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ПОСТАНОВКА И РЕШЕНИЕ ЗАДАЧИ ОПТИМИЗАЦИИ РАЦИОНА КОРМЛЕНИЯ ЖИВОТНЫХ

Обоснована задача оптимизации рациона кормов при создании автоматизированного производства комбикормов и премиксов. Выполнена математическая постановка задачи линейного программирования, построена целевая функция, выбран метод решения задачи и разработано программное обеспечение для реализации метода. Входные данные и полученный рецепт размещены в электронной таблице MS Excel, а обработка осуществлена при помощи встроенного алгоритмического языка Visual Basic for Application.

Ключевые слова: комбикорм, премикс, кормление, оптимизация, метод, алгоритм программы.

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ЕКОЛОГІЧНО-ОРІЄНТОВАНІ ТЕХНОЛОГІЇ ВИРОБНИЦТВА ШКІРИ З ВИКОРИСТАННЯМ ПРИРОДНИХ МІНЕРАЛІВ МОНТМОРИЛОНІТУ І ЦЕОЛІТУ

Ми представляємо екологічно-орієнтовані технології післядубильних процесів виробництва шкіри з використанням серії поліфункціональних матеріалів на основі природних мінералів монтморилоніту і цеоліту. В результаті отримуються шкіри з покращеними експлуатаційними та гігієнічними властивостями, підвищується ефективність використання сировини і хімічних матеріалів, знижується навантаження на навколишнє середовище, зростає конкурентоспроможність виробництва на внутрішньому та світовому ринках.

Ключові слова: *шкіра, технології, мінерал, монтморилоніт, цеоліт, модифікація, поліфункціональні властивості.*

1. Introduction

The production of leather and fur causes a considerable damage to the ecology. It is stipulated by sewage from tanneries. The main pollutants are the products of hides and skins processing and chemical materials which were not made use of. While producing chrome leathers for the upper of shoes 47,0 % of derma collagen is converted into waste and the compounds themselves are used only by 30,0—35,0 %. The purification is a very expensive and complicated task. The problems of sewage purification from tanneries are connected with obsolete technology and low intensity of chemical material use. The increasing requirements as to protection of environment favour the development and introduction of environmentally eco-friendly technologies of leather and fur production. The prospective of environmentally eco-friendly technologies is the development and the use of mineral dispersions on the basis of natural materials with polyfunctional properties [1—3].

Unlimited number of natural minerals montmorillonite and zeolite, their low cost, wide range of adsorption, ion exchange, catalyst, detoxification bactericidal properties and ease of use allow you to create competitive ecologically safe complex materials. Structural and sorption properties of minerals are responsible for the high level of chemical and physical interaction with collagen.

The application of mineral dispersions in leather production, using different technological processes, allows developing environmentally eco-friendly technology, to solve problems of environmental protection and obtain eco-leather.

Analysis of scientific papers emphasizes the possibility of successful use of monmorilonite dispersions in compositions with different functions for filling and retanning of skins [4—10]. However, the use of zeolite mineral dispersions and its impact on the physical, mechanical, operational and hygienic properties require additional research. The difference between the lattice structure of zeolite in comparison with montmorillonite and its specific physical characteristics, particularly high thermal stability (up to 700 °C), allow to suggest that as a filler zeolite will improve not only hygienic and deformation parameters but also heat resistance of leather.

2. Objects and investigation methods

Natural leather for shoe uppers, modified at the stage of liquid finishing with organic mineral compositions (OMC) has been studied.

In accordance with the technological requirements for the materials of leather production, more appropriate is the use of minerals, which are characterized by the maximum exchange capacity, high dispersion and surface area, as well as moderate hydrophilicity. Montmorillonite and zeolite satisfy these demands to a greater degree, palygorskite, hydromica, kaolinite, vermiculite, montmorillonite and palygorskite mixture — to a lesser degree.

