

**NEW EFFECTIVE
ECOLOGY-ORIENTED
TECHNOLOGIES OF LEATHER
AND FUR MATERIALS
PRODUCTION**

Monograph

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The monograph is aimed at scientists, experts in the fur and leather industries. It will be useful for postgraduate students and masters of specialized higher education institutions.

The monograph covers the theoretical substantiation and practical application of the results of the development of ecology-oriented technologies for the production of fur and leather materials in the manufacturing of competitive products. Structural transformations of protein raw materials in colloid-chemical processes of their multi-stage processing have been considered. In addition, considerable attention is devoted to resource-saving technologies for the production of natural elastic materials. The publication can be used to improve the standard eco-friendly technologies of fur and leather production and develop new ones.

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LIST OF ABBREVIATIONS

ACEL	– alkyl carboxyl ethanolamine
ADG	– anionic dark green
ANC	– acrylic nitrocellulose
AST	– ammonium sulfatotitanilate
ATS	– ammonium titanyl sulfate
BBЖ	– Barvacryl brown Ж
BCS	– basic chromium sulfate
BET	– Brunauer-Emmett-Teller method
CCRD	– central composite rotatability design
CHCM	– chromium hydroxocomplex montmorillonite
CJSC	– Close Joint-Stock Company
CPU	– colored polyurethane
CSE	– collagen structural element
DEGE	– diethylene glycol ester
DEL	– double electric layer
DPGE	– dipropylene glycol ester
DPGSE	– dipropylene glycol sulfonic ester
FCP	– fermented collagen product
FTHS	– fermentation thermal stability
HS	– hide substance
HSCC	– hydroxo sulfatochromium complex
IEP	– isoelectric point
LQ	– liquid coefficient
MAC	– modified acrylic composition
MAUC	– modified acrylic urethane composition
MMD	– modified montmorillonite dispersion
MMT	– montmorillonite
NC	– nitrocellulose
OA	– oiling agent
OFCP	– oxidized fermented collagen product
OMC	– organic mineral composition

List of abbreviations

OSL	– one-stage liming
PZC	– point of zero charge
SCP	– standard contact porosimetry
SEOS	– substances extracted by organic solvents
SLP	– soaking and liming process
SLS	– sodium lignosulfonate
TOA	– titanyl oxalate acid
TSL	– two-stage liming
T_w	– temperature of welding
T_b	– temperature of the beginning of mass loss (collagen de- hydration)
T_t	– temperature of the termination of mass loss (destruction termination)
T_{fm}	– temperature of fusion maximum
T_{ms}	– temperature of the destruction maximum speed
T_{bthd}	– temperature of the beginning of thermal destruction
Δm_{300}	– mass loss up to 300 °C
ΔH	– heat of fusion
ε_r	– relative elongation at rupture
σ_{100}	– elasticity module at 100 % elongation
σ_s	– tensile strength
v_{ml}	– mass loss rate

INTRODUCTION

The production of leather and fur materials, characterized by multiple stages, high material consumption and technogenic character, has been known for more than five thousand years. In the context of increased technological and economic requirements for modern production, limited resources, the rising cost of energy and materials and a reduction in production costs, these issues are given particular attention.

In recent years, there has been an increase in manufacturing a new range of leather materials of lesser thickness and specific weight of fur products, an urgent need has arisen to develop efficient production technologies that would meet the increased requirements of environmental safety as well. This is largely due to the deterioration of the general state of the environment resulting from the high consumption of materials and, accordingly, the waste of industries that process leather and fur raw materials.

In the conditions of competition for product sales markets, insufficient attention is paid to the technogenic character of existing technologies. In this regard, a necessary prerequisite for the effective development of leather and fur production is the use of resource-saving, low-waste, environmentally oriented technologies.

This monograph is based on the research work carried out at the Department of Biotechnology, Leather and Fur of Kiev National University of Technologies and Design over the past years, on the following topics:

- physical and chemical principles of the transformation of collagen of the dermis during its processing into the leather;
- theoretical foundations of environmentally friendly leather processing technologies;
- physical and chemical principles of biopolymer modification in leather production;
- the latest and resource-saving technologies in power engineering, industry and agro-industrial complex;

- development of low-waste ecologically safe technologies of chromium-free leather production;
- the use of domestic environmentally friendly materials to improve the quality of leather and fur;
- development of environmentally oriented technologies for the production of fur sheepskins for medical purposes;
- development of resource-saving, environmentally friendly technology for complex finishing of leather and fur semi-finished products;
- orthopedic leather with antimicrobial effect as a product of environmentally oriented technologies;
- protection of the environment and creation of a system for protecting people from adverse effects at work;
- development of resource-saving and environmentally oriented technologies for the production of leather and fur based on modern efficient materials.

Part of the research work was carried out in the framework of international research projects with financial support from the Ministry of Education and Science, Youth and Sports of Ukraine. Most of the executed research work is implemented in the industry.

Section 1 analyzes the work of the authors concerning the study of the structure of collagen and keratin, the electrical surface properties of collagen of the dermis and its structural transformations in the main technological processes of natural protein-containing material formation.

Physical chemistry of soaking and liming processes is described in Section 2. After the presentation of the features of the dermis interaction with chemical reagents, the developed technologies of soaking and liming processes for processing raw cattle hides, which involve reducing the costs of chemical materials and the processing cycle, as well as hair utilization in the production of leather, have been considered. At the same time, a multi-criteria optimization of the process of raw material recovery based on the implementation of the central rotatable composite design and the Harrington function is presented.

Section 3 is devoted to the technology of complex formation of structuring agents with organic reagents in the processes of formation and stabilization of the dermis collagen after preparatory soaking processes.

The developed technology of anion-cation chrome tanning of hide and fur, the ways of rational use of chromium compounds, chromium-free technology of combined tanning and post tanning treatments of the leather semi-finished product are considered.

Section 4 of the monograph is devoted to the resource-saving environmentally oriented technological processing of fur raw materials. The use of electrochemically activated water can be promising here. The developed technologies have been introduced into production, they are distinguished by minimizing the costs of chemical materials and provide an opportunity to obtain leather and fur materials with special properties.

Section 5 is devoted to new technologies for finishing leather materials: aniline and emulsion finishing, including the use of modified polyacrylurethanes. The developed technology for the formation of polymer coatings on leather materials ensures the production of a wide range of elastic leathers.

Mathematical processing of the research results has been carried out using the software developed under the guidance of Professor A. G. Danylkovych and posted on the website <http://mnk-online.narod.ru>, and the software Statistica 6.1 as well.

Solving this scientifically practical problem will enhance the efficiency of soaking and liming, tanning and finishing technologies in general, saving of raw materials and chemical reagents and obtaining top-quality leather and fur materials, as well as improving safety conditions and the environmental situation of production. Ultimately, this will contribute to the economic and social progress in Ukraine.

1. PROTEIN BASIS OF FUR AND LEATHER MATERIALS

A prerequisite for the effective operation of enterprises of the fur and leather industry is the availability of raw materials that would meet the certified requirements, taking into account the range of finished products. Depending on the quality of raw materials, the company should have a wide range of technologies for their processing into high-quality products for special purposes. In particular, the outer cover of animal hides and skins can be used for the production of natural products for polyfunctional purposes.

Industrial enterprises use fur and leather raw materials of various types [1, 2]: of cattle, pigs, horses, etc., of both large and small sizes, as well as fur materials of a wide range. Some of the most valuable and common types of cattle rawhides are, in particular, still-born calfskin, calfskin, grasser skin, heifer, bull-calf and cow hides. According to the weight, they are divided into the following groups: light, medium and heavy; bull and steerhide are light and heavy. Rawhides also include hides of buffaloes and yaks. These types of hides are processed into a wide range of materials. Raw furs are mainly classified according to the species of animals: mink, nutria, Arctic fox, fox, rabbit, fur calf skins, fine-wool, semi-fine wool, coarse wool and semi-coarse wool sheepskins, fur kid and the like. Collagen and keratin proteins are the basis for fur and leather raw materials. In addition, collagen is more susceptible to biological destruction, so green animal hides are cured for two hours [2]. The necessity of this process is caused by the impossibility of bacteria and microorganisms reproduction and the action of the hide enzymes on its protein components.

1.1. Physical and chemical structure of collagen and keratin

In chemical terms, collagen, as a biopolymer of amphoteric nature, has an amorphous-crystalline structure, which is synthesized in tissues

of living beings with a certain sequence of amino acid residues [3, 4]. At the molecular level, the polypeptide chains $\alpha 1(I)$ and $\alpha 2$ form macromolecules (**Fig. 1.1**), with $\alpha 1(I)$ repeated twice [5–7]. Each polypeptide chain, located in a macromolecule at some distance between the centers of 0.6 nm, forms a spiral, swirled to the left, with three amino acid residues on one turn (a triad) and a radial angle of $2/3 \pi$ [8]. All triads begin with a glycine amino acid. In turn, macromolecules are twisted in the opposite direction with ten triads of amino acid residues on one turn. In addition, the active functional groups of side radicals of amino acid residues of molecules have a fan-like pattern around their propellant line with the angle of inclination to the plane of the cross section of 64° and the diameter of about 0.14 nanometers.

The structure of polypeptide chains of the collagen molecule [$\alpha 1(I)$] $_2\alpha 2$ has sequences in amino acid residues in the triads with a frequent presence of proline and hydroxyproline in the crystalline parts of the structure that belong to the hydrophobic ones. Hydrophilic parts in the structure of collagen form amino acid residues with permanently renewed bonds at the presence of acid and basic groups – glutamic acid and lysine or arginine, etc. in amphoteric areas. In this case, the amino acid residues of collagen have both a stabilizing effect on the spiral and a destabilizing one, which depends on the chemical nature of the molecule radical [9, 10].

The destabilizing effect of amino acid residues of the acidic and basic nature on protein molecules manifests itself depending on the magnitude of the charge of the side groups, when stabilizing hydrogen bonds are dominated by repulsion forces of the same charges. In this regard, the structure of the native collagen is in a side state under normal conditions. This is confirmed by the planar configuration of peptide bonds due to the rotation around the axis of $C_\alpha-N$ -bond by φ angle and the rotation of $C_\alpha-C$ -bond by

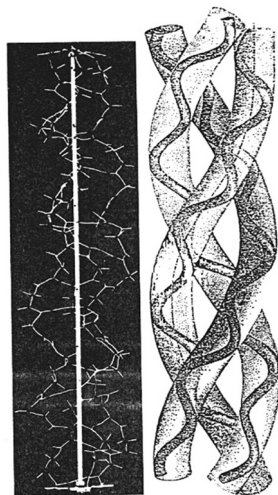


Fig. 1.1. Segment of a collagen macromolecule

ψ angle with clockwise rotation when observed from C_α atom. In this case, the angle of $C-N$ atom bond rotation equals zero. Because of steric constraints, during the interaction of lateral radicals of amino acid residues only about 15 % of possible values of φ and ψ angles are actually realized, which determine the spatial placement of the polypeptide chains. It should be noted that with the increase in collagen temperature, its denaturation occurs, which is manifested in the reduction of φ and ψ angles with an appropriate increase in the diameter of microfibrils. In this case, natural raw materials become unsuitable for processing. Therefore, it is necessary to control the temperature conditions of the industrial treatment in technological processes in order to prevent irreversible structural transformations.

According to modern views, collagen of the dermis has a multilevel hierarchical structure [10–15]. The lower structural level is formed by the sequential arrangement of amino acid residues in the polypeptide chains of protein macromolecules, and the upper one forms the dermis of the animal hide. There are some other structure levels between them (**Table 1.1**). Thus, a spatial combination of three polypeptide chains into a spiral is a macromolecule.

At the supramolecular level of the structure, five macromolecules are combined into a microfibril (pentamer) and interact with the adjacent collagen molecules in the presence of electrically charged functional groups of its molecules (**Table 1.2**) [6, 16]. The table shows 8–16 microfibril triads with the symbols of stable sections by the lines on the left, carboxyl-containing amino acid residues — in bold type and amino acid residues of the basic character — in italics. These groups are located in amorphous unstable sections of collagen molecules. It is also evident from Table 1.2 that charges are unevenly distributed along microfibrils and form structurally weak sections of the pentamer. They appear in the centres of concentration of positive and negative charges of side radicals of collagen amino acid residues, which are asymmetrically superimposed over the polypeptide chain due to different lengths of side radicals and create amorphous sections of the microfibril structure. There are both positive and negative charge carriers that constantly interact both in the polypeptide chain and between the atoms of side radicals. The charged groups also facilitate the external orientation of the side radicals of col-

Table 1.1

Structural levels of collagen

Structure	Level of the structure	Elements of the structure	Average diameter of elements, nm
Molecule	Polypeptide	Polypeptide chains with molecule mass of 100 000	
	Macromolecule	Spatial placement of three polypeptide chains in a spiral	~ 1,5
Supramolecular	Microfibrillar	Conformation of 5 macromolecules	~ 3–5
	Fibrillar	Combination of 900–2000 microfibrils	~ 50–200
Suprafibrillar	Elementary fibre	Formation of 900–1000 fibrils	~ 5 000
	Secondary fibre (fibre bundles)	Aggregates of 30–300 elementary fibres	~ 200 000
	Dermis	Interlacing of elementary fibre bundles lined up in different directions	

lagen macromolecules in the process of collagen fibril formation. At the supramolecular level, microfibrils interact with the adjacent molecules of collagen microfibril forming covalent bonds with the displacement of one molecule concerning the adjacent one at the distance of D period, which corresponds to 234 amino acid residues or 67 nm.

At the suprafibrillar level, fibrils create elementary fibres and their bundles. At this level, the parallelism of the fibers is broken with the formation of their branches and the appearance of a large number of pores (**Fig. 1.2**) [3, 9], but chemical bonds between the fibres are preserved, which ensures the cohesion of the dermis.



Fig. 1.2. The scheme of the dermis macrostructure after asic treatment

Table 1.2

Microfibril section with possible charges of the structure

Triad number	Number of the macromolecule fragment that contains microfibrils					Charge
	1	2	3	4	5	
8	G G G F F F Q Q Q	G G G E E E P'P'P'	G G G A A L P'P'P'	G G G K K K E E E	G G G P P P A A A	-3, +3 -3
9	G G G P P P P'P'P'	G G G A A P P'P'A	G G G P P P S S A	G G G S S T K K K	G G G P P P R R R	+6
10	G G G E E E P'P'P'	G G G N N S K K K'	G G G A A A R R R	G G G P P P R R R	G G G P P P P'P'A	-3 +9
11	G G G E E E P'P'P'	G G G D D E T T S	G G G E E E R R R	G G G E E D T T Q	G G G S S P A A S	-12 +3
12	G G G A A Q S S T	G G G A A N K K L	G G G F F F P'P'P'	G G G P P P A A V	G G G S S P P'P'A	+2
13	G G G P P P M M A	G G G E E E P'P'P'	G G G E E E R R P'	G G G R R R P'P'S	G G G K K K D D I	-6, +6 +2, -2
14	G G G P P A R R R	G G G P P A T T V	G G G V V A E E A	G G G E E S V V T	G G G L L R N N I	-2, +1 +3, -2
15	G G G P P P P'P'P'	G G G I I Q Q Q P'	G G G P P P P'P'T	G G G P P A P'P'S	G G G L L Q P'P'P'	
16	G G G P P P P'P'P'	G G G P P P P'P'P'	G G G P P P A A I	G G G P P P P'P'P'	G G G P P P I I A	

Note. IUPAC names of amino acid residues [17]: A – alanine, V – valine, L – leucine, I – isoleucine, M – methionine, F – phenylalanine, Q – glutamine, P – proline, N – asparagine, G – glycine, E – glutamic acid, D – aspartic acid, R – arginine, K – lysine, T – threonine, S – serine, K' – hydroxylysine, P' – hydroxyproline

Depending upon the sequence of amino acid residues in polypeptide chains and the geometric form of elementary fibers in the animal hide dermis, there are seven types of collagen. The main types are I, III, IV, and V (**Table 1.3**) [10].

The structural elements of Types I, III collagens are covalently bonded together. In Types V, VI and VII collagens, formation occurs predominantly on the surface of fibrils. Fibrils of Types I, III, V collagens are characterized by a transverse banding at the frequency of 700 nm.

Table 1.3

Main types of collagen in animal skins and hides

Type	Molecule formula	Location in tissues	Schematic form
Collagens of the fibrillar structure			
I	$[\alpha_1(\text{I})]_2 \alpha_2(\text{I})$	Skin, bones, sinews, bands	
III	$[\alpha_1(\text{III})]_3$	Skin, blood vessels	
V	$[\alpha_1(\text{V})]_2 \alpha_2(\text{V})$	As for Type I	
Collagen of the lamellar structure			
IV	$[\alpha_1(\text{IV})]_2 \alpha_2(\text{IV})$	Basement membranes	
Collagen with fibrils of the anchor structure			
VII	$[\alpha_1(\text{VII})]_3$	Multilayered scaly epithelium	

Type IV collagen is present in the producing layer of the epidermis, it creates a reticular structure and, after removing the stratum corneum, forms a grain pattern on leather.

The considered collagen structure is characterized by numerous interchain and intercoil bonds, which are formed because of the interaction of functional groups of side radicals of the adjacent protein molecules. Each polypeptide group can form two hydrogen bonds with other groups. Elementary chains of macromolecules are arranged with the formation of the maximum possible number of hydrogen bonds between the adjacent coils of the spiral, which keep them in a tense state.

Hydrophilic and hydrophobic surface of collagen structural elements is covered with glycosaminoglycans, proteoglycans, glycoproteins, which are removed during alkaline treatment as a result of the destruction of chemical and physical bonds. That is to say, the microstructure of fibrous collagen is characterized by the alteration of unstable and stable sections of macromolecules, which are identified, respectively, by the presence or absence of electrical charges of the functional protein groups. At the same time, the distribution of positive and negative charges along microfibrils is uneven.

The features of the collagen structure make it possible to purposefully change and transform its fibrous structure during technological treatments and influence porosity, colloid-chemical, physical-mechanical and structural properties, taking into account the intended use of the leather material [4]. In addition, each structural level of the dermis has an appropriate number of capillaries and pores. Considering this, the dermis as a porous material includes pores of different sizes, which vary in the range from 1 to $200 \cdot 10^3$ nm and form a micro- ($r_{por} \leq 1$ nm), meso- ($1 \text{ nm} \leq r_{por} \leq 200 \text{ nm}$) and macroporous ($r_{por} \geq 200 \text{ nm}$) [18, 19] structure. The percentage of pores of different diameters varies widely and depends on the physical and chemical treatments and technological influences of the reagents used [20–23].

In the process of technological treatments of fur and leather raw materials under the influence of chemical reagents, structural transformations of the biopolymer occur, an important aspect of which is the collagen reactivity [24]. It is caused by the presence of various functional groups in side chains of macromolecules: carboxyl, amino and

hydroxyl, etc. Because of this, the bonds of different nature and location can be formed in the collagen structure – longitudinal intrachain and intramolecular, transverse interchain and intramolecular, transverse intrachain and intermolecular [3, 12]. The presence of hydrophilic and hydrophobic sections in the collagen structure of the dermis significantly affects the effectiveness of its interaction with chemical reagents and their diffusion according to the size of molecules and compatibility with the dermis [16, 25]. A structural idea about the structure of collagen plays an essential role in understanding the formation of the dermis volume, its structure and porosity fixing [26].

