted that the optimization of the generalized desirability criterion may be accompanied by computational difficulties due to the complex structure of this criterion. The search process is partially simplified by preliminary visual analysis of response surfaces, which provides a priori information about the most "promising" ranges of factor space [30].

The numerical solution of a complex nonlinear optimization problem requires the use of special methods for finding the global extremum, for example, the use of random search methods. Given this, the authors conducted a multi-goal optimization that combines the desirability function with the genetic algorithm [31] as an evolutionary method of global nonlinear optimization. Therefore, the optimization of liming technology was performed according to the following procedure:

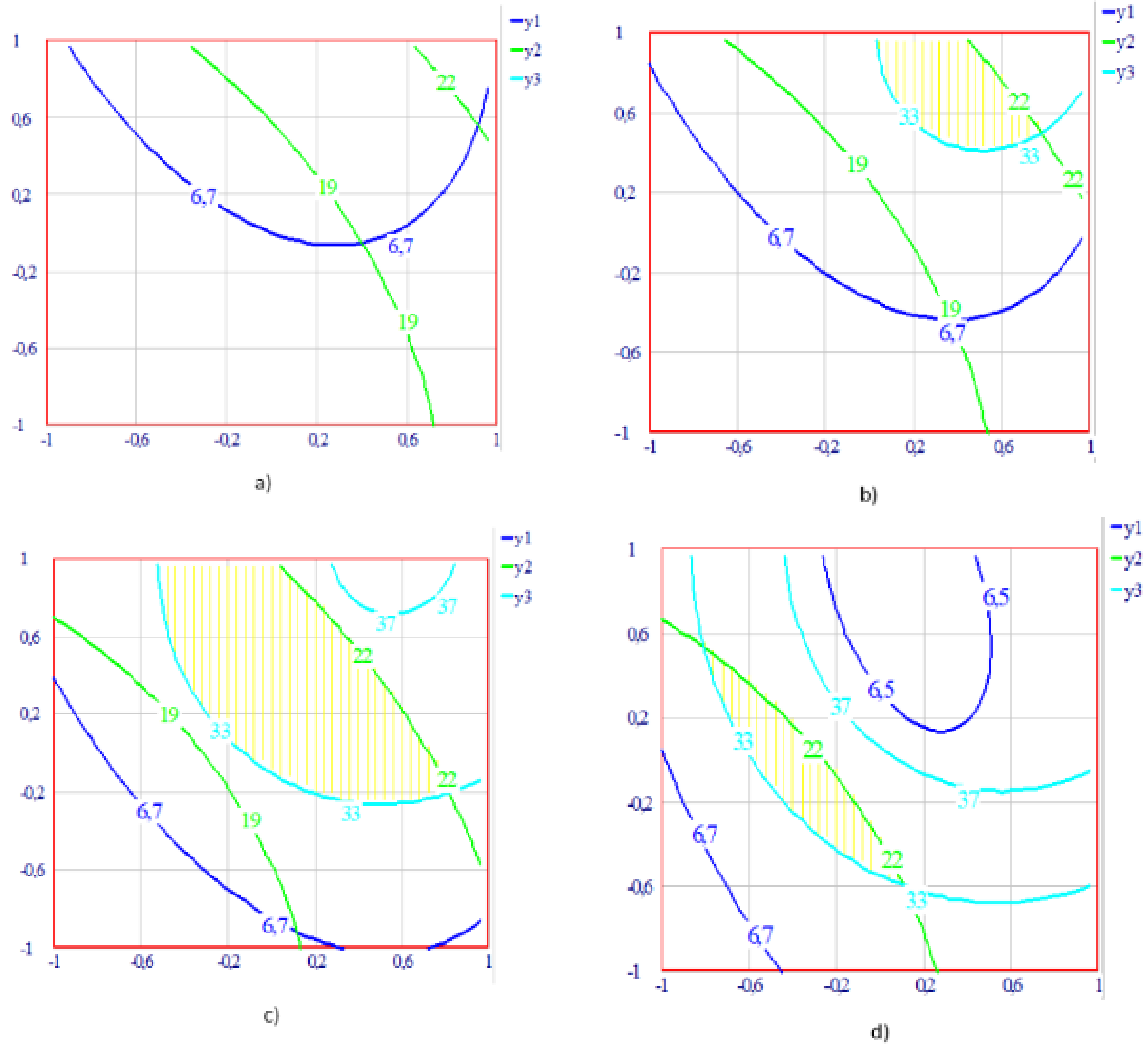


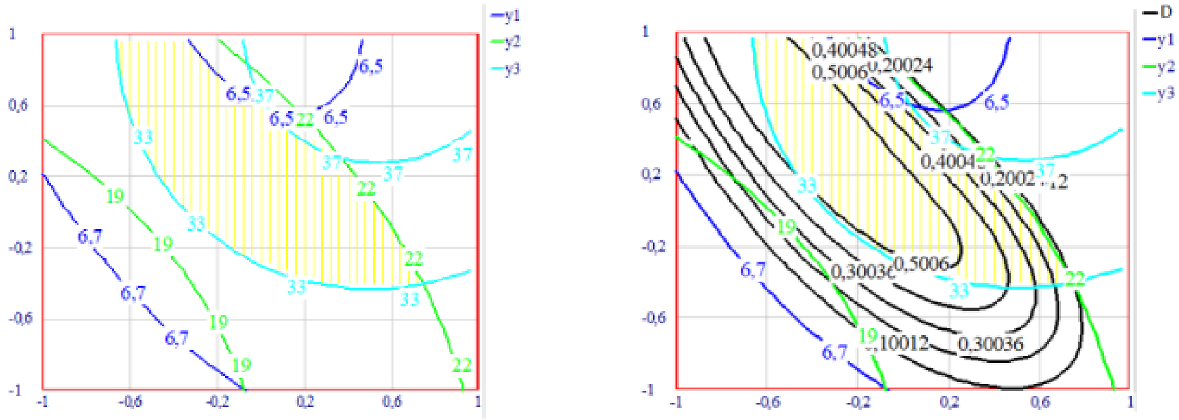
Figure 5. Response graphs of hide liming process. **Note 1.** Factor x_3 was fixed at the level of: a) –0.8; b) –0.6; c) –0.2; d) 0.9. **Note 2.** The compromise area is marked in yellow.

1. Preliminary visual analysis of response surfaces.
2. Construction of a generalized criterion using the Harrington desirability function.
3. Search for the optimum of the generalized criterion of desirability function and decision-making based on the results of optimization. This procedure uses a genetic algorithm of the GENOCOP type [32], which with sufficient probability guarantees the achievement of the global optimum of the generalized criterion of desirability.

The analysis of response surfaces (Figures 5, 6) included simultaneous visualization and study of graphs for all criteria, i.e., construction and study of projections of target surfaces y_1, y_2 and y_3 on the x_1-x_2 plane. During the analysis, the value of the factor x_3 consistently varied within the applicable domain of this factor. The analysis showed that the maximum value of the area of the compromise area can be achieved in the range of change of the factor $x_3 \in [-0{,}6, 0{,}6]$ (Figures 5(c), 6(a)). At the same time, as the factor x_3 moves away from the medium level, the area of the compromise region decreases (Figures 5(b), 5(d)) until it disappears (Figure 5(a)).