Montmorillonite combines maximum sorption, ion exchange, hydrophilic properties and a high dispersion of crystals of an isometric particle shape and possesses the ability of the internal crystalline to swell and random dispersion.

Clinoptilolite has adsorption, ion exchange, catalytic, detoxification, bactericidal and other valuable properties. Each particle of zeolite flour has a plurality of pores with a diameter of 2—10 Å. It is a good sorbent of liquid and gaseous phases. Only molecules, the size of which does not exceed the size of the input windows can penetrate into the inner molecular space of the zeolites. Therefore, zeolites are also called molecular sieves.

Montmorillonite and zeolite are a group of layered hydrated silicate of alumina of lamellar structures, formed in the form of tetrahedra tightly bound in a single plane and weakly bound in the perpendicular direction. Due to the very high dispersion (1—10 microns) and specific surface area (20—800 m^2/g) minerals actively enter the various physicochemical interactions.

The objects of investigation were the processes of retanning and filling of leather semi-finished item by modified montmorillonite (MDM) and zeolite (MDZ) dispersions.

The types of materials on the basis of MDM and MDZ for technological processes are presented in Tabl. 1.

For technological investigation, chrome semi-finished item of light steers from butt was used. The thickness of wet-blue samples after shaving was 1,4—1,6 mm. The raw material treatment was performed according to traditional technology of chrome leather for the upper of shoes production used by Public Joint Stock Company «Chinbar».

Table 1

Technological materials for leather manufacture

Mineral dispersion	Type of technological material	Method of obtaining technological material
Montmorillonite (MDM)	Retanning agent	Modification by sodium carbonate, chromium tannin and sodium lignosulfonate
Zeolite (MDZ)	Filling agent	Modification by sodium polyphosphate and acrylic polymer

For investigation of technological processes, 3 batches of chrome semi-finished item of light steers from butt were used. Each batch included 10 of wet-blue samples, which size was 10 × 12 cm. Two batches were experimental and one — control. For a comparative analysis of the efficiency of using MDM and MDZ, the control samples were treated according to the traditional technology of chrome leather production for the uppers of shoes. The technological processes of the experimental batches were performed by retanning agent (experiment 1), next experimental batches were performed by filling agent (experiment 2).

Retanning agent was obtained by means of montmorillonite dispersion modification with sodium carbonate, chromium tannin and sodium lignosulfonate. Then, in order to achieve the maximum dispergation of montmorillonite the was carried out using sodium salt in the amount of 6,0 % on mineral weight. Further, in the obtained montmorillonite dispersion the solution of chrome tannin was introduced in the amount of 10,0 % on minerals weight in terms of chromium oxide. The production of retanning agent includes introducing lignosulphonate solution in the dispersion of chromium-montmorillonite (the content of tanning substances — 40 % in technical product) with the aim of lignosulphonate adsorption on the surface of mineral particles. Retanning agent was used for retanning-filling of leather semi-finished item in the amount of 2,5 % of the shaved semi-finished item weight. The duration of process constituted 90 minutes. Then, aluminium potassium sulphate and sodium formiate in the amount of 1,5 % and 0,4 % was introduced in the suspension for maximum deposition of retanning agent.

Filling agent was obtained by zeolite dispersion modification with sodium polyphosphate. For this, in dispersion which concentration was 60,0 g/l, at mechanical agitation, the solution of sodium polyphosphate in the amount of 10,0 % on zeolite weight was introduced. The modification temperature was 40—45 °C. The time of agitation was 1,5—2,0 hours. The production of filling agent includes introducing zeolite dispersion in the acrylic polymer. The obtained filling agent was employed for semi-finished item filling in the amount of 3,0 % on shaved semi-finished item weight. The duration of process constituted 60 minutes. Then, aluminium potassium sulphate in the amount of 2,0 % was introduced in the for maximum deposition of filling agent.