The gradual formation of natural materials provides the corresponding porosity, the amount of protein substance per unit of volume, the average angle of inclination of bundles to the surface of the dermis, the number of intermolecular bridges and the strength of cohesive bonds of adjacent microstructure elements [27, 28]. All these indicators affect the mechanical properties of the finished material. In this case, the porosity is determined by the degree of separation of collagen structural elements and formation of the dermis volume. During the treatment of animal hides and skins, there occur dynamic disorders of various types of bonds between the structural elements of the dermis of raw materials and the formed bonds under the influence of chemical reagents.

The native dermis of animal hides and skins contains up to 75 % of water against the dry mass, which is bound with collagen as a result of its hydration, diffusion swelling, wetting and capillary condensation [11, 12, 24, 29]. When swelling in water, elements of the dermis structure increase in volume, and the intervals between them decrease. During the drying of the native dermis, the adhesion of structural elements occurs in the air atmosphere and it leads to the disappearance of pores. This is confirmed by the fact that the specific mass of collagen, according to the results of mercurial porosimetry, corresponds to its actual specific mass [24]. And the use of organic liquids makes it possible to avoid adhesion of the dermis, preventing pore size reduction, but it does not prevent collagen macromolecules convergence [30]. According to the analysis of the skin by volumetric method [31], the total pore volume after disinfection with the ethyl alcohol of the native structure is 43.7 %, which corresponds to the volume of open pores.

Compared with collagen, keratin is less hydrophilic, despite the fact that it has a higher concentration of polar groups (**Table 1.4**) [9, 32].

Table 1.4

Amino acid composition of collagen and keratin in the wool

Amino acid	Content of amino acids, mol. %				
	molecule	hair	cuticle	epicuticle	cortical layer
Glycine	32.85	7.93	9.61	14.27	8.86
Alanine	11.62	4.92	5.66	4.28	5.17
Valine	2.15	5.09	6.59	5.32	5.28
Leucine	2.46	7.08	5.98	5.07	7.27
Isoleucine	0.94	2.88	2.53	2.34	3.04
Methionine	0.62	0.46	0.38	0.03	0.41
Phenylalanine	1.21	2.68	1.86	1.72	2.90
Aspartic acid	2.81	5.87	3.92	5.42	6.29
Glutamic acid	4.61	10.98	8.94	9.91	10.81
Asparagine	1.66	0.00	0.00	0.00	0.00
Glutamine	2.74	0.00	0.00	0.00	0.00
Lysine	2.84	2.82	2.88	4.49	2.65
Histidine	0.45	0.86	0.96	0.96	0.70
Hydroxylysine	0.59	0.00	0.00	0.00	0.00
Argenine	5.10	6.30	4.79	3.97	6.34
Serine	3.33	9.45	13.55	12.69	9.57
Threonine	1.60	5.99	4.91	3.34	5.18
Proline	11.48	5.46	9.29	5.39	5.51
Hydroxyproline	10.48	0.00	0.00	0.00	0.00
Tyrosine	0.45	3.66	2.92	1.92	3.89
Cysteine	0.00	9.67	14.43	0.31	8.57
Cysteine acid	0.00	0.07	0.36	10.76	0.13
Ornithine*	0.00	0.03	0.17	0.68	0.01
Citrulline*	0.00	0.04	0.31	0.15	0.00

* Secondary transformation products in keratin

This can be explained by the presence of a large number of disulfide bonds in its molecules, which are formed along the polypeptide chains and between them, stabilizing the protein macromolecules; by significantly less availability of functional groups to interact with chemical reagents.

As for the amino acid composition, keratin significantly differs from collagen. Thus, the content of destabilizing amino acids (aspartic and glutamic acid, serine and glycine) is higher by two-four times, respectively. However, stabilizing amino acids (alanine and leucine) are less by two-three times. The presence of a large amount of cystine in the keratin, which is absent in collagen, results in a higher stability and lower chemical activity of keratin.

In keratin, unlike collagen, three, seven or eleven macromolecules are combined into a microfibril depending on the type of the hair, and they are its basic structural element. The structure of the hair is marked by a non-uniformity in the cross-section and has the smallest density in the cortical layer, and the largest — in the cuticle one. At the same time, peptide bonds of keratin are sufficiently resistant to a short-term influence of acid solutions, especially at temperatures below 40 °C.

The kinetics of dehairing is determined by the presence of a dense stratum corneum of the epidermis [33, 34], which consists of keratinous, anucleated scale-like cells — corneocytes. They are formed of keratin microfibrils and have a shell of proteins and covalently bound lipids that interact with lipid intercellular spaces through hydrophobic segments. In this case, the stratum corneum of the epidermis is regenerated by means of the granular layer cells, where lamellar bodies (lamellae) are formed, which usually contain polar lipids and catabolic enzymes [35], which provide lipids with a keratinous layer. Lamellae are moved to the highest cellular granular layers due to cloning of the producing layer cells, then merge with plasmolemma and release their contents in the intercellular spaces. The resulting lipids gradually turn into intercellular scales, which are oriented almost in parallel to the surface of corneocyte cells. They are free fat acids, cholesterol and ceramides (**Fig. 1.3**), which completely fill the intercellular spaces of the stratum corneum [36], forming a barrier for the diffusion of reagents [37]. Interstructural layers at the suprastructure level are formed by Landman units consisting of two lipid, densely joint double layers. Physical and chemical properties of cells remain for a long time after removing the skin from the animal carcass [35]. As a result of such structural changes in the epidermis, a very dense packing of the stratum corneum is supported.

Keratin-phospholipid stratum corneum is a major obstacle for the diffusion of chemical reagents to the basement membrane. At the beginning of the hair removal, the diffusion of chemical reagents can occur mainly through the sweat glands and places where hair shafts emerge from the skin and sebaceous glands connected to them (Fig. 1.4). The diffusion of reagents through the epidermis is also possible in the intercellular and transcellular way (Fig. 1.3). In this case, due to the practical impermeability of the epidermis stratum corneum, the diffusion of chemical reagents can occur along a winding path between corneocytes. Their transportation is significantly facilitated in the presence of defects in the stratum corneum, which are formed due to mechanical and chemical influences during the appropriate treatment of hides. Keratin has a high density of the hair surface layer and therefore less

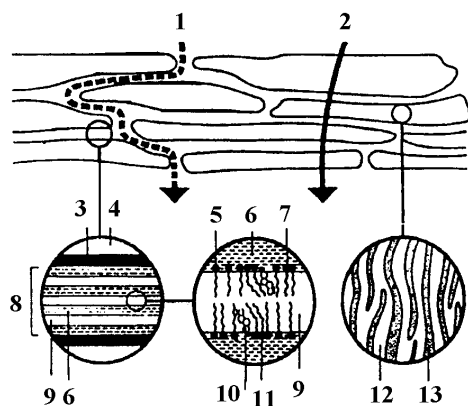


Fig. 1.3. Possible micro-ways of reagent diffusion through the dermis of the hide: 1 – intercellular, 2 – transcellular, 3 – plasma membrane, 4 – cytoplasm of the cell, 5 – fatty acid, 6 – water, 7 – ceramide, 8 – intercellular gap, 9 – lipid, 10 – cholesterol, 11 – transglyceride, 12 – minimum lipid, 13 – keratin

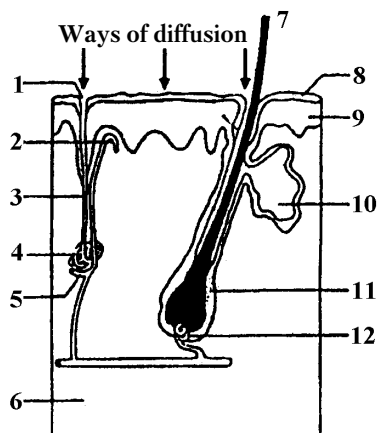


Fig. 1.4. Possible ways of reagent diffusion to the basement membrane: 1 – sweat gland, 2 – subepidermal capillary, 3 – exocrine sweat duct, 4 – gland, 5 – choroids plexus, 6 – dermis, 7 – hair shaft, 8 – stratum corneum, 9 – viable epidermis, 10 – sebaceous gland, 11 – hair follicle, 12 – dermal papilla

accessibility of functional groups of macromolecules to various types of external influences.

Therefore, the dermis of leather and fur raw materials is characterized by a complex fibrous hydrophilic and hydrophobic hierarchical structure formed by polypeptide biopolymer molecules. That is why its technological treatment is multi-stage, and only performing effectively all physical and chemical processes with the use of a wide range of chemical reagents, it is possible to obtain leather and fur materials with the required operational, hygienic and consumer properties [26, 38].

1.2. Electro-surface properties of collagen in the dermis

In technological solutions that come in contact with collagen, the interaction between particles of chemical compounds can lead to their adhesion. Similar processes occur between them and the structural elements of collagen that sorb fixing chemical compounds. The mechanism of such colloidal and chemical phenomena is complicated and depends on the dispersion and stability of chemical systems.

According to modern views about the course of technological processes [39–44], the effect of chemical reagents on the structure of the dermis should be regarded as a complex process that covers simpler, interconnected processes, which occur both gradually and simultaneously. Thus, any technological process begins with the mass transfer and diffusion of the chemical compound particles from the capillaries to the active centers of the direct contact in the dermis. At the same time, there is an adsorption interaction and the formation of chemical bonds between the functional groups of collagen and the chemical compound. The interconnection of such phenomena is that each stage of the process is predetermined by the previous one and vice versa. During the interaction of reactive groups of collagen with chemical compounds, a significant role is played by surface forces that regulate the diffusion of particles and depend on the nature of the interacting phases.

The diffusion of chemical compounds into the dermis collagen is caused by electrostatic interactions. The attraction between differently

charged ions (particles) and repulsion between the same charged ones manifests itself at a distance between them up to 10 nm and is determined by surface forces of a long action [45]. Chemical interaction occurs only at a distance less than 0.4 nm, and it is accompanied by the formation of covalent and hydrogen bonds. It affects the diffusion of chemical reagents into the dermis structure and provides a strong fixation of collagen fibrils.

A significant role in ensuring effective mass transfer and equal distribution of particles and molecules of chemical compounds in relation to the active centers of collagen is played by surface forces. A different diffusion rate and the binding of oppositely charged particles with the protein structure and the emergence of a potential difference between collagen and the working solution is determined by the predominant adsorption of one type of ions (particles) [20]. Identifying the role of electric-surface phenomena in the diffusion processes of particles or molecules of a chemical compound into the collagen structure makes it possible to predict the efficiency of technological processes that are accompanied by structural transformations. Most of the scientific papers [46–52] are devoted to certain stages of chemical or physical changes in the collagen structure, the result of which is the disclosure of chemical interactions of substances with functional groups of collagen or their physical diffusion into the capillary porous structure of the dermis biopolymer of animal hides.

Far-range surface forces affect not only the monolayer of the phase separation boundary but also act at a distance of tens and hundreds of molecules adjacent to the surface layers [45]. In contrast to the homogeneous bulk phase, in the transition zone between the two phases there is a field of electrical and molecular forces that fades as it deepens into each adjacent phase. Surface forces cause the appearance and equilibrium of the interfacial tension and interphase potential jump and include intermolecular, ion-electrostatic and structural interaction forces. Lyophilic systems, which can include the collagen structure of the dermis, are characterized by the formation of boundary layers of a solvent with a special structure, which necessitates the account of structural interaction forces in the balance. Thus, in “collagen — a chemical particle” colloidal systems, there exist forces of attraction of

the intermolecular nature and the forces of repulsion of electrical and structural origin between the reagent particles and collagen fibrils. The result of collision of particles with the surface of collagen structural elements depends on the ratio of attraction and repulsion forces.

In explaining the colloid-chemical processes of diffusion and fixation of chemical particles by the surface of the collagen structure, one must take into account the geometric state of each surface. Because of the hierarchical structure of collagen, its structural elements are considered as cylinders, then the contact with particles of chemical compounds can occur on its flat surface. In this case, the colloidal particle of the chemical compound tends to have a spherical structure with radius r or a section that characterizes its dimensions. At the same time, the balance of surface forces at the presence of colloid-chemical interactions of surfaces and particles, considering their structural and charge characteristics, makes it possible to formulate the fundamentals of technological processes of structural transformations of the dermis taking into account the electrochemical behavior of collagen:

- the formation of the dermis structure, which is the result of the progressive, consistent physical and chemical effects of chemical substances in the aquatic medium, is associated with basic structural and electrochemical transformations of the dermis collagen;
- the influence of chemical reagents on the properties of a biopolymer is their diffusion and distribution in the collagen structure of the dermis at the first stage of treatment and subsequent chemical interaction between the functional groups of collagen and the chemical compound;
- diffusion mass transfer of chemical particles and their interaction with collagen of the dermis regulate the near-range and long-range surface forces, covering the ratio of attraction and repulsion forces between the contacting surfaces, collagen structure and a chemical particle;
- for effective diffusion of the chemical compound into the structure of the dermis, it is necessary for the colloidal system to be characterized by aggregation stability under the influence of long-range surface forces; for the repulsion forces between the surface of the collagen structure and the particles of the

chemical compound to prevail over the forces of their attraction, the minimum distance between the contact surfaces should be determined by a potential barrier [60] $\Delta U_1 = 5 \div 15 kT$, where ΔU_1 is a potential barrier preventing the particle convergence, k – Boltzmann constant, T – temperature, K;

- for a strong fixation and bonding between functional groups of collagen and a chemical particle it is necessary that the forces of attraction between the surface of the collagen structure and particles of the chemical compound, on the contrary, prevail over the forces of their repulsion, the long-range surface forces become the chemical forces of the near-action, and the distance between the contact surfaces was less than the distance corresponding to the potential barrier $\Delta U_1 = 5 \div 15 kT$;
- diffusion and fixation of chemical compounds in the dermis are caused by structural and charge characteristics of both collagen and the chemical particle, covering the sizes of the capillary-porous dermis structure, the radius of the chemical compound particle, taking into account their ratio and charges, and the electrokinetic potentials of surfaces. The intensity and range of surface forces are determined not only by their sizes, but also by the magnitude of potentials of the particle and the structural element of the surface.

In general, the effectiveness of purposeful changes in physical and chemical properties of collagen of the dermis, controlled by surface forces both at the diffusion stage and during the interaction of chemical reagents with collagen, depends on the structural-sorption and electrochemical characteristics of the dermis. The presence of various ionogenic groups in the polypeptide chains of collagen plays an important role in stabilizing its structure and determines the reactivity towards other substances. Due to the simultaneous presence of acid and basic groups, the dermis behaves like a typical ampholytic, that is, depending on the *pH* of the medium can carry both positive and negative electrical charges. At the same time, in the native state there is a mutual compensation of positively and negatively charged biopolymer groups corresponding to the isoelectric state, and the *pH* value – to the isoelectric point of the collagen (IEP). It has been long established for proteins [53] that at

the IEP, there is an appropriate correlation between the concentration of H^+ -ions and the constants of electrolytic dissociation of water K_w , hydrogen solutions of the basic K_{bas} and the acidic K_a forms of collagen:

$$[H^+] = \sqrt{K_\kappa K_w / K_{basic}} .$$

In solutions of electrolytes, the pH value, which characterizes the IEP of ampholyte, decreases or increases. The charge of the dermis in this case is determined not only by the presence of H^+ and OH^- -collagen ions, but also by the anion and cation of the electrolyte. In the case of absorption of the same number of H^+ and OH^- ions by an ampholyte, the collagen of the dermis is in the isoionic state [54], which corresponds to the point of zero charge (PZC). Only for the native state of collagen, the IEP and PZC coincide by the pH values.

According to the pH , the IEP and PZC of the dermis determine the structural stability of the collagen organization and its mechanical properties. The collagen of the dermis with the pH of the IET and the possible simultaneous electrolytic dissociation of carboxyl and amino groups can form a double ion — a zwitterion:



This assumption confirms the nature of changes in the mechanical properties of the dermis: strength, hardness, resistance to friction, etc. (Fig. 1.5).

It is possible that in acidic and basic zones of the pH , there is a mutual electrostatic repulsion of the same charges arranged along the polypeptide chain, which dramatically reduces the strength of the dermis. This significantly simplifies friction and shredding of the dermis and obtaining stable dispersions of

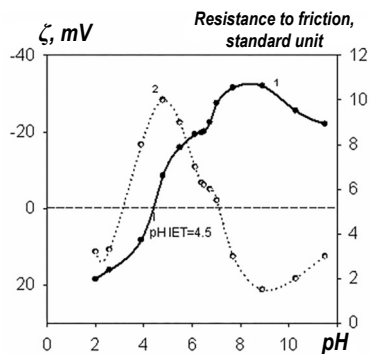


Fig. 1.5. Dependence of electrochemical (1) and mechanical (2) indicators of collagen of the dermis on the pH medium

the biopolymer. On the contrary, in the zone of the pH of the IET, due to the mutual attraction of different charges, the strength of the dermis is maximal, which significantly slows down and complicates friction and shredding and destabilizes the stability of the biopolymer dispersion. Undoubtedly, such interactions of charges accompany the corresponding conformational changes in the hierarchical structure of collagen, which determines the mechanical properties of the dermis.

The IEP and PZC values are closely interconnected with their acidic and basic properties, that is why the identification and study of the relationship in accordance with the basic technological processes will contribute not only to the disclosure of the mechanisms of leather production, but also to the optimization and regulation of the technological conditions of collagen treatment. Due to effective chemical effects on the collagen structure of the dermis during the main technological stages of leather production and the corresponding chemical interactions with the main reactive-capable protein groups, the magnitude and type of charge of the collagen element surface are constantly changing. Such transformations result in shifting the pH of the IEP and PZC of protein, respectively, which significantly changes both its acidic and basic properties, and electrochemical characteristics. The physical effects of such changes are connected with structural transformations and corresponding changes in structural and sorption properties of the collagen organization, which in turn determines the accessibility of the dermis to diffusion, mass transfer and fixation of chemical substances in its structure.

In this regard, for the analysis of electrochemical and structural characteristics of collagen at the main technological stages of leather production, samples of the corresponding state of the dermis have been obtained according to the standard technology of production of elastic upper shoe leather. Applying a wide range of colloidal and chemical methods for determining adsorption parameters of the dermis, one can estimate the specific surface of the collagen structure of the dermis at various stages of its transformation and formation (**Table 1.5**).