As a result of the analysis of response surfaces, the range of factors variation during multicriteria optimization of the liming process was previously determined to reduce the number of calculations: $x_1 \in [-0.6, 0.9]$, $x_2 \in [-0.5, 1]$, $x_3 \in [-0.6, 0.6]$. The subsequent numerical search for the extremum based on the desirability function (Figures 5b, 6b) confirmed that these intervals were chosen correctly.

For parametric identification of partial desirability criteria according to a priori data, reference marks on the desirability scale were set (Table 3). The reference marks establish a correspondence between the "less desirable" and "more desirable" key values of the response variables y_i (i=1, 2, 3) and the values of desirability.



a) b)

Figure 6. Response graphs of the multi-goal optimization problem in the neighborhood of the extremum. **Note 1.** The compromise area is marked in yellow. **Note 2.** The factor x_3 is fixed at the average level; a) compromise area, b) correlation of the compromise area with the desirability function D isolines.

Table 3. Reference marks on the desirability scale for the response variables

Response values	**Desirability**		
	"bad" (d_i=0,2)	***"good" (d_i=0,8)***	***"bad" (d_i=0,2)***
y_1	–	6.47	6.58
y_2	17	21	26
y_3	32	36	–

It should be noted that for variables y_1 and y_3 one-sided desirability profiles were applied, while for variable y_2 a two-sided profile was applied, since the desired range of existence of the variable y_2 was known.

After determining the partial desirability criteria di (*i*=1, 2, 3) a generalized desirability criterion (2) was constructed:

$$D = \sqrt[3]{d_1 \cdot d_2 \cdot d_3} \qquad (2)$$

The maximum value of the generalized desirability criterion D = 0,707 corresponds to the compromise-optimal values of the factors in the coded form: x_1 = –0.1233, x_2 = 0.4405, x_3 = 0.0497.