After retanning and filling of experimental variants, the samples were fat-liquored, squeezed out up to humidity of 55—60 %, dried on contact drier up to humidity of 26—28 %, dried up in the free state at the temperature of 35 °C, damped, stretched, dried in the free state to humidity of 14—15 %.

Further, leather performances were determined. Chemical analysis and physico-mechanical indices of the finished leather were determined according to the methods [11, 12].

The influence of the time factor, peculiarities of material deformation, their ability to take shape and keep it fully characterize one cycle characteristics. These tensile properties were obtained by applying the complete test cycle «loading — unloading — rest» to sample material. Identification of the components of the strain of modified skins was performed according to the method of study of relaxation phenomena with the help of relaxometer «Rack» with accuracy ± 0,1 mm, scheme is shown in Fig. 1.

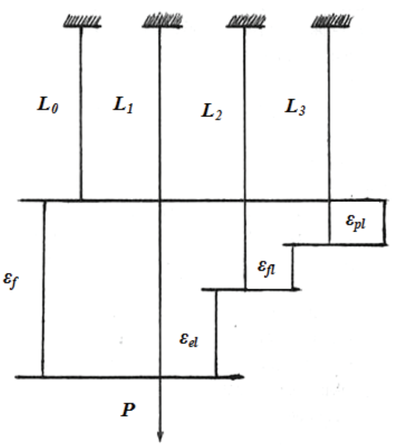

Fig. 1. The scheme of materials samples testing on relaxometer «Rack»: L_0 — the initial length of the sample, mm; L_1 — length of the working section of the sample at the final measuring under load, mm; L_2 — length of working area immediately after unloading, mm; L_3 — length of the sample after rest for a certain time, mm

To estimate the degree of anisotropy in the skin according to relaxation and deformation properties, uniformity coefficient $K_{unif.}$ of the properties of leather in the area was determined — the ratio of the average values of relative elongations in a transverse direction relative to the backbone line, to the average value in the longitudinal direction by the formula (1)

$$K_{\text{unif.}} = \frac{\varepsilon_{\text{transverse}}}{\varepsilon_{\text{longitudinal}}}. \quad (1)$$

Calculations of one cycle characteristics of new ecologically friendly leather materials with mineral content were carried out according to methods presented. The width and thickness of the standard sample of skin for tensile were measured in five areas and according to mean data its average cross-sectional area was calculated. The cross-sectional area was multiplied by the voltage value of 10 MPa and received steady current load, which is necessary to hang on the sample. With set screws relaxometer was installed by level, and the samples were inserted so that the distance between the two clamps was L_0 = 50 mm. Then rated load was hung to the lower clamp. After 60 min the length of the sample between the clamps increased to L_1 and by the formula (2)

$$\varepsilon_f = \frac{L_1 - L_0}{L_0} \times 100\%, \quad (2)$$

full (general) deformation was determined.

In 5 sec load was removed, sample length L_2 was measured and elastic deformation $\varepsilon_{\text{elastic}}$ was calculated using the formula (3)

$$\varepsilon_{el} = \frac{L_1 - L_2}{L_0} \times 100\%. \quad (3)$$

Then the working length of the sample was measured in 2, 30, 60, 120, 1440 and 20160 min after removing the load from the lower clamp and measurements $L_{3(2)}$, $L_{3(30)}$, $L_{3(60)}$, $L_{3(120)}$, $L_{3(1440)}$ and $L_{3(20160)}$ were used to calculate the conditional relative flexible deformation $\varepsilon_{\text{flexible}}$, which manifests itself in 2, 30, 60, 120, 1440 and 20160 min as follows:

$$\varepsilon_{fl} = \frac{L_2 - L_3}{L_0} \times 100\%. \quad (4)$$

Conditional relative plastic deformation $\varepsilon_{\text{plastic}}$ was calculated by the formula in 2 hours of rest of the sample:

$$\varepsilon_{pl} = \frac{L_{3(120)} - L_0}{L_0} \times 100\%. \quad (5)$$

The error of determination did not exceed 5 % for physico-mechanical tests, 3 % for chemical analysis.