The use of the methylene blue adsorption method for the study of adsorption parameters of the semi-finished product after chrome tanning can not be considered reliable, since the charge of the same name on the surface of the structural elements of the dermis and the cations

Table 1.5

Adsorption parameters of the collagen structure of the dermis [55]

Adsorbent	Specific surface of a semi-finished product, m ² /g, after					
	Chrome tanning	neutralization	organic retanning	mineral filling	liquid colouring	emulsion greasing
1. Methylene blue	—	14.6	24.7	58.5	—	—
2. Nitrogen	12.1	21.4	19.6	25.6	21.4	8.2
3. Nitrogen	16.7	29.5	26.5	35.7	28.9	11.3
4. Octane	216.0	—	197.0	195.0	—	—

Note. Methods that have been used: 1 – adsorbent, 2 – BET method, 3 – Langmuir method, 4 – ECP method

of the dye causes electrostatic repulsion, which inhibits the diffusion into the semi-finished product and fixation of the methylene blue cations therein. Neutralization and reduction of positive charges of the surface in accordance with the technological treatment contributes to the increase in the dye adsorption and the specific surface of the dermis structure. A similar tendency and a sharp increase in the level of adsorption and, consequently, in the specific surface of the samples occur at the stages of liquid finishing, which involves the implementation of standard retanning and mineral filling. The dominant contribution to this tendency is the filling of the semi-finished product with the MMT modified dispersion. Due to the dispersion and highly developed specific surface with the level of 750 m²/g, the mineral particles are adsorbed, shielding structural elements of the dermis and creating an anti-adhesive layer on their surfaces. In this way, they prevent adhesion and increase the accessibility of the structure to the diffusion of chemical reagents at subsequent technological stages of its treatment.

According to **Table 1.3** the determined values of the specific surface of the dermis by different methods have significant differences. This is due to the difference in the nature of adsorbates and sizes of their molecules, which are used to evaluate the adsorption parameters. Therefore, the micropores of the dermis are less accessible for the

adsorption of organic cations of a methylene blue dye ($\omega_0 = 135 \text{ \AA}^2$, where ω_0 – the area occupied by the adsorbed molecule) compared with a low molecular sorbate. It should be noted that adsorption of nitrogen is insensitive to the nature of the dermis surface. Taking into account the smaller size of the nitrogen molecule ($\omega_0 = 13\text{--}14 \text{ \AA}^2$), higher surface area values should be expected than those actually obtained. Presumably, a low temperature of a liquid nitrogen (-193 K), according to the BET research method, causes the consolidation of the collagen structure that leads to significantly lower values. This, in turn, affects the obtaining of abnormally high values of the density of the surface charge of the dermis. Significantly higher values of the specific surface area of $216.0\text{--}195.0 \text{ m}^2/\text{g}$, obtained by studying the adsorption parameters by the ECP method, characterize the greater accessibility of the dermis structure after the application of appropriate technologies. This makes it possible to estimate the surface charge density and the corresponding electrochemical properties of collagen, taking into account technological treatments.

An informative way of identifying the nature of changes in the acid-base and electro-surface properties of collagen of the dermis in the course of treatment is the overlapping of the potentiometric titration curves of protein dispersions after the technological processes in the presence of an indifferent electrolyte of 0.1 M . The results of the potentiometric titration and the data of the specific surface of the dermis (**Table 1.5**) permitted to estimate the amount of bound acid and alkali depending on the *pH*-medium and determine the corresponding surface-charge density and the PZC of the dermis after the main technological processes of the leather production. Together with the parameters of the electrokinetic ζ -potential of the dermis and the corresponding values of the IEP dependence on the *pH* of the medium, these data are necessary for controlling, optimizing and forecasting the technology of leather production.

The influence of the main technological processes of leather production on the acid-base properties of the dermis is clearly traceable during the dependence analysis of $\Delta pH = f(pH_{eq})$, where $\Delta pH = pH_0 - pH_p$ corresponds to the difference between the *pH* of the initial background solution and the *pH* of the equilibrium dermis suspension (**Fig. 1.6**).

Thus, the amplitude of ΔpH changes decreases in the direction from the semi-finished product, dehaired before chrome tanning. If for the native dermis the pH value of the IEP coincides with the PZC and corresponds to 6.5 and quantitatively confirms the collagen amphotericity through the equilibrium of positive and negative charges, the number of acidic groups of the dermis predominates in the state of the pelt (dehaired semi-finished product). The basic volume of the pelt by a quantitative value is higher than the corresponding indicator for the native derma, and the acidic one is much lower by the data [14]. This explains that the true maximum binding of the acid can only be achieved at the pH of 1–2. In addition, the values of the dissociation constants pK for $-NH_2$ – and $-COOH$ -groups can vary considerably under the influence of the near position of polar groups in the dermis structure [3, 29].

According to the analysis of the titration curves, all subsequent processes lead to a decrease in the amount of absorbed alkali, that is, to a decrease in the number of $-COOH$ -groups. The maximum reduction of the alkaline capacity of collagen is observed after chrome tanning and filling. This is due to the entry of a large number of carboxyl groups during tanning into the inner sphere of the chrome complex and blocking its ability to interact with alkali.

The data from **Fig. 1.6** indicate violations of the acid-base equilibrium under the influence of technological treatments. The intersection of dependencies $\Delta pH = f(pH_{eq})$ with the pH_p axis corresponds to the

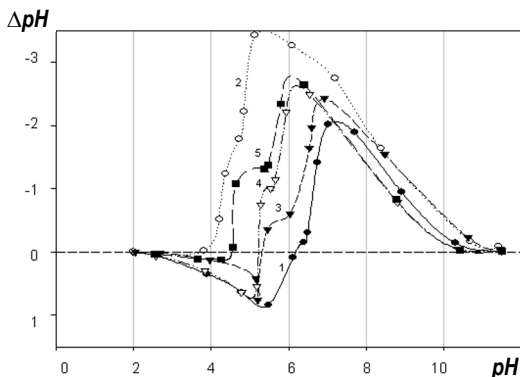


Fig. 1.6. The shift of pH 0.01 M of the solution KCl from its equilibrium value pH (ΔH) after its contact with the dermis at different technological stages of the semi-finished product treatment: 1 – the pelt, 2 – of chrome tanning, 3 – filled with montmorillonite, 4 – dyed, 5 – greased

PZC as for the state of the dermis. The PZC for dehaired semi-finished products at the $pH = 6.3$ after chrome tanning is significantly shifted to the acid zone from the PZC at the pH level of 3.8–4.0, and subsequent liquid treatment processes move the PZC to a more neutral zone. A comparison of the dependencies of charge characteristics on the pH at each technological stage, taking into account the previous process of treatment, makes it possible to analyze the change in the charge and potential of the dermis.

The analysis of co-located dependences of the ζ -potential and the surface charge density σ_0 of the dehaired semi-finished product of the basic treatment (the pelt) on the pH of the medium with a constant ionic strength of the background solution *KCl* allows us to substantiate the following ideas:

- the position of the IEP and PZC of the pelt indicates that its acidic character is more than the alkaline one;
- the position of the IEP of the pelt ($pH = 4.3$) and the zone of negative and positive charge of the dermis surface characterize the degree of affinity of the dermis to anionic or cationic substances;
- S-shaped nature of the dependence of the charge and the potential of the dermis on the pH of the medium indicates the dissociative mechanism of the origin of the electric charge of the dermis;
- the limits of changes in the charge density of the dermis σ_0 ($10\text{--}150 \mu\text{C}/\text{cm}^2$) make it possible to label it as a high-charged colloidal and chemical object in the pH range from 2.0 to 12.0 and a low-charged one – in the pH range from 3.5 to 7.0;
- the plateau zone with a minimum charge, which depends on $\sigma_0 = f(pH)$ ($pH = 3.5\text{--}7.0$), indicates the area of maximum stability of the dermis to acid and alkaline treatments (**Fig. 1.7**).

Chrome tanning sharply changes the nature of dependence of ζ -potential of the dermis on the pH of the medium (**Fig. 1.8**). This occurs primarily due to the recharge of the surface of collagen structural elements (CSE) of the dermis, which acquires a positive charge within the pH range of 2.0–7.5, and the shift of the entire dependence to the alkaline zone by more than 3 units of the pH .

The interaction of the dermis with chromium sulfate tannin is accompanied by strong charge effects, and it manifests itself in the shift

of the PZC to the acid zone from the pH of 6.0 to 4.0 and the simultaneous shift of the IEP to the opposite positive pH zone from 4.3 to 7.5 (Fig. 1.8 and 1.9). Compared to the pelt, the charge density of the chrome tanned dermis in the acidic and, in particular, in the alkaline zone, the pH is reduced (Fig. 1.9), that confirms the participation of carboxylic and amino groups in the interaction with chrome polyoxycations and their entry into the internal coordination sphere of chrome complexes.

The level of a negative charge reduction indicates that only by $\sim 1/10$ part, the $COOH$ -groups link themselves to chrome complexes. However, since the adsorption of cationic complexes often reaches 50–60 % of amino acid residues in the collagen structure [3, 18, 29], along with coordination bonds, electro-valence ones are formed between the ionized collagen groups and the complex chromium ions of the opposite charge, which accompany the van der Waals forces of attraction. In accordance with Fig. 1.9 and 1.10, the stability area of the semi-finished chrome tanned product is limited by the pH values of 2.0–7.0. Beyond these borders, detanning of the dermis occurs.

In accordance with [56], such phenomena as surface recharging and significant shifts of the IEP and PZC are caused by the specific adsorption of ions. The direction of the shift points to the sign of the ion, which is adsorbed predominantly in a specific way. If it is an anion, the ΔPZC has a positive sign and the ΔIEP – a negative one. The signs change during cation adsorption. Depending on the dermis, for which the potential significant ions are H^+ and OH^- and which determine the values of its IEP and PZC in the absence of specific adsorption, the IEP and PZC coincide. However, after dosing an electrolyte, for example, a

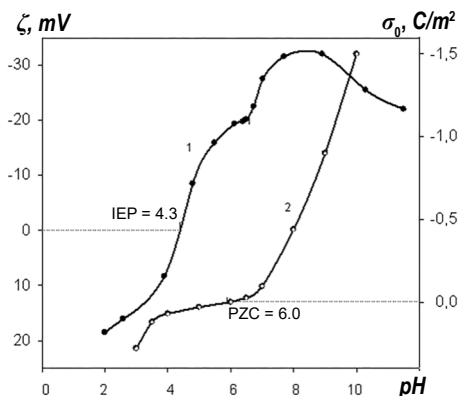


Fig. 1.7. Dependence of ζ -potential of the pelt (1) and density of its surface charge σ_0 (2) on the pH -system with a steady ionic force KCl of 0,01M

solution of the main chromium sulfate during the tanning of the pelt, hydrochromate cations are adsorbed specifically, and SO_4^{2-} anions – only non-specifically due to electrostatic forces. In this situation, complex chromium cations accumulate on the surface of the available CSEs and significantly affect the equilibrium of the H^+ and OH^- -ions while determining the PZC before the adsorption of $\Gamma_{H^+} = \Gamma_{OH^-}$ chromium ions, and after the adsorption of $\Gamma_{H^+} < \Gamma_{OH^-}$, as the adsorption of OH^- hydroxyls increases and H^+ protons decreases under the influence of a positive charge of the chromium cation. To restore the condition of the PZC ($\Gamma_{H^+} = \Gamma_{OH^-}$), it is necessary to increase the concentration of H^+ -ions in the appropriate volume. Therefore, after the chrome tanning, the PZC is theoretically and practically (**Fig. 1.8** and **1.9**) shifted to the acid zone.

As a result of the specific adsorption of hydroxychromium cations, the ζ -potential becomes more electropositive, and the IEP of the chrome tanned dermis can be achieved due to the adsorption of more hydroxyl OH^- -ions. Thus, the IEP of the dermis after chrome tanning with cationic chrome complexes is shifted to the alkaline zone (**Fig. 1.8**).

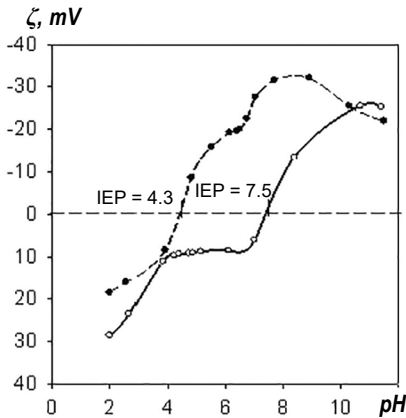


Fig. 1.8. Dependence of ζ -potential of the pelt (1) and the chrome-tanned semi-finished product (2) on pH -system with a constant ion force of the background solution KCl 0.01M

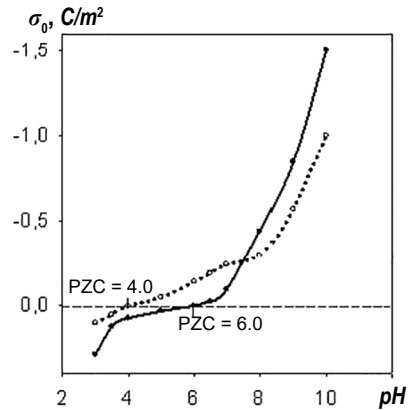


Fig. 1.9. Dependence of a surface charge σ_0 of the pelt (1) and the chrome-tanned semi-finished product (2) on (2) on the pH -system

A similar trend is also reproduced during the specific adsorption of anions, which is common for technological processes of liquid finishing with negatively charged particles – retanning, filling, colouring and greasing of the semi-finished product. **Table 1.6** presents a comprehensive assessment of changes in the acid-base properties of collagen of the hide dermis according to the type of its technological treatment. The most significant charge changes are observed for the pelt and chrome semi-finished products.

Developed for leather production, the neutralization of the semi-finished chrome tanned product fosters further strengthening of the bonds of fixed chrome complexes and their modification through the displacement of acid residues from the internal sphere by functional groups of collagen and the entry of neutralizing agents, including hydroxyl groups, into the complex of anionic residues. It is an additional entry into the inner sphere of chrome complexes during the neutralization of *COOH*-groups of collagen that explains the effect of the PZC shift of the neutralized semi-finished product to the *pH* of 4.0, and the density of the dermis increasing the *pH* > 7 decreases (**Fig. 1.10**). The degree of neutralization is of positive significance for the subsequent liquid finishing processes

Table 1.6

The *pH* value of the isoelectric point and the point of zero charge of the dermis at various technological stages of its treatment

Dermis		<i>pH</i> values at	
		PZC	IEP
Raw stock		6.5	
Semi-finished product	dehaired	6.0	4.3
	of chrome tanning	3.8	7.5
	neutralized	4.0	5.2
	retanning with organic compounds	4.5	4.8
	of mineral filling	5.0	4.3
	coloured	5.0	3.3
	of emulsion greasing	4.5	3.8

and it determines the quality of the finished leather. In contrast to the changes in the electric surface characteristics of the pelt, which lead to structural transformations of the protein, the reason for the PZC shift of the semi-finished chrome tanned product and the subsequent liquid finishing processes is connected with the specific adsorption of anions in the dense part of the double electric layer (the Stern layer).

Further processes of liquid finishing of the semi-finished product have a lesser effect on the change of the acid-base properties of collagen and its electrochemical behavior, but are more directed towards its volume formation, and therefore provide treatments with such chemical materials that would ensure the fixation of porosity, filling of the structure, increasing the density of the outer layer. The influence of organic tanning materials of anionic nature on the transformation of the dermis during standard organic retanning is accompanied by the PZC shift of the neutralized semi-finished product with the pH from 4.0 to 4.5 (Fig. 1.11). This is characterized by almost a twice reduction of the charge density of the dermis throughout the pH range, which

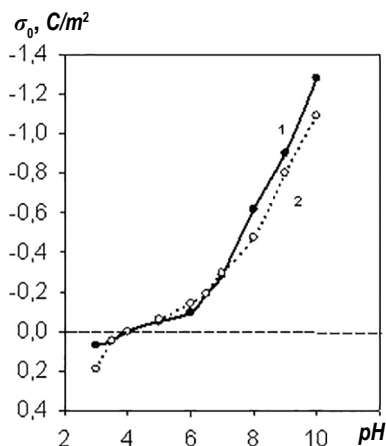


Fig. 1.10. Dependence of surface charge density σ_0 of the chrome-tanned semi-finished product (1) and neutralized (2) on the pH of the medium

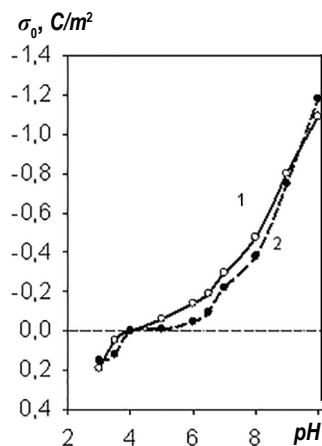


Fig. 1.11. Dependence of surface charge density of the semi-finished product σ_0 neutralized (1) and retanned with organic compounds (2) on the pH of the medium

positively affects the diffusion quality of chemical compounds for the subsequent liquid treatment processes.

The general tasks of filling the semi-finished product are equalizing the thickness and density of the leather according to hide sections, increasing the material's resistance to external influences and forming a volume structure of the dermis. Due to the similarity of the effects achieved after the action of organic tanning materials, in practice, vegetable and synthetic tanning agents are used for filling. At the same time, the filling process is carried out differentially depending on the purpose of the leather material.

During the production of leather with a natural outer layer, two-phase retanning is used. In the first phase, synthetic tanning agents are used and they give the surface tenderness, density and ability to be uniformly painted over. The second phase is associated with the use of tannin tanning, which fills well and increases the volume output of the finished leather. In accordance with colloid and chemical changes, synthetic tanning materials lower a positive charge of the dermis that prevents the tannin binding by the dermis on the outer and flesh surfaces and contributes to the diffusion of the latter into the depth of the structure.

In modern leather production, water soluble polymers are widely used as fillers. Unlike aqueous dispersions of polymers that reduce the hydrophilicity of leather material, their hygienic properties, surface yield [56], water soluble polymers can chemically interact with collagen, form additional cross-sectional links of the “protein-polymer-protein” type or “protein-polymer-tanning material-protein” one and, therefore, structure and fill the dermis.

Among the most common polymer fillers, acrylates increase the shrinkage resistance of the dermis during dehumidification, and storing material, prevent its drying and strength retrogression. However, a significant influence on the formation of the structure of the dermis is made by mineral fillers, which are modified dispersions of montmorillonite. Their application is accompanied by many positive effects, which are manifested in increasing the volume yield of the dermis and are the following:

- reverse structuring as a result of filling;
- preventing adhesion of the dermis microstructure due to the shielding of active centers of the surface of the structural elements;

- the damping effect of MMT particles fixed by the dermis during deformation and drying of the semi-finished product, which ensures fixation, preservation of porosity and an optimal angle of collagen bundle that prevents shrinkage of the structure.

As a result of filling and shielding of active centers of the structural elements of the dermis, there is a decrease in the density of the surface charge of the dermis (**Fig. 1.12, 1.13**) and the grading of electrochemical properties of the semi-finished product: $pH_{IEP} \approx pH_{PZC} \approx 4.3-5.0$ (**Table 1.6**). At the same time, organic retanning and filling of the chrome tanned semi-finished product with negatively charged particles of montmorillonite are accompanied by a change of its positive charge and ζ -potential on the negative (**Fig. 1.14**) within a wide range of the pH . At the same time, the IEP of the chrome semi-finished product is shifted from the pH of 7.5 to 4.3, that in the subsequent treatments contributes to its more qualitative dyeing and greasing [57].