Therefore, based on the results of optimization of the liming process of wet salted extreme light steer hides, the following values of the consumption of chemical reagents (% by weight of raw materials) were recommended: hydrosulphide and sodium sulphide 0.57; calcium hydroxide 1.10. The recommended process duration is 12.2 hrs. The consumption of raw material of 6.5 kg per 1 m^2 of product, as well as a degree of swelling of 21% by weight of raw materials and stretch elongation 36.0% at 9.81 MPa, can hereby be achieved.

THE TESTING OF THE DEVELOPED TECHNOLOGY

The industrial testing of the developed low-waste technology of soaking and liming was carried out in the "Chinbar" stock company (Kyiv City, Ukraine), in the production of elastic leather for shoe uppers from wet salted extreme light steer hides. All soaking and liming processes were carried out in the liming drum "Volcano" manufactured by "Olcina" (Spain) at a speed of 3-4 min^{-1} at a stable temperature. Soaking of raw materials was carried out in accordance with the regime described above (in the section "Materials and methods of research"). The following mixture (% by weight of raw material) was used for liming: sodium hydrosulphide – 0.57, sodium sulphide – 0.57, calcium hydroxide – 1.1. The spent technological solution had the following characteristics: pH equal to 11,5-12,0 and density equal to 1.020-1.035 g / cm^3. After washing at a float ratio of 2 for 40 min, the limed semi-finished product was subjected to fleshing and splitting.

Before the reliming, using ammonium sulfate 1.6–1.8%, the splitted semi-finished product is washed at float ratio 1.2 for 20 minutes. The semi-finished product then undergoes bating, washing and pickling processes at a float ratio of 0.6. The characteristics of the spent solution were as follows: the pH value is 2.9–3.4 and the density is 1.027 g / cm^3. Tanning of the obtained semi-finished product is carried out with basic chromium sulfate with a basicity of 38–42% with a consumption of 1.8 in terms of Cr_2O_3 using the spent solution. The tanning agent is dosed in two stages with an interval of 2 hours.

Further technological processes and operations were performed according to the current technology [21] which acts as a reference technology. The results of determining the physicochemical properties of the obtained hides are shown in Table 4.

Table 4. Conditions for soaking and liming processes and hide properties.

Effectiveness measure	Technology	
	offered	*pre-existing*
Float ratio, [dm^3] per 1 kg of raw material, when soaking	–	1.5
Float ratio, [dm^3] per 1 kg of raw material, when liming	1.3	1.5
Float ratio, [dm^3] per 1 kg of raw material, when calcinationing	–	1.5
Consumption of materials, [%] by weight of raw materials	2.7	8.8
Process temperature [ºC]	27–29	20–22
Duration of the process [hours]	17–19	40.0
The degree of swelling of the sheared skin [%]	21.0	26.0
The degree of rendering of gelatin, [%] of the dry residue	9.0	12.0
Enzyme-thermal stability [min]	55.0	52.0
Porosity of raw material [%]	44.0	44.0
Porosity of sheared skin [%]	52.0	50.0
Porosity of product [%]	54.0	53.0
Hydrothermal stability of raw material [ºC]	65.0	65.0
Hydrothermal stability of sheared skin [ºC]	56.0	54.0
Loose grain hides [%]	–	18.0
Consumption of raw materials, [kg/100 m^2]	647.2	669.5
Yield of hide area [%]	92.5	89.0

The hides obtained by the developed technology are characterized by savings of natural raw materials (3.5% yield higher) and the absence of loose grain defects. This is confirmed by the higher resistance of the limeless semi-finished product of the developed technology to the melting of gelatin and the smaller amount of its swelling. At the same time, the developed technology is characterized by significantly lower consumption of environmentally hazardous chemical reagents and reduced duration of the technological process.

CONCLUSIONS

The process of defibrillation of raw hide collagen in the production of elastic skins has been studied. The study involved determining the optimal parameters of the liming process of the semi-finished product, which provides the best colloid-chemical properties of the mentioned semi-finished product. It was found that during the caustic treatment of raw materials with an increase in the ratio of process medium to its mass from 0.5 to 3.0 (at a temperature of 27–29 °C), the degree of defibrillation increases corresponding to the swelling of derm collagen. In this case, the hydrothermal stability and the yield of the hide area approaches 107 ºC and 92% of the area of the soaked raw material, respectively. It is shown that in the case of a decrease of the Na_2S/NaHS ratio, the degree of swelling decreases, and the area yield reaches the maximum value at a ratio of these reagents 1/1 and the optimal degree of defibrillation of the derm collagen. Multigoal optimization of raw leather liming process using the Harrington desirability function was performed. According to the results of optimization, the optimal values of technological factors of the process (the total consumption of reagents) were established: hydrosulphide and sodium sulphide – 0.57, calcium hydroxide – 1.1 (% by weight of raw materials).