3. Task formulation

The aim of the given investigations was to study the effectiveness of the employed materials on the basis of modified montmorillonite and zeolite used for technological leather production processes.

4. Results and Discussions

Special features of the collagen structure can purposefully change and transform its fibrous structure during processing treatments and influence the porosity, the colloid, chemical, physical, mechanical and deformation properties with the ultimate purpose of produced leather.

During the processing of hides and skins collagen undergoes profound intra-structural and intermolecular changes. Introduction of chemicals into the dermis and their interactions with the protein contributes to the production of leathers with the desired properties. Thus, if pre-tanning processes are aimed at dispersing the collagen structure of the dermis and remove of non-collagenous proteins, and in tanning the obtained microstructure is fixed, the final formation of the dermis is reached by post tanning. During retanning-filling, dyeing and greasing the necessary operational and hygienic properties of finished leathers are laid, including indicators of comfort, stiffness, softness, weight, hygienic and thermal insulation properties (thermal conductivity and total thermal effect).

The quality of derma structure formation in many respects depends on the character of interaction and distribution of mineral particles in chrome semi-finished leather structure. The high ability of mineral particles to disperse stipulates their power for diffusing and absorbing on microfibres of derma collagen. In that case, the leather structural elements are separated, and the leather qualitative and operational properties are improved.

The use of retanning agent, filling agent on the basis of modified montmorillonite and zeolite dispersions allow to obtain leather with filled, highly formed structure, large yield of leather area and also guarantees the rise of the quality of the finished leather. It has been found that the physical and mechanical properties of skin are formed at the macro level of collagen structure and depend on the type of mineral filler. Changes in the microstructure of the dermis as a result of mineral filling lead to increased strength, significant increase of seal temperature (Fig. 2), reduced elongation of the dermis and increase the coefficient of uniformity of mechanical properties in the longitudinal and transverse directions.

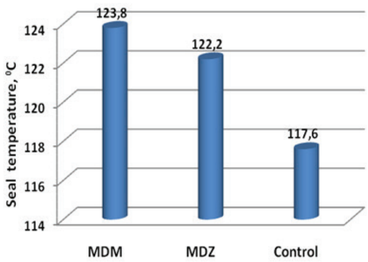

Fig. 2. Seal temperature of leather with mineral filling MDM and MDZ

The emergence of adsorption centers in the form of mineral dispersion particles with high sorption surface promotes deeper diffusion and more uniform distribution of them in the structure of semi-finished leather, as evidenced by the increase in the coefficient of uniformity. Interacting with the functional groups of the dermis collagen modified dispersions of montmorillonite and zeolite contribute to its formation and the formation of spatial structures. Penetration of minerals nanoparticles into interfibrillar spaces reduces the ability of the collagen structure to bonding when semi-finished product is dried, promotes the ordering of the elements of the dermis structure and provides the formation of oriented macromolecules and supramolecular structures. So, we believe that elastic-plastic properties of experimental skins are characterized by a pronounced deformation compared with unfilled skins. The results of the analysis are presented in Tabl. 2.

Curve of linear characteristics of modified skin samples after removal of the load over time (Fig. 3) shows a positive effect of the mineral content of semi-finished leather on the relaxation and deformation characteristics of the leather for shoe upper.