Therefore, in retanning and filling processes, there is a shift of the IEP of the semi-finished product to the region with lower pH values, which later on will lead to a decrease in the degree of binding of

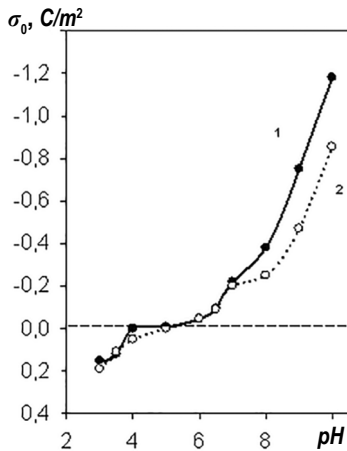


Fig. 1.12. Dependence of surface charge density of the organic retanned semi-finished product (1) and filled (2) on the pH -medium σ_0

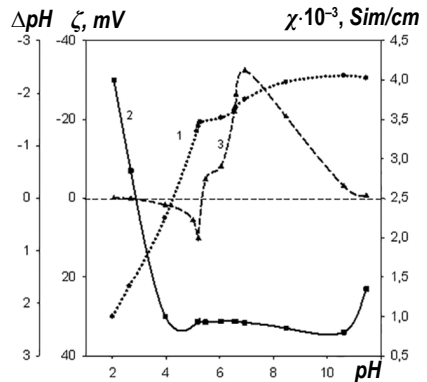


Fig. 1.13. Dependence of ζ -potential (1), specific electric conductivity (2) and density of the surface charge of the semi-finished product σ_0 (3) filled with a constant ionic force KCl 0.01M on the pH -medium

anionic dyes by the structure of the dermis and will facilitate the dye diffusion into the depth of the dermis. In this regard, the dyeing of the semi-finished product should start at the pH of the solution close to the pH of the IEP, and to fix the dye, it is necessary to reduce the pH to the specified electrochemical characteristics of collagen of the dermis. When coloring the chrome tanned semi-finished product with acid dyes, the pH of the solution is maintained within the range of 4.5–5.0.

During traditional coloring with anionic dyes, particularly with the direct black, the electrochemical properties of collagen of the dermis are significantly altered (**Fig. 1.15**). By doing so, the IEP of the dyed semi-finished product is shifted to the acid region to the pH of 3.25, and the PZC – to the pH of 5.0. In addition, the size of the negative ζ – potential increases. All charge effects are caused by the specific adsorption of the dye anions on the surface of the collagen structure elements.

At the final stage of the standard liquid finishing of the semi-finished product, emulsion greasing, the particles of the emulsion are diffused into the depth of the dermis, and after its splitting, they are adsorbed by structural elements. The absorption of greasing substances by the

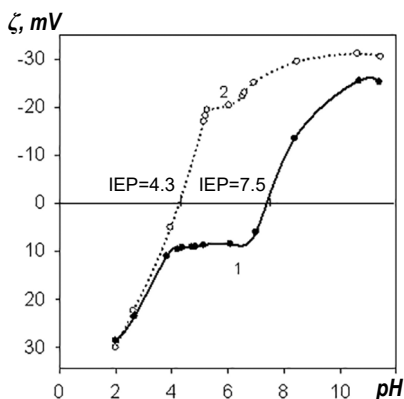


Fig. 1.14. Dependence of ζ -potential of the chrome tanned semi-finished product (1) and filled with montmorillonite (2) on the pH of the environment

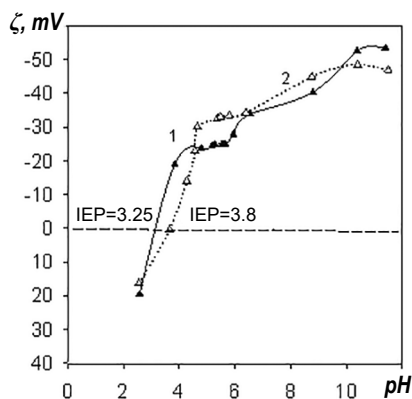


Fig. 1.15. Dependence of ζ -potential of the chrome tanned semi-finished product (1) and filled with montmorillonite (2) on the pH of the environment

semi-finished product and their distribution in the depth of the dermis, as a rule, depends on the chemical nature, electrochemical properties and aggregate stability of the greasing emulsion, the method of tanning and the nature of previous technological processes [26]. The charge and ζ -potential of the dermis caused by its pre-treatment are of particular importance. The smaller the ζ -potential between the surface of CSEs and the particles of the greasing emulsion, the deeper can diffuse the greasing materials into the depth of the semi-finished product.

For deep diffusion and increased uniformity of the distribution of greasing substances in the semi-finished product, it is important to provide its treatment at the pH close to the pH values of the IEP, which the dermis has gained after its pre-treatment. Moreover, the greasing effect of the semi-finished product on the electrical properties of collagen (**Table 1.6, Figure 1.16**) is in shifting the PZC to the acid zone from the pH of 5.0 to 4.5, and the IEP – to the pH of 3.8, which is due to the interaction of sulfo groups of the greasing material with the dermis, corresponding increase in collagen alkaline capacity and increase in a negative charge and ζ -potential of the semi-finished product.

A comparison of the dependences $\sigma_0 = f(pH)$ for the reticular and papillary layers of the dermis revealed some differences in their electrochemical behavior. It can be seen from **Fig. 1.17** that after almost all treatments, the curves of the dependences $\sigma_0 = f(pH)$ for the reticular layer, both in acidic and alkaline media, are characterized by higher intensity compared with the curves for the papillary layer. This behavior is determined by the different accessibility of the structure for the particles of chemical compounds, which determines different speed and the level of efficiency of a technological process.

The general dependences of the electro-surface properties of

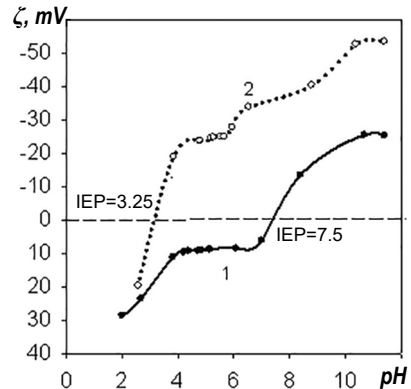


Fig. 1.16. Dependence of ζ -potential on the dyed (1) and greased semi-finished product (2) on the pH of the environment

collagen, which are given on the pH -dependences of charge density and ζ -potential during technological treatments (Fig. 1.18, 1.19), made it possible to reveal a natural decrease in the surface charge density of the dermis in both acidic and alkaline media, and gradual shift of curves into the zone with higher pH . Thus, taking into account the fact that the structure may be retained at $3 > pH > 7$ [3, 29], it is obvious that with each process of liquid finishing, in particular after filling, there is a gradual increase in the stability of the structure of the semi-finished product to the effects of external factors.

Performed according to the principles of electro-surface phenomena and the theory of colloid system stability, the study of electrochemical and structure-sorption properties of the dermis collagen at the basic technological stages of its treatment makes it possible to measure the optimal parameters concerning the effective diffusion and fixation of chemical substances in collagen structure. Weakly charged state of collagen structure and regions of a low surface charge density for every kind of semi-finished products define the pH limits for the effective diffusion and distribution of particles of chemical compounds in the depth of the dermis. The values of pH at the IEP and zones of positive and negative charge of the dermis point to the affinity of collagen

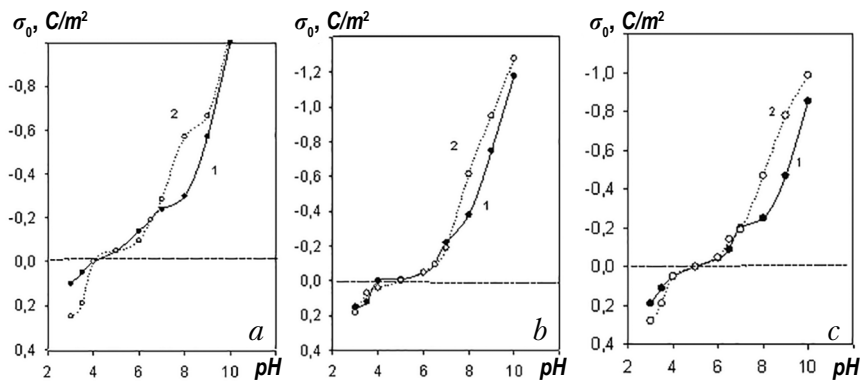


Fig. 1.17. Dependence of surface charge density on the pH of the medium of the semi-finished product: of chrome tanning (a), vegetable retanning (b), filled with montmorillonite (c) for the dermis layer
1 – papillary, 2 – reticular

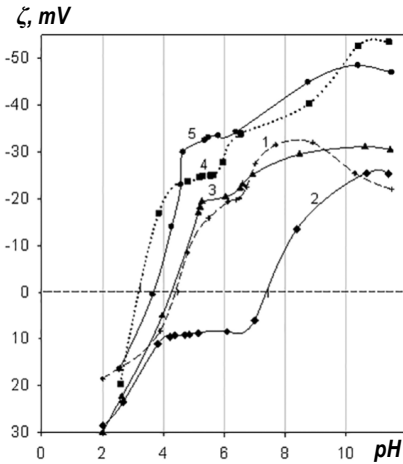


Fig. 1.18. Dependence ζ -potential of the dermis on the pH of the medium: 1 – pelt; the semi-finished product 2 – of chrome tanning; 3 – filled with montmorillonite; 4 – dyed; 5 – greased

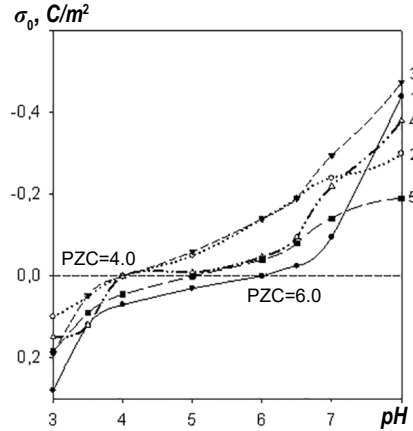


Fig. 1.19. Dependence of surface charge density σ_0 of the dermis on the pH of the medium of the semi-finished product: 1 – dehaired; 2 – of chrome tanning; 3 – neutralized; 4 – retanned with organic compounds; 5 – filled with montmorillonite

structure to the interaction with appropriate chemical compounds, leading to their effective diffusion or chemical fixation. Considering the changes in electrochemical properties of the semi-finished product, determined by the use of appropriate chemical materials, the course of technological treatments of the dermis in leather production can be predicted and monitored.

1.3. Structural transformations of raw materials in the treatment processes

While forming fur and leather materials, collagen and keratin are exposed to the action of reagents of different chemical activity with various sizes of molecules. A special role in the transformation

of collagen structure of the dermis is played by preparation processes, which involve its watering, separation of fibers, and removal of soluble proteins and other non-collagen constituents of a hide after the chemical action of alkaline reagents, enzymes and acids [58]. In addition, at the first stage of the process, cured rawhides are to be treated with water solutions of electrolytes. At the same time, reagents with minimal sizes of molecules are readily diffused into a hydrophilic dermis containing both soluble and insoluble components. Because of the pre-treatment, the hide dermis is close to the green condition by the content of water. At first, soluble proteins are removed from it, and then under the influence of an alkaline or acidic solution – hydrocarbon, fat substances, and the like. Furthermore, the alkaline solution is able to destroy the hair keratin, and in the case of a prolonged action of acid-salt solution on it, no noticeable changes are observed.

During the interaction of collagen with aqueous solution of reagents, the hydration of its molecules occurs. In this case, the intermolecular distances significantly and practically linearly increase (Fig. 1.20) [9, 12] in the studied interval of the dermis watering. An increase in the moisture of its collagen is accompanied by an increase in the cross-sectional area of fibrils while maintaining the cross-sectional area of molecules.

Thus, with a fixed length of microfibers and 60 % humidity, the cross-section area of fibrils will increase from 7.85×10^3 to $31.4 \times 10^3 \text{ nm}^2$, with intermolecular gaps increasing up to 0.6–0.8 nm, and inter-microfibrillary – up to 2.74 nm. That is, aqueous solutions of reagents actively influence the structure of collagen, especially on the microfibrillary level. Therefore, there are conditions for diffusion and effective interaction of reagents of larger molecule sizes.

Acid-salt treatment, in which partial dehydration of polypeptide

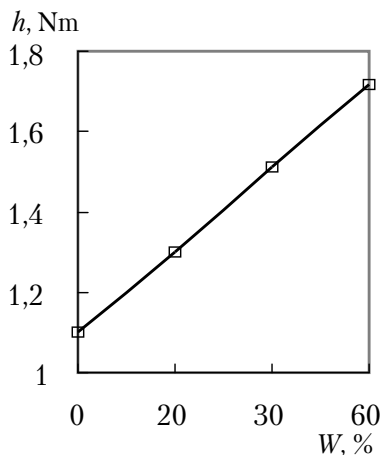


Fig. 1.20. Dependence of the distance between molecules on the content of water in collagen

chains of macromolecules and the growth of intermolecular gaps occur, facilitates the increase in interstructure distances in the dermis collagen, accompanied by an increase in the accessibility of collagen functional groups to the interaction with reagents. Unlike collagen, long acid-salt treatment of keratin, required to remove hydrocarbon compounds from the rawhide dermis, does not lead to significant structural changes in the hair. In the case of leather raw materials, degradation of the dermis collagen occurs during long alkaline treatment.

The character of structural changes of the dermis collagen is seen in the treatment of wet salted steerhides, which have the most uniform structure of the hide sections. Comprehensive studies on the change in the microstructure and sorption characteristics of water and water vapour absorption by the semi-finished product while forming the pelt and leather [59] make it possible to reveal the peculiarities of discharging of non-collagen formations by the dermis collagen structure and their substitution for cluster aqueous solutions [58, 60] of chemical reagents. Due to this, a raw hide has a consolidated fibrous structure after soaking, its fibers are combined into bundles, between which there are gaps filled with a technological solution (**Fig. 1.21a**) [27]. It is shown in the change in the amount of total capillary moisture from 81.0 to 109 % (**Table 1.7**). Appropriate chemical reagents force out cluster water at the first technological stage of leather formation. After this mechanism of the pelt and leather formation, a high speed of diffusion and appropriate reduction in the duration

Table 1.7

Sorption properties of the semi-finished product at different stages of rawhide treatment

Semi-finished product after the process of	Specific surface, m ² /g	Maximum sorption of water vapour, %	Absorbability, %	Total capillary moisture, %
Soaking of raw materials	47.0	45.0	57.0	81.0
Liming	108.0	48.0	59.0	93.0
Deliming and bating	119.0	55.0	64.0	109.0
Tanning	88.0	38.0	56.0	91.0

of soaking and liming processes are achieved. Under the action of a lime solution, the dermis structure is changing (**Fig. 1.21b**) due to a temporary structuring and formation of calcium-collagen complexes, expressed by the destruction of polypeptide bonds between the chains and formation of new cross-section bonds with the participation of calcium ions.

During the subsequent liming and bating, liming reagents, mucopolysaccharides, discharge from the dermis structure, and the content of water decreases. These changes are shown in **Fig. 1.22a** as clearly outlined bundles of fibers and enlarged gaps between them. Under the action of acid-salt treatment, a further dewatering of the dermis fibrillar structure occurs, which is fixed at the chemical structuring of HSCCs in the tanning process (**Fig. 1.22b**). In this case, elementary fibers of

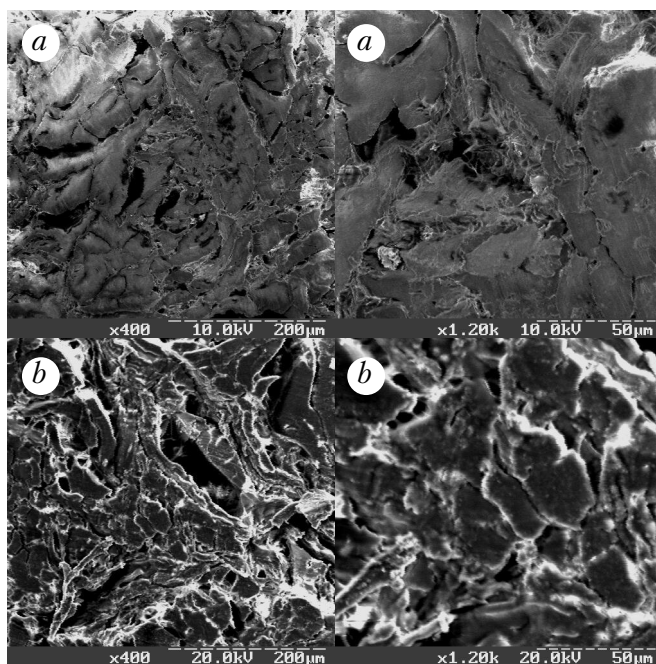


Fig. 1.21. Submicroscopic image of a cross-section hide cut after soaking (a) and alkali treatment (b)

the dermis collagen within 2mcm in size are well seen and they form a stabilized capillary cellular structure.

Possible formations of chemical bonds with the participation of HSCCs interacting with collagen macromolecules in the volume $1D$ of the microfibril section are given in **Fig. 1.23** [9], where dashed lines show possible interactions between the most active carboxyl groups of collagen macromolecules and hydroxosulphate chromium complexes (HSCCs) with the size of molecules 0.7 nm (**Fig. 1.24**) [61]. The bonds of the three types are possible and they are located between:

- adjacent polypeptide spirals, and their triads of amino acid residues are situated on the same or adjacent levels (the first type);
- amino acid residues that belong to the adjacent polypeptide spirals but are situated one-three triads farther (the second type);

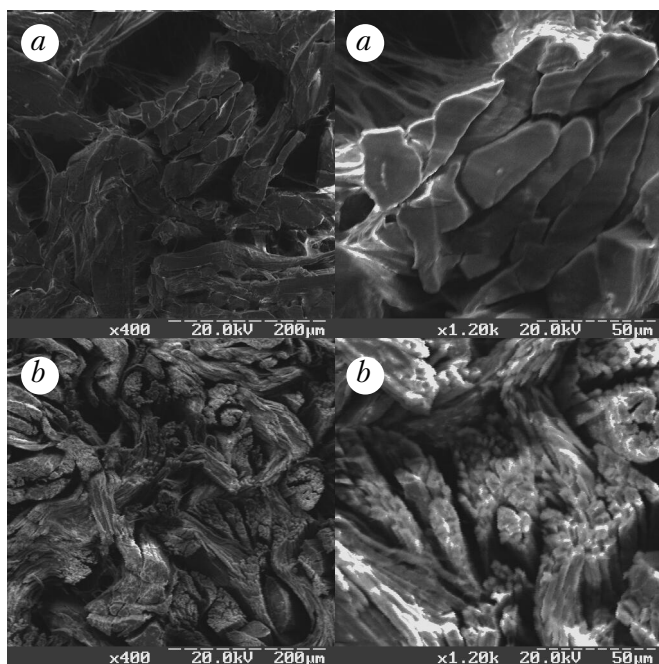


Fig. 1.22. Submicroscopic image of a hide cross-section cut after bating (a) and tanning (b)

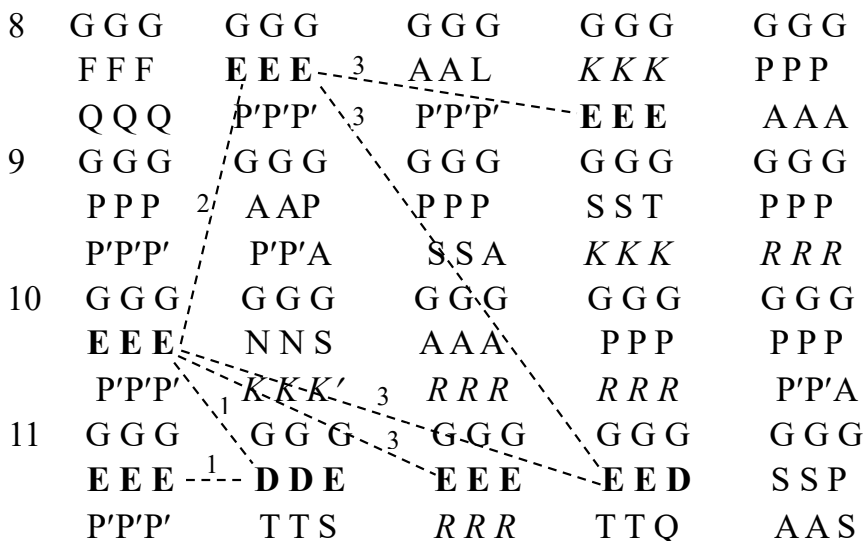


Fig. 1.23. Possible interactions of HSCCs with active groups of a microfibril

– amino acid residues, situated one polypeptide spiral farther on the same level and one or two triads farther (the third type).