The optimized soaking and liming technology was tested under industrial conditions, in the production of shoe upper leather. The analysis of the results of practical evaluation showed that the implementation of the optimized technology (in comparison with the current technology) provides the reduction of environmentally hazardous reagents consumption by more than three times, as well as the halving of the duration of leather raw materials caustic treatment. At the same time, the low-waste technology ensures the production of elastic leather materials that meet the requirements of state standards of Ukraine, with an increase in the area by 3.5%.

The developed technology of leather soaking and liming can be used in the development of innovative processes for the production of leather materials from the wide range of raw hides and skins.

REFERENCES

1. Skyba M., Synyuk O., Zlotenko B., et al.: A new modern theoretical view of the structural model of the structure of natural leather, Fibres and Textiles 28(2), 2021, pp. 82-90.
2. Andreyeva O., Atamanova A., Maievska T., et al.: Utilization of enzyme-containing products obtained from fish waste in leather production processes, Fibres and Textiles 28(4), 2021, pp. 3-10.
3. Orgel J. P. R. O., Irving T. C., Miller A., Wess T. J.: Microfibrillar structure of type I collagen in situ. Proceedings of the National Academy of Sciences 103(24), 2006. pp. 9001–9005. https://doi.org/10.1073/pnas.0502718103
4. Berber D., Birbir M.: Determination of major problems of raw hide and soaking process in leather industry, International Journal of Advances in Engineering and Pure Sciences 2, 2019. pp. 118–125. https://doi.org/10.7240/jeps.470865
5. Thanikaivelan P., Rao J.R., Nair B.U., et al.: Recent trends in leather making: processes, problems, and pathways, Critical Reviews in Environmental Science and Technology 35(1), 2005. pp. 37–79.
6. Siggel L., Bulo R. et. al.: Leather related collagen modeling: the challenges of modeling hierarchical structures. Journal of the American Leather Chemists Association. 102, 2007. pp. 333-336.
7. Steshov G.I., Golovteyeva A.A.: Influence of the type of salt on the change in the properties of collagen during alkaline salt treatment (Vliyaniye vida soli na izmeneniye svoystv collagena pri shcholochno-solevoy obrabotke), Izvestiya

vysshikh uchebnykh zavedeniy. Tekhnologiya logkoy promyshlennosti 2, 1965. pp. 75–79. (In Russian).