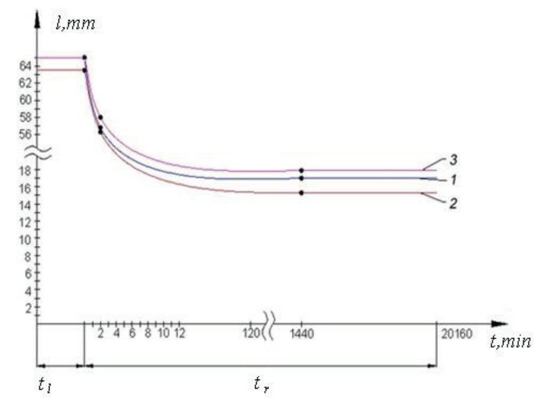

Fig. 3. The dependence of the deformation of tension of filled leather from the time under load (t_l) and at rest (t_r): 1 — control, 2 — MDM, 3 — MDZ

Table 2

Indices of qualitative and operational properties of leather

Indicator	Semi-finished material, filled		
	MDM	MDZ	Control
Derma structure formation			
Yield of leather area, % from control leather	105,8	103,8	100
Yield of leather thickness, % from control leather	104,9	102,9	100
Volume yield, cm3/100g derma	289,2	287,6	284,5
Physical and mechanical properties			
Breaking load, H	487 K_{unif} = 0,91	428 K_{unif} = 0,94	396 K_{unif} = 0,90
Tensile strength at break, MPa	29 K_{unif} = 0,79	27 K_{unif} = 0,78	26 K_{unif} = 0,77
Relative elongation, %, at 10 MPa	22,3 K_{unif} = 0,87	23,4 K_{unif} = 0,9	24,95 K_{unif} = 0,73
Relative elongation, %, at break	67,3 K_{unif} = 0,91	65,6 K_{unif} = 0,95	65,3 K_{unif} = 0,90
Conditional modulus of elasticity, MPa	34,4	32,8	32,3
Stiffness, H	468	492	484
Physical and chemical analysis			
Moisture, %	14,4	13,9	13,6
Mineral matter*, %	8,1	8,4	5,7
Substances extracted by organic solvents*, [%]	6,4	6,3	6,2
Hygroscopicity, %	10,25	9,93	8,09
Water yielding capacity, %	8,24	9,03	7,55

Remark: * — based on the weight of dry substance

Experimental leathers are characterized by increasing yield of leather thickness in comparison with control ones. Yield of leather area and volume yield of control and experimental leathers are practically identical. As a whole, the MDM and MDZ can be applied in the production of eco-leather as alternative of foreign technical materials.

5. Conclusion

The paper is devoted to the investigation of the efficiency of leather manufacture with modified minerals dispersions. It has been shown that modification of montmorillonite and zeolite dispersion allows to obtain technological materials with polyfunctional properties. While leather retanning, filling with MDM and MDZ dispersion particles are absorbed into the collagen fibrous structure and allow to form derma volume on account of screening its structural elements.

Thus, as a result of the research:

— it has been found that the introduction of dispersions of montmorillonite and zeolite to the structure of the dermis improves the durability of semi-finished leather products, the growth rate uniformity of mechanical properties in the longitudinal and transverse directions;

— it has been shown that the use of modified montmorillonite and zeolite dispersions allows to obtain leathers with high formation of volume, perfect physical and chemical indices and developing environmentally eco-friendly technology.

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ЭКОЛОГИЧЕСКИ-ОРИЕНТИРОВАННЫЕ ТЕХНОЛОГИИ ПРОИЗВОДСТВА КОЖИ С ИСПОЛЬЗОВАНИЕМ ПРИРОДНЫХ МИНЕРАЛОВ МОНТМОРИЛЛОНИТА И ЦЕОЛИТА

Мы представляем экологически ориентированные технологии последубильных процессов производства кожи с использованием серии полифункциональных материалов на основе природных минералов монтмориллонита и цеолита. В результате получаются кожи с улучшенными эксплуатационными и гигиеническими свойствами, повышается эффективность использования сырья и химических материалов, снижается нагрузка на окружающую среду, растет конкурентоспособность производства на внутреннем и мировом рынках.

Ключевые слова: кожа, технологии, минерал, монтмориллонит, цеолит, модификация, полифункциональные свойства.

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