The distances between ionized carboxyl groups of macromolecules, which depend on the types of bonds and their number in 1D volume of the microfibril section, are given in **Table 1.8** [9].

It can be seen from the Table that the number of active centres of collagen macromolecules, approachable for dinuclear HSCCs to

Table 1.8

**Equivalent number of possible bonds
in 1D-volume of a microfibril**

Type of bonds	Distance, nm	Number of bonds	
		internal	external
first	0.6–0.8	27	42
second	over 0.8 to 1.4 incl.	29	54
third	over 1.4	27	45

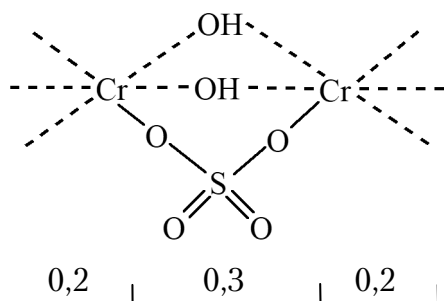


Fig. 1.24. Structure and size, nm, of hydroxosulphate chromium complexes

interact with carboxyl groups at the initial stage of collagen structure stabilization in their equivalent proportion to chromium (III) atom, amounts to 61 % of a total number of ionized carboxyl groups in 1D-volume of a microfibril being 226, and only 113 chromium (III) complexes can interact with them.

At the second stage of the collagen structure stabilization, the size of HSCCs grow due to their hydrolysis when alkalinizing the medium. In addition, hydroxo bridges are formed between chromium (III) cations and carboxyl groups, located at the distance of three- and four-nuclear complexes and interacting making bonds of the second type, become approachable for them. Additional 22 % of carboxyl groups can start interacting with chromium (III) complexes by this type of bonds. In the final phase of the second stage of the collagen structure stabilization due to furtherolation of chromium (III) complexes, located inside fibrils and on their surface, sulphate groups are pushed back from the adjacent zone of chromium and replaced with hydroxo bonds, which facilitates the formation of interstructural bonds of the third type. Furthermore, as the calculations show, with 100 % participation of carboxyl collagen groups in the interaction and bonding with one carboxyl group of one chromium atom, it is necessary to have 5.5 of Cr_2O_3 against 100 g of collagen. In case of higher nuclearity of HSCCs, formed at the second stage of collagen structure stabilization, the amount of fixed chromium increases.

Experimental study of hydrothermal stability of unsplitted pelt, treated with HSCCs adding 0.4 % of electrolitho-resistant emulsion after acid-salt treatment, shows (**Table 1.9**) that the content of BCS in collagen in equivalent to Cr_2O_3 – 3.5 %, being enough to achieve the temperature of welding, exceeds 100 °C. Within studied limits and decreasing the basicity, the content of BCS in collagen grows by 17 % Cr_2O_3 , showing an incomplete interaction of basic chromium sulphate with collagen. In addition, an appropriate number of chromium (III)

Table 1.9

**Change in hydrothermal stability of collagen
under the effect of HSCCs**

Consumption of HSCCs		Content Cr_2O_3 , % of a dry residue	Hydrothermal stability of the dermis collagen, °C		
Cr_2O_3 , % of the pelt weight	with basicity, %		after stabiliza- tion	after 12 hours	after shaving
1.1	34.0	3.47	101.0	105.0	102.0
1.2	42.0	3.78	104.0	107.0	104.0
1.3	34.0	4.12	107.0	111.0	107.0
1.3	26.0	4.89	106.0	113.0	108.0

complexes can interact with 60–65 % of a total number of carboxyl groups in collagen.

Thus, the analysis of the interaction of BCS with collagen shows that almost all carboxyl groups in the dermis collagen structure are favourably located to interact with hydroxosulphate chromium complexes, and most of them are approachable at the first stage of interaction with dinuclear HSCCs. The rest of carboxyl groups of collagen macromolecules can bond with chromium (III) complexes of higher nuclearity at the second stage of its structure stabilization by the bonds of the second and third types.

Therefore, both collagen and keratin have a potential ability to interact with different reagents due to the presence of functional groups of the acid-base character. However, for its realization appropriate technological conditions should be created preparing collagen and keratin structures of raw materials for accessibility of active protein groups to suitable reagents in order to successfully perform subsequent technological treatments. As collagen has a more mobile structural organization in the technologies for processing of leather and fur raw materials, showing increased activity and variation of the complex of operational properties of leather materials for various purposes. Calculations for the approachability of functional groups of collagen macromolecules after the dermis degradation indicate that active groups are well located and

potentially accessible for chemical reagents. In particular, the distances between acid and base groups in microfibrils provide the approachability and effective interaction of collagen with hydroxo sulfatochromium complexes. When developing new technologies with effective colloid and chemical processes, it is necessary to take into account peculiarities of collagen and keratin structure, accessibility and activity of functional groups of macromolecules to chemical reagents, purposeful regulation with the mode of technological treatments for their prediction in leather and fur production.

Taking into account the benefits of each type of tanning, it is advisable to combine several methods of tanning in the technology in order to obtain high quality leathers [15]. The use of chrome tanning gives the leather a high wear resistance and heat resistance; tannins – plasticity and thickness; zirconium tanning agents – density and strength; aldehydes – softness and resistance to perspiration [38]. In this regard, chrome-tannin, chrome-syntane-tannin, chrome-titanium-synthetic tanning, etc., are wide-spread in the practice of leather production [39]. With organic and mineral tanning, the total porosity of the semi-finished product is increased in comparison with raw materials [20, 40], which is related to the formation of small pores and as the appearance of closed pores. The use of chrome tanning of semi-finished products is accompanied by an increase in their porosity due to the formation of a wider range of pores. Probably, smaller chromosome structural elements of the dermis are accessible to chromium compounds [61], and the structural effect of chromium salts also reduces the number of large pore. At the same time, the kind and consumption of the tanning agent [26, 62] have a significant influence on the nature of the formation of the tanned semi-finished product structure. The largest part of the porous leather structure is formed at the consumption of 0.5 % of Cr_2O_3 . In this case, pores appear with $(10-20)\times 10^3$ nm diameter, and there is also a significant number of pores with $(0.1-5)\times 10^3$ nm diameter. The final state of the porous structure of chrome tanned leather is formed at the consumption of a tanning agent of 1.5–2.0 % of the pelt weight.

Using tannins of organic nature with significantly larger particle sizes that have the diffusion capacity lower than HSCC [59], the structuring process takes place at the microfibrillary level and effective collagen

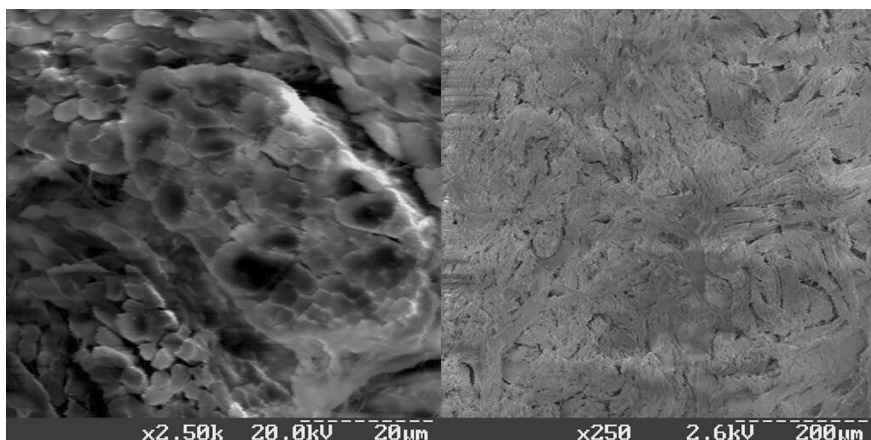


Fig. 1.25. Submicroscopic image of a hide cross-section cut after syntan and tannin tanning

interaction occurs in larger pores (**Fig. 1.25**) [63]. Chrome-free tanning methods with the consumption of aldehyde compounds of 9 % of the pelt weight provide a complete formation of the porous structure of the dermis with the main volume of pores with $(5-20) \times 10^3$ nm and $(0.5-2) \cdot 10^3$ nm diameters. A further increase in the consumption of tanning agents up to 12 % is not accompanied by any significant changes in the porous structure, with the exception of a decrease in the proportion of pores with $(20-100) \times 10^3$ nm diameter. The chrome-free tanned semi-finished product can be considered as coarse-pored. The appearance of bulky defects (openness and looseness) can be explained by this kind of treatment. Given the peculiarities of the porous structure of chrome-free tanned leather, it is necessary to adjust the following methods of the semi-finished product finishing in order to obtain elastic and soft leather [46]. In addition, leathers of aldehyde tanning are characterized by a smaller thickness. By physical and mechanical properties, leathers of glutar tanning have high resistance to perspiration and alkali, they are soft and elastic.

Capillary condensation of vapours is higher in leathers of tannin tanning than in chrome-tanned leathers [30] due to a larger number of narrow pores. The presence of a significant amount of condensed moisture in capillaries has a significant effect on the mechanical properties

of the semi-finished product, since water, which fills the pores of the corresponding structural elements, acts as a plasticizer of the dermis [20]. Not only the chemical interaction with active groups of the dermis collagen but also the space deposition in macropores of the semi-finished product structure are characteristic of tannins [4]. As a result of this effect, the leather acquires important properties – greater thickness, plasticity, etc.

In the tanning process, the average angle of inclination of bundles of air-dried leather fibers to its surface increases, its growth by 4° causes almost 8 % shrinkage [23]. Reducing the length of fibers by 5.9–6.4 % at the average angle of 38° leads to a 10 % decrease in the area of the semi-finished product. The change in microstructure causes the formation of the dermis volume, the quantitative characteristic of which is the change in porosity or the ratio of pores to the total size of leather.

An important role in the formation of leather properties is played by filling-retanning, due to which the porous structure of the finished leather is fixed [4]. In addition, there is a significant decrease in the number of large pores. If, in the process of tanning, pores of a smaller size with the diameter of $(0.6\text{--}0.8)\times 10^3$ nm are fixed, the fixation of larger pores with $d > 1\times 10^3$ nm [25, 65–67] primarily occurs during filling. At the same time, the maxima of the pore distribution by diameters are shifted to the micropore side, indicating that the leather porosity is aligned according to the sections. This distribution of pores of the central part and its peripheral regions is observed in the leather of a combined tanning using mineral and vegetable tanning agents. The following processes of greasing and dyeing of the semi-finished product are accompanied by a decrease in the porosity of the collagen structure that significantly influences the hygienic properties of finished leathers [27]. Closing transverse pores with coating films while finishing the leather grain leads to a decrease in their air and vapor permeability.

An important characteristic of the leather structure formation is the volume yield, which is determined by the chemical composition, the size of tannin particles and the method of tanning. At the same time, the level of the dermis structure fixation is reflected mainly in the leather yield in terms of area. A wide range of the volume yield ($143\text{--}400$ cm³/100 g of collagen [68]) indicates a significant influence of the dermis structure

level on which a tanning agent interacts with collagen. Porosity indicators are also related to the physical and chemical properties of the leather [48, 49]. A greater porosity of the macrostructure is more specific for a fillet part compared to the central one (butt). This indicates a lower density of packaging of collagen structural elements of the front part and it is manifested in reducing the strength and extension of elongation compared to the butt. The quotient of strength and elongation in the longitudinal and transverse directions has different values, which indicates and confirms the level of orientation of interlaced elements of the fibrous structure of the dermis. This results in a smaller increase in the thickness of the peripheral parts of the leather, and the unevenness of the thickness grows with the increase in its area.

Fatliquoring of the semi-finished product and its filling with polymer dispersions contributes to increasing the uniformity in the thickness and physico-mechanical parameters of the semi-finished product. In this case, the properties throughout various sections of the leather improve [23]. The final formation of the leather structure determines its application properties: stiffness, plasticity, specific mass, hygiene and heat protection — thermal conductivity and total thermal resistance [68]. At the subsequent stages of the pelt tanning, retanning and filling of the semi-finished product, the chemical composition of the dermis, as well as the specific surface, porosity and pore volume distribution in size, and the interarrangement of the structural elements of the dermis, vary considerably.

The nature of gradual structural changes in the dermis collagen, observed in submicroscopic images of the corresponding specimens, correlates with the peculiarities of changing their sorption characteristics (**Fig. 1.26** [69], **Table 1.8** [70]). The obtained isotherms of sorption of water vapors in the samples differ significantly depending on the pre-treatment of the semi-finished product, and this concerns both their shape and absolute values of moisture content. At the same time, the nature of the change in the shape of the sorption curves indicates a wide distribution of pore sizes and relatively high porosity of the samples under study, since most of the sorbed water corresponds to the section of large values of relative water vapor pressure, i.e., capillary condensation.

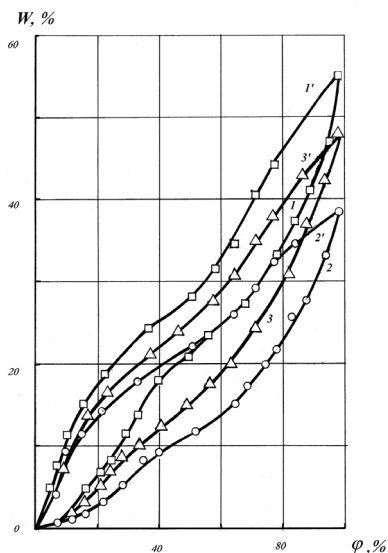


Fig. 1.26. Sorption (1–3) and desorption (1'–3') isotherms of water vapor with the semi-finished product samples at the temperature of 20°C: after liming and bating (1, 1'); chrome tanning and squeezing out (2, 2'); alkali treatment and fleshing (3, 3')

between the samples of the tanned dermis and delimed-bated pelt, the moisture content of which is 55.0 %. This may lead to a decrease in the concentration of hydrophilic groups due to the formation of compounds with the participation of dinuclear HSCCs and ionized carboxyl groups. At the same time, the obtained data on the moisture content of the tanned semi-finished product show a high degree of hydrophilicity of the studied samples in the absence of fat substances, which, depending on their chemical composition, could significantly reduce the moisture content of the finished leather.

A similar effect is observed in the limed pelt, which is manifested in reducing the sorption of water by 7 % compared with the delimed and

At the beginning of sorption, the curves of the isotherm have a linear dependence $W = f(\varphi)$ on $P/P_s = 0.1-0.2$. The desorption curves form a hysteresis with the sorption curves. On the sorption-desorption curves, three main areas without sharp transitions are distinguished, and the first area corresponds to a small water sorption (2.0–3.0 %), but in desorption, much larger values of residual water correspond to it (10.0–12.0 %). This may indicate a high hydrophilicity of the internal structure of the dermis collagen at various stages of processing, starting with the soaked raw material.

The most significant differences between the samples on sorption isotherms are already manifested at low values of the relative pressure of water vapor and remain until the total completion of the capillary condensation process. The maximum difference in sorption reaches 17.0 %

bated pelt. In addition, complex processes take place, on the one hand, connected with the destruction of inter- and microfibrillary bonds between the amino and carboxyl groups of polypeptide chains, which may cause a decrease in the sorption capacity of the semi-finished product, and, on the other hand, they form complex compounds of calcium with the amino acid residues of collagen macromolecules, which accompanies a decrease in the amount of adsorbed water. The obtained data show the prevailing role of the second process in the alkaline treatment of leather raw materials. The maximum moisture content of the delimed and bated semi-finished product is caused by a decrease in the content of chemically bound calcium in the dermis due to the transformation of its complex compounds into a soluble state under the influence of an excess of anesthetic reagent – ammonium sulfate and its partial removal from the structure. In addition, removal of the remains of keratin destruction products from the hair sacks, mucopolysaccharides from interfibrillary gaps due to the partial destruction of relatively weak interfibrillary bonds also contributes to increasing the hydrophilicity and moisture content of this such semi-finished product.

The specific surface of semi-finished samples at different stages of the technological process, calculated by the BET equation in the range of relative humidity of 0.05–0.25 %, varies in the range of 47.0–119 m²/g (**Table 1.7**), and this indicator acquires the maximum value in case of the delimed and bated semi-finished product. The increased hydrophilicity of raw materials is not manifested at the low pressure of water vapor, but it is observed at its increase. The reason for this can be the dislocated tension in the dermis pores, which grows with the increase in the sorption of water vapor.