8. O'Flaerti F., Roddi V.T., Loller R.M.: Chemistry and technology of leather. Vol. 1. Literary Licensing, LLC, 2013.
9. Oliynyk M.M., Ponomariov S.H., Zhuravskyy V.A.: Influence of concentration of lime on properties of clay, semi-finished product and finished skin (Vplyv kontsentratsiyi vapna na vlastyvosti holyny, napivfabrykatu y hotovoyi shkiry), Lehka promyslovist 1, 1980. Pp. 50–52. (in Ukrainian).
10. Levenko P.I., Volpert G.R.: Influence of some factors on dehairing and consumption of raw materials (Vliyaniye nekotorykh faktorov na obezvolashivaniye i raskhod syr'ya), Leather and footwear industry 10, 1997. pp. 17–20. (in Russian).
11. Reich G.: Collagen report: A Review about the present state. Das Leder 46, 1995. pp. 192–199.
12. Gumbiner B.M.: Cell adhesion: the molecular basis of tissue architecture and morphogenesis, Cell 84 (3), 1996. pp. 345–357. https://doi.org/10.1016/S0092-8674(00)81279-9
13. Saran S., Mahajan R.V., Kaushik R., et al.: Enzyme mediated beam house operations of leather industry: a needed step towards greener technology, Journal of Cleaner Production, 54, 2013. pp. 315–322. https://doi.org/10.1016/j.jclepro.2013.04.017
14. Jayanthi D., Victor J.S., Chellan R., Chellappa M.: Green processing: minimising harmful substances in leather making, Environmental Science and Pollution Research 26, 2019. pp. 6782–6790. https://doi.org/10.1007/s11356-018-04111-z
15. Sizeland K.H., Edmonds R.L., Basil-Jones M.M., et.al.: Changes to collagen structure during leather processing, Journal of Agricultural and Food Chemistry, 63, 2015. pp. 2499−2505. https://doi.org/10.1021/jf506357j
16. Kayed H.R., Sizeland K.H., Kirby N., et. al.: Collagen cross linking and fibril alignment in pericardium, RSC Advances 5, 2015. pp. 3611−3618. https://doi.org/10.1039/C4RA10658J
17. Maxwell C.A., Wess T.J., Kennedy C.J.: X-ray diffraction study into the effects of liming on the structure of collagen, Biomacromolecules 7, 2006. pp. 2321−2326. https://doi.org/10.1021/bm060250t
18. Danylkovych A.H.: Practical training on chemistry and technology of leather and fur (Praktychnekerivnyctvo z himiji I tekhnologii shkiry i khutra): 2nd ed. Kyiv: Phoenix, 2006. (in Ukrainian).
19. Danylkovych A., Mokrousova O., Zhyhotsky A.: Improvement of the filling-plasticizing processes of forming multifunctional leather materials. Eastern-European Journal of Enterprise Technologies 2/6 (80) 2016, pp. 23–31 https://doi.org/10.15587/1729-4061.2016.65488
20. Danylkovych A.H.: Basic materials and technologies of leather production (Osnovni materialy i tekhnolohiyi vyrobnytstva shkiry). Kyiv: KNUTD, 2016. (in Ukrainian).
21. Technological methods of production of leathers of various assortment for shoe uppers and shoe linings, haberdashery from cattle hides and horse hides (Tekhnolohichna metodyka vyrobnytstva shkir riznomanitnoho asortymentu dlya verkhu vzuttya i pidkladky vzuttya, halantereynykh vyrobiv iz shkur velykoyi rohatoyi khudoby ta kins'kykh shkir). Kyiv: Chinbar, 2003. (in Ukrainian).
22. Box G.E.P., Draper N.R.: The choice of a second order rotatable design, Biometrika 50, 3−4, 1963. pp. 335–352. https://doi.org/10.1093/biomet/50.3-4.335
23. Hong C., Chen S.: Optimisation of multi-response surface parameters of the roving twist factor and spinning back zone draft, Fibres & textiles in Eastern Europe 27, 5(137), 2019. pp. 28−33. https://doi.org/10.5604/01.3001.0013.2898
24. Andonova S., Baeva S.: Optimizing a function linking an quality criterion to input factors on the thermo-mechanical fusing process, Fibres and Textiles 3, 2020. pp. 19-24.
25. Danylkovych A. G., Shakhnovsky A.M.: Development of a filling-hydrophobic composition in the production of velour from nutria skins: experience of multi-goal optimization (Rozroblennya napovnyuval'no-hidrofobizuyuchoyi kompozytsiyi u vyrobnytstvi velyuru zi shkurok nutriyi: dosvid bahatoparametrychnoyi optymizatsiyi), Kompjuterne modelyuvannya v khimiyi ta tekhnolohiyakh i systemakh staloho rozvytku: Zbirnyk naukovykh statey, Kyiv: Igor Sikorski KPI, 2020. pp. 161-168.
26. Oliveira L., Saramago S.: Multiobjective optimization techniques applied to engineering problems, Journal of the Brazilian Society of Mechanical Sciences and Engineering 32, 2010. pp. 94−105. https://doi.org/10.1590/S1678-58782010000100012
27. Costa N.R., Lourenço J., Pereira Z.L.: Desirability function approach: A review and performance evaluation in adverse conditions, Chemometrics and Intelligent Laboratory Systems 107, 2, 2011. pp. 234–244. https://doi.org/10.1016/j.chemolab.2011.04.004
28. Danylkovych A.H., Korotych O.I.: Optimization of leather filling composition containing SiO2 nanoparticles, Journal of the American Leather Chemists Association 114, 2019. pp. 333–343.
29. Danylkovych A., Lishchuk V., Shakhnovsky A.: Improvement of structure determining qualitative characteristics of hydrophobized velour, Fibres and Textiles 3, 27, 2020. pp. 41−48.
30. Sivertsen E., Bjerke F., Almøy T., et al.: Multivariate optimization by visual inspection, Chemometrics and Intelligent Laboratory Systems 85, 2007. pp. 110−118.
31. Pasandideh S.H.R., Niaki S.T.A.: Multi-response simulation optimization using genetic algorithm within desirability function framework. Applied Mathematics and Computation, 175(1), 2006. pp. 366–382. https://doi.org/10.1016/j.amc.2005.07.023
32. Michalewicz Z.: A personal perspective on evolutionary computation A 35-year journey. Evolutionary Computation 2023. pp. 1-33. https://doi.org/10.1162/evco_a_00323