The processing of the aqueous vapor desorption curves from the leather semi-finished samples using the Kelvin-Thomson equation made it possible to determine the peculiarities of the change in the porous structure of the studied semi-finished product during its formation. This is expressed in the form and the mutual arrangement of integral and differential curves of pore distribution by size (**Fig. 1.27**). For all samples of the semi-finished product, the presence of micro-, super-micro- and mesopores with the radii of 0.25–8.0 nm is characteristic, which correlates with the classification adopted by the IUPAC, with

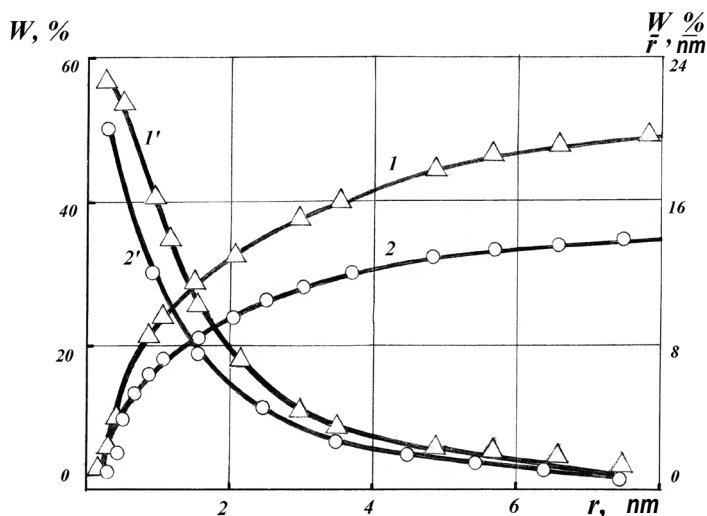


Fig. 1.27. Integral (1, 2) and differential (1', 2') dependences of aqueous vapour desorption on the radius of leather semi-finished product capillar: after delimiting-bating (1); tanning-pressing (2)

micropores corresponding to the size smaller than 0.6–0.7 nm, supermicropores $0.7 < r < 1.5$ –1.6 nm and mesopores $1.6 < r < 50$ nm.

The proportion of meso- and micropores in terms of volume (together with supermicropores) after tanning compared to the samples obtained after the soaking of raw materials and delimiting-bating of the semi-finished product, gradually increases from 4.0/1.0 to 5.5/1.0 and to 6.6/1.0, while the micropore volume decreases by 38.0 %. This can be explained by the difficult desorption of water molecules from the microporous microfibrillar structure of the dermis collagen after chrome tanning.

The state of water in the pores of the leather semi-finished product at various stages of its treatment can be shown by the results of thermogravimetric studies [59] of water desorption at critical points on the curve of kinetics of the sample temperature variation under isothermal conditions of dehydration at 80 and 100 °C. Due to the research carried out on the samples of semi-finished products selected at different technological stages of treatment on the corresponding kinetic curves

in the process of gradual dehydration, the presence of sections that may correspond to different state of water in the semi-finished product and its bond with collagen (**Table 1.10**) has been determined. Watered samples of the leather semi-finished product are characterized by a large amount of water absorption by its structure. As a result of watering, the distances between macromolecules, microfibrils and other elements of the fibrous structure of the dermis collagen are increasing as a result of the destruction of hydrogen and a part of ionic bonds. The structuring of the dermis should counteract this process, both as temporary during its liming and permanent in chemical structuring.

According to the experimental data, the nature of the changes in the watered samples of the semi-finished product at the successive stages of its treatment correlates with the maximum values of the aqueous vapor sorption with significantly higher values for the watered samples. The relative increase in the volume of water in the meso-, micropores for the watered samples is due not only to the deeper loosening of the fibrillar collagen structure, but also to the possible formation of a denser outer layer of the structure through which the water is removed. In this

Table 1.10

State of water in a cellular structure of watered semi-finished product at different technological stages of its treatment

Semi-finished product after technological stage	Differential moisture capacity, %			
	capillary		of adsorbing layer	
	macropores	meso-, micropores	polymolecular	monomolecular
Liming-fleshing	46,0	47,0	19,0	8,0
	52,0	47,0	22,0	13,0
Deliming-bating	52,0	57,0	22,0	12,0
	90,0	50,0	22,0	11,0
Tanning-pressing	56,0	55,0	13,0	4,0
Filling	41,0	38,0	12,0	4,0
	35,0	56,0	15,0	4,0

Note. The numerator and denominator show the indicators of the studied and reference variants of the semi-finished product treatment.

case, the ratio of capillary water in the macro- and meso-, micropores is minimal (1.4 times), while this ratio is maximum and equals 3.5/1.0 for the delimed and bated samples. This indicates an excessive watering of the pelt during liming accompanied by increased loosening and, accordingly, requires a significant amount of filling materials to prevent bulky defects in the finished leather. The adsorption water remaining in the structure of the leather semi-finished product after the removal of the capillary tends to reduce its content in its structure as it approaches the finished leather. The quantities of water absorption and sorption of aqueous vapor are in correlation dependence for the semi-finished product samples at different stages of the technological process.

Thus, the implementation of a number of technological treatments of leather semi-finished products, aimed at loosening the fibrillar structure of the dermis when liming and its release from non-collagen formations, contributes to the formation of semi-finished and natural material. In this case, the volume of collagen mesopores of the dermis increases during its liming and subsequent structuring. Accordingly, the number of macropores, which requires additional complex filling of the tanned semi-finished product with the use of dispersions of polymers, vegetable and synthetic tannins and greasing materials, is growing. The specific surface of the studied samples after the chemical structuring of the dermis decreases by 17 %. As the structure of the leather material is formed during the process, the specific surface area and the maximum adsorption of aqueous vapor before a constant structuring of the dermis with hydroxosulfate chromium complexes grow, and after the tanning, these parameters decrease by 26.0 and 31.0 % respectively. The observed effect can be explained by two processes — loosening of the collagen structure of the dermis in the alkaline treatment of raw hides and the chemical structuring of the semi-finished product, with the dominant role of the first process before the tanning.

The pore size distribution curves in the leather semi-finished product made it possible to determine that the porous structure is characterized by the presence of micro-, supermicro and mesopores, with the transition from the meso- to the microstructure in the range of values of pore radii of 1.5–1.6 nm depending on the processing stage of the leather semi-finished product. In this case, the ratio of meso- and micropores

of the structure increases after soaking of skins and hides from 4.0/1.0 to 6.6/1.0 for the tanned samples with a total reduction of mesopores after tanning by 26.0 %. At the same time, research on the desorption of water from semi-finished products made it possible to determine its availability in different kinds and their ratio in the capillary-porous structure of watered samples. While forming the leather material, the ratio between capillary water in the meso- and micropores and the water content that forms the polymolecular layer increases from 2.4/2.5/1.0 to 3.4–4.3/3.2–4.2/1.0, respectively, with a 34 % decrease in absolute volume of water corresponding to adsorption water. The obtained results of the research show deep structural transformations while tanning the dermis collagen, as indicated by its interaction with water at the maximum watering compared to the interaction with aqueous vapor. At the same time, the process of water absorption and water delivery by the semi-finished product after tanning is reversed. Absolute high values of moisture capacity indicate the necessary replacement of the part of the water of macro- and mesopores with chemical materials of hydrophobic nature to obtain a water-resistant material structure.

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Questions for self-control

1. Prerequisites for the effective operation of enterprises of the fur and leather industry.
2. Physical and chemical structure of collagen and keratin.
3. Multi-level structure of collagen of the hide dermis.
4. The scheme of the dermis macrostructure after its alkali treatment.
5. Influence of hydrophilic and hydrophobic regions on the structure of the dermis collagen.
6. Electro-surface properties of the dermis collagen.
7. Principles of technological processes of the dermis structural transformations considering electrochemical behaviour of its collagen.
8. Methods to determine the specific surface of the dermis.
9. Comprehensive assessment of changes in acid and alkali properties of the dermis collagen according to the technological treatment.
10. Features of two-stage retanning of the leather semi-finished product.
11. The use of water-soluble polymers as fillers in modern leather production.
12. Influence of mineral fillers (modified montmorillonite dispersions) on the dermis structure formation.
13. Structural transformations of fur and leather raw materials during treatment.
14. Pre-treatment processes of fur skins and hides — watering, separation of fibers, removal of soluble proteins and other non-collagen constituents.
15. Influence of lime solutions on the dermis structure.
16. Sorption properties of the semi-finished product at different stages of rawhide treatment.
17. Influence of liming-bating on the dermis structure.
18. Characteristics of the main changes in hydrothermal stability of the dermis collagen under the influence of hydroxosulphate chromium complexes.
19. Combination of several types of tanning in treatment technology of fur skins and hides.
20. Significance of filling and retanning in the formation of finished leather properties.
21. Factors that greatly affect porosity of the finished leather.
22. Influence of fatliquoring on the increase of leather thickness uniformity and physico-chemical parameters of leather semi-finished products.
23. State of water in the cellular structure of watered leather semi-finished product at different technological stages of its treatment.

2. TECHNOLOGIES OF RAW MATERIAL PREPARATION BEFORE THE SEMI-FINISHED PRODUCT TANNING

The effectiveness of the developed technology is primarily determined by the degree of the use of raw materials and chemical reagents, including water, by their duration and the amount of waste after some leather and fur production processes. These factors directly affect the technogenicity of production, which is caused by the use of a large number of chemical reagents that are hazardous to the environment in soaking and liming processes (SLPs) [1]. In this regard, the development of energy-efficient technologies involves reducing the use of toxic reagents, as well as establishing technological modes that ensure their more efficient use to produce high quality products.

In order to effectively carry out the process of the leather semi-finished product tanning, it is necessary to obtain a high-quality pelt after performing scientifically grounded processes of soaking, dehairing, liming, deliming and bating.

As a result of complex scientific and chemical research into the processes of interaction of alkaline reagents with the dermis components, energy-saving technologies of SLPs have been developed. These technologies are ecologically oriented and they are different from the previous ones by a minimum use of water and chemical reagents.

2.1. Features of interaction of aqueous solutions of reagents with raw stock

Since skins and hides of animals are highly hydrophilic biological raw materials, all technological processes of the leather production, starting with the uncuring of raw materials during the soaking process

and ending with finished products, are related to the interaction of collagen with aqueous solutions of chemical reagents. In this regard, the study of their interaction mechanism is of theoretical and practical significance, especially at the cellular level, where processes occur in the presence of electrolytes. As all liquid treatments of hides occur in a dynamic mode and aqueous medium using a large number of chemical reagents, the issue of the state of water as a chemical reagent in the transport medium, as well as the mechanism of its interaction with other technological components of the processing liquors in the presence of collagen of the dermis, is of paramount importance.

In the interaction of raw materials with alkaline solutions, water absorption with the skin swelling, of the dermis structure “opening”, partial removal of globular proteins, polysaccharides and fatty substances due to the destruction of the main substance cells, epidermis and hair, occurs initially. The chemical nature of the skin protein components, first and foremost, affects the formation of the pelt structure. Due to its amphoteric nature, collagen can substantially change its properties depending on the *pH* of the medium. It reacts energetically with aqueous solutions of chemical reagents used in technological processes.

The dynamic nature of the structure formation in aqueous solutions determines the unique properties of both water itself and solutions of substances with different chemical characteristics. According to the cluster model of water [2, 3], in which there is a certain dynamic equilibrium between the groups of its dipole molecules, connected in clusters and individual non-associated water molecules (**Fig. 2.1**). The presence of orderly formations in water, clusters that have a structure close to a spherical form, and disorderly individual molecules, can lead to specific effects that depend on the chemical nature and structure of the reagents introduced into the water. In case of ionic compounds, there may be three-hydrated layers around the ion, which differ by the force of interaction and the degree of water molecules ordering. In addition, the inner layer directly surrounds the cation or anion of the molecules of the reagent and corresponds to the hydration layer of the orderly water molecules, the second one is less orderly and the third one is actually volumetric water.

The distances between ions in the aqueous solution of the electrolyte do not depend only on its concentration, but also on the nature

of the ion. Thus, in a 0.1 mole of the electrolyte solution, the average distance between ions is 2 nm, so the water molecules are separated from ions by no more than 1 nm or 0.36 of the water diameter [4]. In the transition to more concentrated electrolyte solutions, this model turns into a two-layer one. In case of cations and anions with a high electric charge density, a hydrated layer of bound water with a high ordering is formed around them, and in case of cations, the oxygen atoms are oriented in the direction of the ion, and in case of anions – hydrogen atoms do the same [5]. Such ions include Na^+ , Ca^{2+} , Al^{3+} , OH^- . The water around such ions has a higher density in comparison with volumetric water. This solution diffuses more rapidly through membranes that are neutral to it, in comparison with ions of a large size, such as K^+ , NH_4^+ , Cl^- , ClO_4^{2-} , NO_3^- [6]. And due to the interaction of collagen with the processing liquor, its reticular structure loses its orderliness, although it exists directly around the ion. In this case, the viscosity of the solution decreases and the permeability of the membrane increases.

In the presence of non-ionic substances, for example in aqueous alcoholic solutions, the structure is ordered due to a strong interaction between OH^- groups of alcohol and water. In contrast to hydroxyl-containing substances, inert substances, in particular aliphatic hydrocarbons, can undergo a so-called hydrophobic hydration in water,

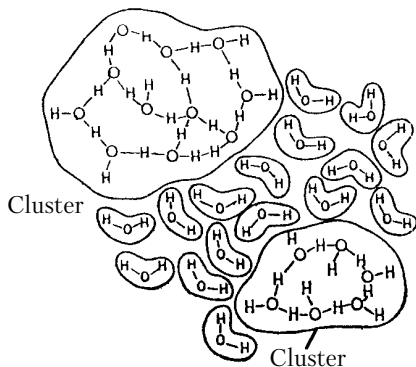


Fig. 2.1. Clusters and free molecules in liquid water

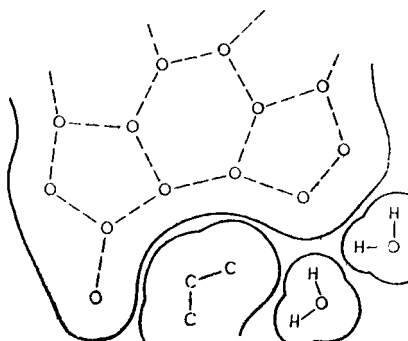


Fig. 2.2. Cluster section close to a hydrocarbon molecule of the dissolved substance

according to the scheme shown in **Fig. 2.2**, and have a guiding influence on the structure of water [2]. This occurs due to the repulsion of water molecules by the molecules of the inert substance in such a way that non-associated molecules of water turn around and increase its overall ordering, which leads to an increase in the interphase surface tension. In case of surfactants, this effect largely depends on the hydrophobic and hydrophilic balance of their molecules.

The study of a dynamic state of water in surfactant and electrolyte solutions made it possible to determine the contribution of collective and individual movements of water molecules in the overall coefficient of its self-diffusion [7], and receive the information on the sorption mechanism, the structure of adsorption layers of surfactants on the surface of sorbents. The studies of hydrophobic and hydrophilic interactions in surfactant solutions on sorbents and membranes give some grounds to predict and regulate the amount of bound and free water in surfactant-sorbent, surfactant-membrane systems of collagen of the dermis.

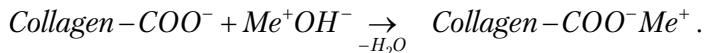
The water in the hide collagen exists in another structural state. According to the data of the nuclear magnetic resonance [8], it has been found that a large amount of water in collagen is bound with hydrophilic groups in the form of hydrates, and the lifetime of water molecules in the bound state is 10^{-6} s, that is by 10^5 – 10^6 times more than in a cluster of volumetric water. The study of sorption processes in the collagen-water system [9, 10] has proved that water in collagen, polarized under the influence of ionogenic collagen groups, is ordered and forms adsorption layers. In these layers, one coil of collagen macromolecules (2.86 nm) contains six repeating chains of water molecules of 0.474 nm long with the length of a hydrogen bond of 0.29 nm. In the bound water, the equilibrium concentration of Na^+ ions, which are always present in the preparatory processes for the formation of the pelt structure, is only 10 % in collagen and the dermis cells in terms of its concentration in the external sphere of the adsorption layer [10].

Consequently, water interacting with electrolyte and surfactant solutions, other reagents, collagen membrane cells of the dermis and the main substance, changing their physical and chemical properties and structure, as well as the structure of chemical reagents and their reactivity, can significantly affect the kinetics and the mechanism of preparatory

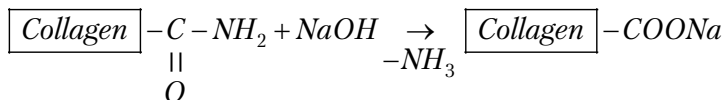
processes for the pelt structure formation. The interaction of collagen with alkaline solutions leads to the dissociation of its carboxyl groups due to the neutralization of a positive charge of nitrogen-containing groups by hydroxyl groups of alkali with a release of thermal energy of 15.32 kJ/g of the dermis collagen [3] when sodium hydroxide is being used. At the same time, due to the ionization of collagen carboxyl groups and their electrostatic repulsion, intermolecular interactions in the dermis structure weaken. This contributes to additional water absorption and swelling of the pelt. At the same time, there is an uneven distribution of ions, capable of diffusion, in the technological solution. After a complete ionization of carboxyl groups in the side chains of collagen macromolecules, the increase of the fixed ions stops. The mechanism of the dermis swelling may be caused by the occurrence of osmotic pressure due to the emergence of a gradient of concentrations between fixed ions of collagen of the dermis and in the technological solution. Simultaneously, there is an electrostatic repulsion and dipole interaction in polypeptide collagen chains. In this case, the polypeptide chains are deformed and macromolecules unfold and shrink. This process is facilitated by the attraction of charged centers of collagen polar water molecules, which intensifies swelling of the dermis.

Thus, swelling is a total effect of the three factors: osmotic pressure in the dermis, electrostatic repulsion of the same charged groups and ion-dipole interaction of water molecules with charged groups of collagen macromolecules.

In the alkaline medium, ion bonds in the structure of the dermis collagen are broken and the released carboxyl groups of the side chains interact with the cation of the alkali according to the following scheme:



In the presence of calcium cations, its compound with collagen is formed, and it is weakly dissociating. The main chemical changes of collagen during liming of the dermis are the reanimation of amide groups of asparagine and glutamine according to the following scheme:



which changes the isoelectric properties of the dermis collagen, while the pH of the isoelectric point is decreasing to 4.5–5.5.

These schemes show a simplified interaction of collagen of the dermis with alkali, since its oppositely charged groups do not coincide in quantity. In addition, the acid and basic amino acid residues of collagen macromolecules have different degrees of dissociation. Electrochemical processes in the structure of collagen of the dermis are complicated by the simultaneous destruction of hydrogen, ionic, intermolecular, intramolecular bonds, and the formation of free radicals.

The degree of swelling due to the physical and chemical sorption of water by collagen macromolecules determines the “opening” of its structural elements and strongly depends on the nature of chemical reagents and the composition of the lime solution. Lime solutions of ash cause less than sodium hydroxide and its mixture with sodium sulfide swelling of the dermis. Such differences are caused by higher solubility of sodium hydroxide, on the one hand, and the formation of slightly-dissociated compounds of calcium with collagen, which helps to strengthen the dermis.

As a result of alkaline or acid swelling, the mutual uncoiling of the spirals of polypeptide chains and collagen macromolecules increases, which causes thickening with a simultaneous reduction in the length of microfibrils, elementary fibers and their beams that leads to thickening of the pelt and reduction of its area. Therefore, for the rational use of the raw material surface and minimization of chemical reagents, the degree of swelling is optimized.

According to the degree of influence on the pelt elasticity or swelling of the spatially-stitched collagen structure, the alkaline reagents form the following series: $KOH > NaOH > Ba(OH)_2 > Ca(OH)_2$. However, according to the ability to bind with collagen, chemical reagents, depending on the affinity to it, are arranged in the following sequence [11]: $Ca(OH)_2 > Ba(OH)_2 > KOH > NaOH > Na_2S > NH_4OH$, and according to the speed of washing them out, they have a reverse sequence.

Solutions of strong alkali cause a significant destruction of collagen that in 2 days, at the temperature of 18–20 °C reaches 24.0 % in 10 % $NaOH$ solution [12]. Moreover, even in dilute alkaline solutions, body peptides detach with amino acid residues of tyrosine. Unlike

strong alkali, when using calcium hydroxide, the hydrolysis destruction of collagen is significantly reduced. Thus, in a saturated solution of calcium hydroxide (~ 0.13 %), it reaches only 12 % with a 120-day contact of the components [13]. In the alkaline medium, a number of destructive chemical processes occur, namely detaching of ammonia from the residues of asparaginic and glutamic acids, breaking of ionic and hydrogen bonds, the destruction of transverse intermolecular and intramolecular bonds, which lead to the release of blocked amino-, carboxylic and hydroxyl groups. Along with this, depolymerization may occur as a result of the breakdown of covalent bonds in the main chains to form free amino- and carboxyl groups, as well as the detachment of the guanidine group of arginine [11]. The course of these side reactions is much slower than the interaction of alkali with carboxyl groups in the side radicals of collagen macromolecules.

A more noticeable opening of the fibrillar structure of the dermis is ensured using alkaline solutions with a high content of solids [14] (4.0–4.5 % of calcium hydroxide of the raw material mass). This is due to the active action of dispersed calcium hydroxide particles on the structure of collagen and other proteins. The use of a smaller content of dispersed alkali in liming processes can be considered to be more rational, and it contributes not only to the obtaining of high-quality elastic hides of chrome tanning, but also to the reduction of sewage pollution. Adding salts to the alkaline solution reduces the hydrolyzing effect on the collagen, while swelling of the dermis decreases depending on the nature of salt in alkaline salt treatment. Active collagen groups of the dermis adsorb neutral salts, changing the degree of its rehydration.

There are three groups of salts by the degree of rehydration [15]. Rhodanates, iodides, chlorates, barium, calcium, magnesium and lithium salts cause strong swelling of collagen. It is manifested in significant thickening and reduction of collagen fibers with a simultaneous reduction of their hydrothermal resistance. The influence of salts of the second group is determined by their concentration in the solution. For example, low concentrations of sodium chloride cause significant swelling and high ones – collagen dehydration. Salts of the third group (sulphates, thiosulfates, carbonates) have dehydration ability and do not display any increased adsorption.

In the treatment of hides and skins by liming, calcium hydroxide and a sodium sulfide accelerator, as a reducing agent, are often used. It is also possible to use sodium hydroxide and sodium carbonate. In the presence of sodium hydroxide, the solubility of calcium hydroxide is reduced and the lime solution partially loses its technological properties. The same process occurs during a complex use of calcium hydroxide with one of the potassium or sodium salts-sharpeners, which form insoluble or slightly soluble salts of calcium. In the formation of $CaCO_2$, CaC_2O_4 insoluble salts, there is a direct dependence between the concentration of the added salt and the properties of the lime solution. If the salt is slightly soluble, for example, $CaSO_4$, CaS_2O_3 or $Ca(C_2H_3O_2)_2$, or soluble as $CaCl_2$, in the presence of sodium chloride in the skin, increasing the amount of the added salt, the maximum alkalinity is quickly reached. The formation of double $CaSO_4 \cdot Na_2SO_4$ salt is also possible. The use of sodium hyposulfite in the lime solution has an advantage, since it eliminates the formation of insoluble compounds, and it is possible to control an increase in the alkalinity of the lime solution.

In nourishing liming, a large part of globulin proteins, polysaccharides, fatty substances, contained in the main substance cells, is removed. Proteins of the epidermis and hair disappear almost completely and this significantly increases the specific surface of the dermis and its porosity. The influence of standard alkaline treatments on elastin and reticulin is reduced to their modification [16] with the break of reticulin meshwork. There is some doubt about the use of a “sharpened” lime solution, which may be accompanied by a partial removal of elastin fibers.

Most of the globulin proteins are removed at the stage of soaking, because they are contained in saline solutions of the connective tissue. This process is intensified by the use of surfactants. The splitting ability of collagen fibers is believed to depend on the completeness of globulin proteins and polysaccharides removal, as they are substances that glue the fibrous structure of collagen of the pelt.

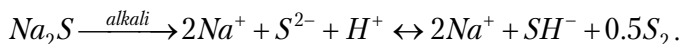
Surface-active substances, used in SLPs, are characterized by poly-functionality. Reducing the surface tension of the processing liqor on the boarder between the phases, they facilitate diffusion of electrolyte aqueous solutions into the skin and its cells. By doing so, they increase the rehydration of the skin dermis, exert a dispersing effect on the

substances to be removed, and plasticize the fibrillar structure of collagen. When used in a soaking sulfonol solution with the concentration of more than 2 g/dm^3 , the yield of hexoses in the processing solution will increase by almost 8 times [17], and proteins — by 4 times. A similar effect, concerning polysaccharides, is achieved with the use of nonionic surfactants and at the liming stage, but the yield of soluble proteins and oxyproline is small.

The removal of the main substance from the structure of the dermis facilitates the division of its fibrous structure and an increase in collagen reactivity. This ability is manifested in a partial disorientation of elements of a fine structure with a decrease in its strength. The degree of hydration and swelling of neutralized dermis and the release of gelatin when heated in water increases, the degree of collagen digestion by enzymes rises. [18].

Therefore, in the process of soaking and liming of raw materials, complex colloid-chemical phenomena connected with the diffusion of alkaline reagents into cells of the main substance take place. This is accompanied by their interaction, division of the structure of the dermis, increase in collagen reactivity and the release of non-fibrous formations into the processing liquor. In this case, irreversible changes in the formation of the pelt structure, whose interstructure spaces are filled with aqueous solutions of reagents containing residues of destroyed proteins, carbohydrates and fats, occur. Along with changes in the dermis structure during liming, there is dehairing, which weakens the connection between the hair and epidermis with dermis that provides their further removal or destruction. Alkaline reagents produce an action on keratin similar to the collagen, but with the hydrolysis of disulfide bonds.

Dehairing effect when using only the lime solution is conditioned by its action, primarily on glycosaminoglycans of the basement membrane of epidermis and hair sacks. The sulfide solution affects keratin of the hair and epidermis [3], however, its effect on collagen of the dermis is much smaller than that of a calcareous solution containing sulfide solution. When interacting with keratin, *SH*-ions do not exert a hydrolysing effect upon it independently. Adding sodium sulfide to the solution, the ionic equilibrium is shifted towards the formation of S^{2-} ions, which is accompanied by the restorative splitting of the cystine group:



This action of a sulfide ash is possible at a high *pH* value of the medium where the concentration of S^{2-} -ions in the solution is significant.

Taking into account a high strength of these bonds, the reducing agents, such as sulfides, bisulfides, etc., are introduced for their effective destruction in lime solutions. In case of the hair destruction technology, the concentration of these reagents is much higher. The rate of the hair destruction depends significantly on the *pH* values and temperature of the solution and significantly increases at the *pH* > 13.5 and the temperature above 25 °C [19]. Weakening of the hair ties with the hair follicles is caused by the hydrolytic destruction of the epithelial tissue, which is the producing layer of the epidermis of hair follicles and hair bulbs. With the increase in the concentration of chemical reagents in the lime solution, sulfide bonds in keratin are destroyed. The most significant changes in the composition of the hair during alkaline treatment are manifested in the loss of sulfur, the basic mass of which is contained in the cortical layer of a mature hair in the form of disulfide bridges.

The analysis of residual sulfur in the hair after the treatment with 0.1n sodium hydroxide solution for 600 hours shows a decrease in its content from 3.5 to 2.4 %, and with an increase in temperature only to 50 °C this value is 1.98 % in 8 hours. After the treatment of the crushed hair and skin in a 0.2 mol *NaOH* solution for various periods, sulfide, polysulfide, thiosulfate, sulfite and sulfate were detected. In addition, the maximum content of sulfide was after 30 hours of treatment, and then it decreased; the amount of polysulphide and sulphite increased, reaching almost a constant value, and the amount of thiosulfate increased with a gradual deceleration. It is possible that, at first, sulfur is removed in a highly dispersed state and interacting with alkali it forms sulfide and sodium polysulfide. In return, sodium thiosulfate is a secondary oxidation product.

The obtained results of physical and mechanical tests of the hair after its long-term treatment with alkaline solution show that the hair keeps its sufficient strength, even when 50 % of sulfur is detached from keratin. Therefore, the destroyed disulfide bridges in keratin were replaced by chemical bonds of another type. Calcium hydroxide, the most

common in lime solutions, has a better effect on keratin, and according to their dehairing effect, alkaline reagents are arranged in the following series: $Ca(OH)_2 > Ba(OH)_2 > NaOH > KOH$. Dehairing is intensified by adding sodium sulfide into a calcium hydroxide solution. In this case, sulfhydrates of these metals are also formed. The use of only sodium sulfide in the lime solution, despite its high propensity to hydrolyze, has no dehairing effect and does not cause swelling of the dermis. The maximum action of calcium hydroxide and sodium sulfide solutions is provided only with the equimolar ratio of hydroxyl and sulfhydryl ions.

The destruction of disulfide bonds in keratin may also occur under the influence of some oxidants of different chemical compositions [20, 21]. So, the use of chlorinated oxidizing agents, such as monochloramin B and the dibasic salt of calcium hypochlorite, causes deep destruction of keratin in the hair. Moreover, the maximum oxidation capacity of the first one manifests itself in the acidic medium at the $pH < 2$. The use of butyl alcohol as a solvent of secondary products of its interaction with acid significantly accelerates the dehairing process. This is due to the formation of the absorption layer of a solvent saturated with an oxidizer at the phase of separation, and it greatly accelerates the diffusion of the oxidant into the structure of the hair and its further destruction. However, in this method of dehairing, products of butyl alcohol oxidation cause the formation of the pelt facial layer cockling and the scub.

The use of urea as a modifier in oxidative dehairing [22] contributed to the formation of mono- and dichloroquine in solution, the weakening of intermolecular interactions in the collagen structure as a result of the destruction of hydrogen and physical bonds, and a decrease in the concentration of active chlorine in the gas phase. Subsequent alkaline treatment of the skin with sodium hydroxide promoted the dissolution of the destroyed hair in the form of salts of keratin sulfonic acids and the formation of alkaline swelling of the pelt. The use of urea significantly accelerated the effect of dehairing of raw materials.

Apart from chemical reagents, enzyme preparations, which have a specific action on keratin, collagen and other components of raw materials, are also used for skin dehairing. Enzymes are characterized by a strong catalytic action and they are by billions of times more efficient than other catalysts in “soft” biological conditions [18]. In leather

production, enzymes that accelerate the reaction of hydrolytic splitting of intramolecular bonds are most widely used: these are hydrolases, proteases, esterases, and epizabases. The action of enzymes, like alkali, is in the destruction of polysaccharides of the producing layer of the epidermis and hair follicles. The activity of each enzyme preparation is maximally manifested only in a certain range of the *pH* of the medium. So, the protosubtilin G10h enzyme preparation has a maximum proteolytic activity at the *pH* of 10.7. Increasing the *pH* to 12.5 leads to a decrease in its activity by 60–70 %.

Thus, dehairing of raw hides using enzyme preparations is characterized by the specificity of their action and high catalytic activity, which depends on the composition of the technological solution and the process parameters. The disadvantage of this method is inequality of weakening of the hair connection with the dermis in different hide sections, and as a result, a part of the hair felts or remains on hides (5–10 %), and then it should be removed in the subsequent liming. Because of a high cost of enzyme preparations, the process of dehairing and liming requires an intensive control of technological parameters with the obligatory accurate identification of the enzymes' activity.

The main condition for obtaining high-quality leather for various purposes is the effective carrying out of dehairing and liming processes based on the modern ideas about their mechanism. However, the study of these processes, compared with the subsequent processing of semifinished products, is paid much less attention, which is manifested in a significantly smaller number of publications. It can be explained by the complexity of physico-chemical phenomena in the formation of the pelt structure and their duration, material capacity with the use of a wide range of chemical reagents, labour intensity of these processes.

Thus, the physico-chemical processes of transforming hides of animals into the pelt should contribute to the formation of its porous structure, the peculiarities of which are determined by the technological treatment mode with the creation of optimal conditions. At the same time, an effective diffusion of chemical reagents into cells of the germic layer of the epidermis, hair bulbs and dermis is realized. It ensures the hair preservation to be utilized, "opening" of the fibrous collagen structure due to the destruction of the main skin substance cells and connections

of hydrocarbon-protein complexes with structural collagen elements. An effective post-diffusion interaction of chemical reagents with the skin cells makes it possible to create moderate swelling of the dermis by adjusting the *pH* of both the medium and the main substance of cells, forming a spatial structure of the pelt to provide maximum output of the skin area.

By changing the composition and structure of clusters formed by ionized molecules of chemical reagents in processing liquors and hydrated layers of water around reagent molecules, one can purposefully influence the kinetics and the degree of the course of physico-chemical processes in the formation of a porous pelt structure. This is achieved by using chemical reagents whose molecules in aqueous solutions form clusters of a predominantly spherical shape, that have greater mobility and penetrate into cells of the main substance and fibrillar collagen structure. Moreover, hydrated ions of a small size with a greater electric charge density penetrate into the structure more easily and cause a greater decomposition effect, which depends on both the nature of the reagent and its concentration. Due to the anisotropic fibrillar structure of collagen, aqueous solutions of diffused chemical reagents are localized in the form of linear clusters, mainly in polar areas.

The use of the established mechanism of physico-chemical processes of the pelt structure formation has become the basis for creation of new energy-saving technologies for dehairing and liming of hides.

2.2. One-stage dehairing and liming

In the process of developing one-stage technology, particular attention is paid to the study of the influence of the main parameters of SLPs on the properties of the hair and the pelt. From the *a priori* information, the complex nature of such dependencies is known and that is why mathematical modeling using the *D*-optimal second-order plan [23] was used to minimize the cost of alkaline reagents and determine the influence of temperature on the course of one-stage dehairing and liming process (OSDL). Dehairing and liming processes of raw materials were studied using the system of automatic scheduling and processing

of experimental data on the computer. The factors influencing soaking and liming processes have been identified: concentrations, g/dm³:

X_1 – of sodium carbonate in a soaking solution;

X_2 and X_3 – of sodium sulfide and calcium hydroxide in a lime solution;

X_4 – the temperature of the soaking and liming process, °C.

The experiment area is determined by the data given in **Table 2.1**.

Table 2.1

Experimental design options

Name	Value of the factor			
	X_1	X_2	X_3	X_4
Zero level	4	9	8	28
Variable interval	4	3	5	4

The plan and the results of the experiment are shown in **Table 2.2**. The investigated technology was assessed according to the grade of the received skins y_1 , % and the consumption of raw materials per 100 m² of skins y_2 , kg/100 m².

The search for the most appropriate models according to the maximum value of F -criterion and the correlation coefficient, taking into account the minimum value of the mean-square deviation, gives an opportunity to obtain the following mathematical models of the liming process in natural values¹:

$$\hat{y}_1 = 640.6 - 4.3X_2 - 7.7X_3 - 6.5X_4 - 1.8X_2X_3 + 3.7X_3X_4 - 2.5X_1^2 + 2.1X_3^2 + 7.9X_4^2;$$

$$\hat{y}_2 = 91.32 + 0.21X_2 + 0.13X_3 - 0.23X_4 - 0.075X_1X_4 + 0.175X_2X_3 - 0.144X_3X_4 + 0.38X_1^2 + 0.13X_2^2 - 0.87X_3^2 - 7.9X_4^2.$$

The analysis of the obtained models made it possible to establish the degree of influence of the main parameters of SLPs on the economic

¹ \hat{y} – predictive value of the output variable by the model.

indicators of the hide. The increase in Na_2CO_3 and Na_2S concentration contributes to reducing the consumption of raw materials and improving the quality, and increase in $Ca(OH)_2$ concentration and the temperature of the liming process reduces the initial values. The estimation of the coefficient significance based on the analysis of the obtained models makes it possible to determine the influence of each factor on the output variables of the liming process. In particular, on the consumption

Table 2.2

Experimental design and results of the research

№ of the ex- periment	Factors of the process				Output variable	
	x_1	x_2	x_3	x_4	y_1	y_1
1	+1	+1	+1	+1	89.4	632.2
2	-1	+1	+1	+1	89.7	631.8
3	+1	-1	+1	+1	88.5	643.5
4	-1	-1	+1	+1	88.8	645,8
5	+1	+1	-1	+1	89.6	644,2
6	-1	+1	-1	+1	89.7	642.5
7	+1	-1	-1	+1	89.8	649.8
8	-1	-1	-1	+1	89.9	649.1
9	+1	+1	+1	-1	90.6	636.2
10	-1	+1	+1	-1	90.8	638.1
11	+1	-1	+1	-1	90.4	649.2
12	-1	-1	+1	-1	89.9	647.1
13	+1	+1	-1	-1	89.5	664.7
14	-1	+1	-1	-1	89.4	663.2
15	+1	-1	-1	-1	89.2	666.2
16	-1	-1	-1	-1	89.2	668.4
17	-1	0	0	0	91.7	638.9
18	+1	0	0	0	91.7	6367.7
19	0	-1	0	0	91.1	646.7
20	0	+1	0	0	91.8	736.1
21	0	0	-1	0	90.2	649.3
22	0	0	+1	0	90.7	635.5
23	0	0	0	-1	90.3	659.9
24	0	0	0	+1	89.7	636.4

of raw materials and quality grade of leather materials, respectively, in mass %: Na_2S – 20 and 8, $Ca(OH)_2$ – 40 and 20, the temperature of the process is 35 and 70 °C. The influence of Na_2CO_3 concentration on the original factors is much lower.

Thus, it has been established that the most influential factor in the consumption of raw materials and quality grade of the leather is the temperature of the soaking and liming process and the amount of calcium hydroxide. This effect of alkaline reagents during liming on the output variables is made by a significant change in the structure of the dermis.

Experiments on the influence of the process temperature and Na_2CO_3 consumption on the soaking kinetics according to the content of moisture in the middle layer of the hide (**Table 2.3**) [23, 24] showed that the rise of the technological solution temperature from 20 to 28 °C accelerates the process of raw materials soaking even with a decrease in Na_2CO_3 concentration. Therefore, with a decrease in Na_2CO_3 concentration from 12 to 4 g/dm³, the time of soaking is reduced by 37–39 %. At the same time, uniform rehydration of raw materials is achieved within 5.0–5.5 hours.

The investigation of the elemental composition of raw material samples at different stages of processing, obtained by the developed technology with a minimum consumption of reagents by the X-ray spectral analysis (**Table 2.4**) [25] using an X-ray microanalyser of “LS-5”

Table 2.3

Kinetics of moisture content in the middle layer of rawhide

Time of soaking, hours	Moisture content, %, at the temperature, °C	
	28*	20**
0	47.5	47.5
2.5	57.0 / 59.0	56.0 / 58.0
5.0	62.5 / 64.5	60.5 / 63.0
6.0	63.5 / 65.5	61.0 / 64.3
8.0	65.3 / 66.5	62.3 / 65.0
9.0	65.7 / 67.0	62.5 / 65.0

Note. The value of moisture content using Na_2CO_3 concentration, g/dm³, is given in the denominator: * – 4, ** – 12.

Table 2.4

**Residual content of chemical reagents elements
in the semi-finished product after technological treatments**

Semi-finished product after the process of	Content of chemical reagents in the dermis, %			
	chlorine	calcium	sulfur	chromium
Soaking	0.85 / 1.00	—	0.10 / —	—
Liming	0.50 / 0.40	0.80 / 1.30	0.50 / 0.60	—
Deliming-bating	0.10 / 0.30	0.25 / 0.40	0.90 / 1.20	—
Tanning	0.20 / 0.35	0.20 / 0.30	2.10 / 2.80	1.20 / 1.60

Note. The value of the semi-finished product elements obtained by the standard technology is given with a slash.

model (Ukraine), showed that the residual content of elements in the semi-finished product at all stages of processing is smaller compared to the samples obtained by the standard technology.

Thus, it has been established that soaking and liming processes are desirable to be carried out at the temperature of 28 °C, with a threefold decreased consumption of sodium carbonate in soaking, reduced concentrations of calcium hydroxide and sodium sulfide in liming according to the consumption of 6–8 and 6–9 g/dm³, and the reduced content of chemical reagents in the semi-finished product in comparison with the standard technology. During SLPs at the increased temperature, through the intensification of the interaction of alkaline reagents with the dermis, partial destruction of collagen macromolecules with the loss of diamino acids and hydroxyproline and, as a result, the appearance of skin defects, is possible. The dependence of the amino acid composition of the bated pelt on the parameters of SLPs by ion-exchange chromatography was investigated thereby. The results were detected on T-339 automatic analyzer of acids manufactured by *Mikrotechna* (the Czech Republic) using Ostin LGANB sulfopolystyrene ion exchange resins in *Li*-citrate buffer single-column mode.

By a comparative study of the content of diamino acids and hydroxyproline in the pelt according to the developed OSL technology and the standard one (OSL-S) at the leather enterprise CJSC *Chinbar*

Table 2.5

**The content of diaminocarboxylic acids
and oxyproline in the pelt after bating**

Amino acid	Content, mol %, in the pelt by the technology	
	OSL	OSL-S
Arginine	5.12	5.31
Histidine	0.83	0.62
Lyzine	3.03	2.96
Hydroxylysine	0.75	0.74
Hydroxyproline	6.33	6.35

(Ukraine), conducted at the temperatures of 27–29 and 20–22 °C, respectively (**Table 2.5**) [26], it has been proved that the amino acid content is practically the same in collagen of the dermis after delimiting and bating of the pelt.

The study of the amino acid composition, as well as the nature of the soaking kinetics, proves the usefulness of activation of soaking and liming processes at the increased temperature. This makes it possible to reduce significantly the consumption of chemical reagents, including those that are toxic to the environment. As one of the main technological parameters is the liquid coefficient (LQ), which can intensify the process and change the degree of the pelt swelling by enhancing mechanical influences, the activity of alkaline reagents, etc., the dependence of elastic and plastic properties of the pelt on the LQ of the technological solution during soaking and liming at the temperatures of 27–29 °C has been studied. The choice of such physical and mechanical parameters has been determined by their sensitivity to relaxation processes in the structure of collagen of the dermis and the degree of its rehydration, during which there is a redistribution of intermolecular interactions of water with protein and reagents, as well as hydrophobic interactions in collagen.

The results of the studies on the rehydration degree and hydrothermal stability are given in **Table. 2.6** [27]. The given data prove an increase in the degree of the pelt swelling with an increase in the LQ, but in the variant without soaking of raw materials, this figure

Table 2.6

Properties of the semi-finished product after liming and tanning

Indicator	Value according to the variant				
	1	2	3	4	5
Liquid coefficient	0.5	1.0	1.5	1.5*	3.0
Degree of the pelt swelling, %	17.0	21.0	21.5	16.0	26.5
Hydrothermal resistance, °C, of the pelt	58.0	54.0	54.0	60.0	57.0
– a semi-finished product	103.0	107.0	108.0	98.0	102.0

Note. * Without soaking of raw materials

was reduced by 5.5 %, and by the pelt rehydration is at the level of the sample received with the LQ of 0.5. The hydrothermal resistance of these samples has the slightest discrepancy: the highest value before tanning and the lowest – after it. With the increase in the LQ and the degree of rehydration, the hydrothermal stability reaches its extreme value for the pelt and the semi-finished product in Variants 2 and 3. In this case, the maximum difference between the hydrothermal stability of the respective samples before and after tanning is observed. The samples of Variant 5, as well as Variant 1, are characterized by an increase in the hydrothermal stability of the pelt and its slight decrease for the semi-finished product.

The observed effects are caused by a number of reasons. First of all, by the change of the processing liqor after the LQ growth and, accordingly, by the nature of interaction with the structural elements of raw materials. In this case, an important role is played by the ratio between the concentration of the chemical reagent and the protein material. According to the cluster model of aqueous electrolyte solutions with the increase in Ca^{2+} , OH^- , Na^+ ion concentration, the degree of processing liqor structuring increases, especially at low LQs, and their diffusion ability and influence on collagen structure of the negatively charged dermis decreases. The increase in temperature and LQ contributes to the reduction of ionized clusters' size and their diffusion into the structure of the dermis. This is confirmed by the fact that during the liming of raw materials without soaking at the LQ of 1.5, they contain a large

amount of electrolyte, and the pelt demonstrates swelling similar to a soaked sample that was limed at the LQ of 0.5.

The mobility of water molecules grows increasing the temperature; the strength of hydrogen bonds weakens in the intercoil areas of helix molecules of collagen. At the same time, probability of the formation of new bonds, with less swelling of the dermis collagen, increases. Accordingly, the hydrothermal stability, which is determined by the dynamic equilibrium of forces that hold the polypeptide spiral in a stressed state at the given temperature influence on it, and elastic forces of the spiral, dramatically changes. The reduced hydrothermal stability of the pelt obtained with the LQ of 1.5 without soaking of raw materials may be explained by its uneven liming due to the surface interaction of ionized clusters and inadequate hydration, which is directly related to the insufficient “opening” of the fibrous collagen structure. Therefore, with the LQ ranging from 1.0 to 1.5, it is possible to get the pelt with a moderate degree of swelling, with a lower hydrothermal resistance, which indicates a satisfactory opening of structural elements of the dermis collagen. This will facilitate the diffusion of chemical reagents at the subsequent stages of treatment into the inter-microfibrillary space formed in liming during the formation of the pelt structure.

The study of the complex of the pelt deformation properties (**Fig. 2.3**) shows that an increase in tension is accompanied by an increase in the deformation ability of the pelt for all LQs, especially in loose areas like bellies. This is confirmed by a two- or threefold increase of the tangent of the angle of the functional dependence of the belly pelt deformation against the butt on tension, with the exception of samples obtained at the LQ of 0.5, during which cations of alkaline reagents clusters are deposited predominantly on the surface of the fibrous collagen structure. This can be explained by insufficient water absorption of a denser butt area. However, it is characterized by a slightly larger deformation with respect to samples obtained at higher LQs, which is evidently caused by a lower internal resistance to deformation of an insufficiently rehydrated structure of the dermis. At the LQ of 3, samples have excessive swelling and due to large internal stresses exhibit the least deformation ability.

The influence of the alkaline reagents concentration on the structural changes of the dermis and the deformation indicators of the pelt

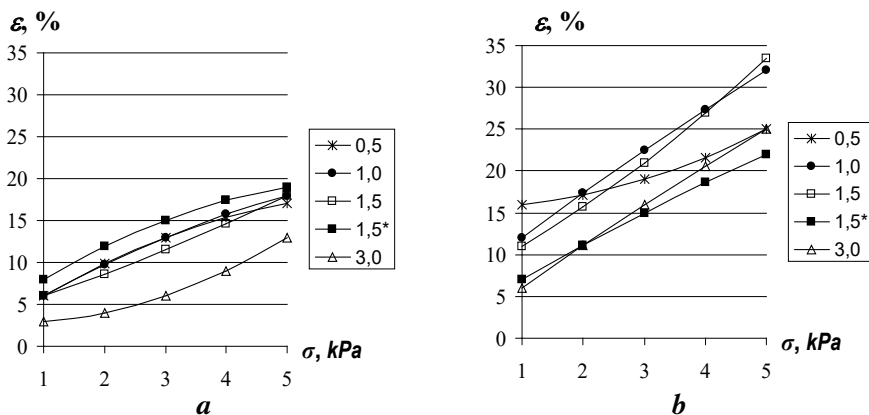


Fig.2.3. Dependence of the butt pelt deformation (*a*) and the belly (*b*) on tension and the LQ: 0.5; 1.0; 1.5; 1.5* (without soaking); 3.0

in the nature of the dependence of the deformation types on the LQ is especially clearly manifested. As can be seen from **Fig. 2.4**, the samples of the butt area, obtained at the LQ of 3, have the greatest elasticity and the least residual deformation. At the same time, there is a growth of residual deformation with a simultaneous decrease of elastic deformation of peripheral areas, which is connected with the nature of the orientation of collagen fibers. At the lowest LQ, the residual deformation of the peripheral areas is sufficiently large with a decreased value of the elastic component of the deformation, explained by insufficient rehydration of the samples, although this effect is not detected on the butt area. The best correlation of the deformation types, as it can be seen from **Fig. 2.4b**, is observed at the LQ of 1.0–1.5 for the samples of the belly area. At the same time, in the butt area, a slight increase in residual deformation occurs at the LQ of 1.0, and the belly area is very deformed. The pelt samples, obtained without soaking, have a minimal deformation.

The study of gelatin smelting during calcareous sulfide liming [28], depending on the temperature and water ratio of 0.8/1.0, shows (**Fig. 2.5**) that at the temperature of the process higher than 28–29 °C and the concentration of calcium hydroxide of 25 g/l there may be a sharp increase in gelatin smelting, indicating the destruction of inter- and intramolecular bonds of collagen macromolecules. This is also shown by

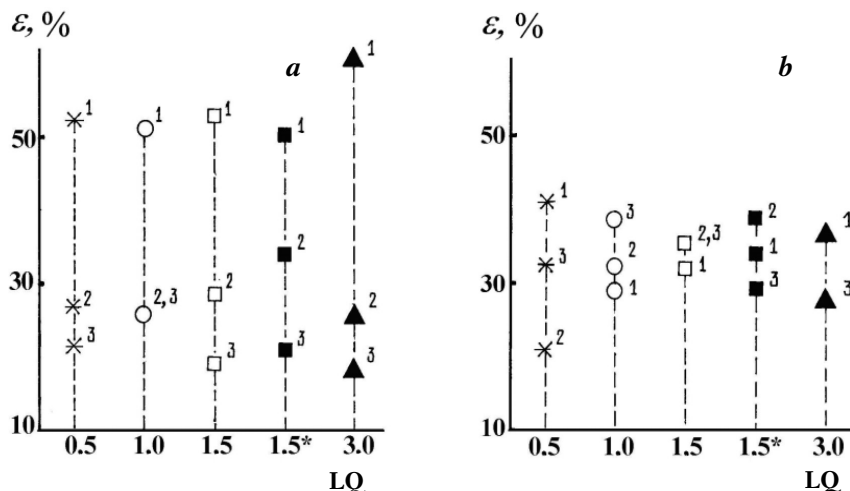


Fig. 2.4. Dependence of flexible (1), elastic (2), residual deformation (3) of the butt (a) and belly (b) pelt on the LQ and tension when compressing the sample

the increase in the protein content in the spent lime solution. At a lower temperature, the process of collagen structure splitting is slowing down and so the technological process is getting longer. After two hours of alkaline treatment for further liming, the ratio of water-raw materials was raised to 1.0/1.0, and sodium sulfide with calcium hydroxide – to 2.0 and 2.4 % of the raw materials weight.

Thus, it has been identified that by deliberately changing the concentration of alkaline reagents during the soaking and liming, the degree of opening of the collagen structure of the dermis, its swelling and hydrothermal resistance of the pelt can be regulated, which will promote more uniform stabilization during tanning. It has been shown that with liquid coefficients of 1.0 to 1.5, the pelt with 21.0–21.5 % swelling is formed having favorable proportions of elastic and flexible indices.

The thermogravimetric analysis of the dermis was conducted on the derivatograph OD-102 (MOM Company, Hungary) in order to identify the peculiarities of the structural transformations after soaking (S), liming (L), deliming and bating (DB) at a heating rate of 10 °/min.

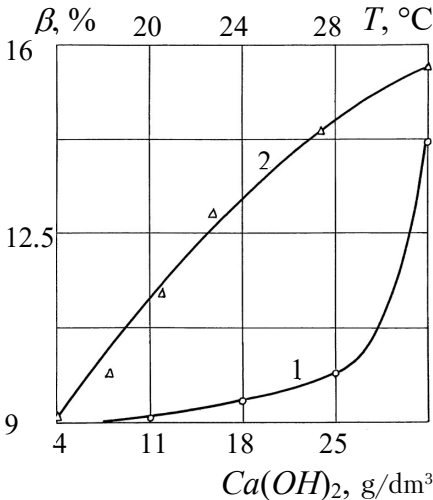


Fig. 2.5. Dependence of smelted gelatin β on the temperature of liming (1) and Ca(OH)_2 concentration (2)

in the air environment using an inert substance – aluminum oxide. At the same time, the temperature of the beginning, the end, and the maximum speed of the endoeffect were determined according to T_b , T_e , T_{ms} ; mass loss velocity v_{ml} in the range of 50–150 °C; relative mass loss up to 300 °C Δm_{300} ; the temperature of the thermal destruction beginning T_{tdb} [29].

The analysis of the thermograms of the studied dermis samples has shown that the loss of its mass begins at 56–60 °C (**Table 2.7**). The loss of moisture, which is mainly about hygroscopic water, corresponds

to this effect. A more extended temperature interval of the mass loss at this stage of heating may indicate a higher degree of splitting of the internal structure of the dermis collagen obtained by a new technology. This is due to a more complete removal of preservative reagents and globular proteins from the dermis during soaking, of mucopolysaccharides during liming along with a partial destruction of reticulin, elastin fibers and lipids. It should be noted that after deliming and bating, the final temperature of the endothermic effect for the samples of a new technology is by 2 °C higher with a lower maximum rate of hygroscopic water loss of 3 °C.

After a significant decrease in the samples' mass loss, two less noticeable endothermic effects are observed in the temperature range of 196–245 and 230–225 °C, which may cause the destruction of interfibrillary and intermolecular bonds. The first of these, apparently is associated with the loss of hydration water during collagen welding. The destruction process of physical bonds of hydrophobic parts of collagen, hydrogen and ionic bonds of its polar areas then transforms into

Table 2.7

**Thermal indices of the dermis samples at different stages
of treatment**

Technology (stage)	Endoeffect temperature, °C			V_{mT}^{mT} %/min	T_{tdb} , °C	Δm_{300} , %
	T_b	T_e	T_{ms}			
OSL (S)	56	125	90	1.9	259	30.0
OSL-S (S)	60	123	91	2.0	255	31.0
OSL (L)	57	125	95	1.4	257	28.0
OSL-S (L)	61	123	103	1.8	255	27.0
OSL (DB)	60	130	100	2.1	259	40.0
OSL-S (DB)	60	128	103	2.2	258	33.6

a noticeable destruction of collagen, caused by the destruction of intra-molecular covalent bonds. This is manifested by a strong endothermic effect on the DTA curves and a significant mass loss of the samples, at the temperatures ranging from 255 to 259 °C. A higher degree of splitting of the collagen structure of the dermis after dehairing and bating of a semi-finished product obtained by a new technology is shown by a greater loss of their mass up to 300 °C by 6.4 %.

Therefore, the thermogravimetric study made it possible to reveal the peculiarities of the collagen structure of the cattle dermis at different stages of treatment, depending on the character of soaking and liming processes. The largest temperature interval of the mass loss at the first endothermic effect and the mass loss to 300 °C after dehairing and bating of a new technology samples may indicate higher porosity and accessibility of collagen structure to the action of reagents.

All processes of the OSL technology were carried out in a suspended-type washer of *Vallero* company (Italy) at a fixed temperature of 27–29 °C [30] that intensifies the process. Preserved raw materials after washing at the LQ of 1.2 for 30 minutes adding sodium carbonate in the amount of 0.3 %¹ go through double soaking at the LQ of 0.8. The first soaking is carried out using a nonionic surfactant – 0.3 % in

¹ In the future, the materials are dosed into a technical product depending on the mass of raw materials.

the presence of sodium carbonate — 0.15 % for 1 hour with the subsequent drainage of the spent solution. The second soaking is carried out for 4–5 hours adding sodium carbonate — 0.5 % and a non-ionogenic surfactant — 0.2 %.

Liming is carried out using a processing liquor after the second soaking with the addition of, mass %: water — 20, sodium sulfide — 2 and calcium hydroxide — 2.4. The process time is 12 hours with a periodic rotation of the drum at the rate of 3–4 min⁻¹, during the first hour — 30 minutes, the second — 10 minutes and the next 10 hours — 5 minutes per hour. Then, the semi-finished product is washed twice at a constant rotation of the drum with a gradual decrease in the temperature up to 20–22 °C for 15 minutes. The pelt is checked for dehairing completeness, moderate swelling, cleanliness of the grain, homogeneity and translucency of the transverse cut made along the vertebral line near the rump.

Thus, the technology of one-stage liming of cattle raw materials with preliminary washing and a two-stage soaking gives an opportunity to receive the pelt with moderate swelling and sufficient splitting of the dermis structure. The pelt, received after deliming, bating, washing and pickling, becomes open to effective interaction with tanning reagents.

2.3. Two-stage dehairing and liming with the hair utilization

In order to avoid the presence of degradation products in waste water of industrial enterprises, a two-stage SLP technology for the utilization of hair [31] has been developed. To implement such a technology, the development of new compositions of chemical reagents, identification of their effective concentrations in processing liquors, treatment conditions and the availability of automated technological equipment are required [32, 33]. At a reduced concentration of chemical reagents in SLPs, the role of physical and mechanical influences in a moving apparatus for the formation of the optimally piled structure of the pelt increases when the raw materials are exposed to the combined

action of stretching, compressing and scrubbing of the epidermis, which is accompanied by its mechanical and chemical activation (**Fig. 2.6**). However, the long mechanical and chemical influence on the hides can lead to the detachment of the papillary layer of the dermis from the reticulate one, causing openness with the possible appearance of the leather material looseness.

According to the given scheme of dehairing and liming [34], at first it is necessary to ensure the destruction of the lipid matrix of the epidermal stratum corneum and openness of microways of chemical reagents diffusion for the basal membrane of the dermis. This is accelerated by the action of mechanical factors during the treatment of hides in a moving apparatus. At the same time, the alkaline medium restricts keratolysis, and conditions, preventing the hair immunization in hair follicles, are created. The enzyme preparation is of primary importance

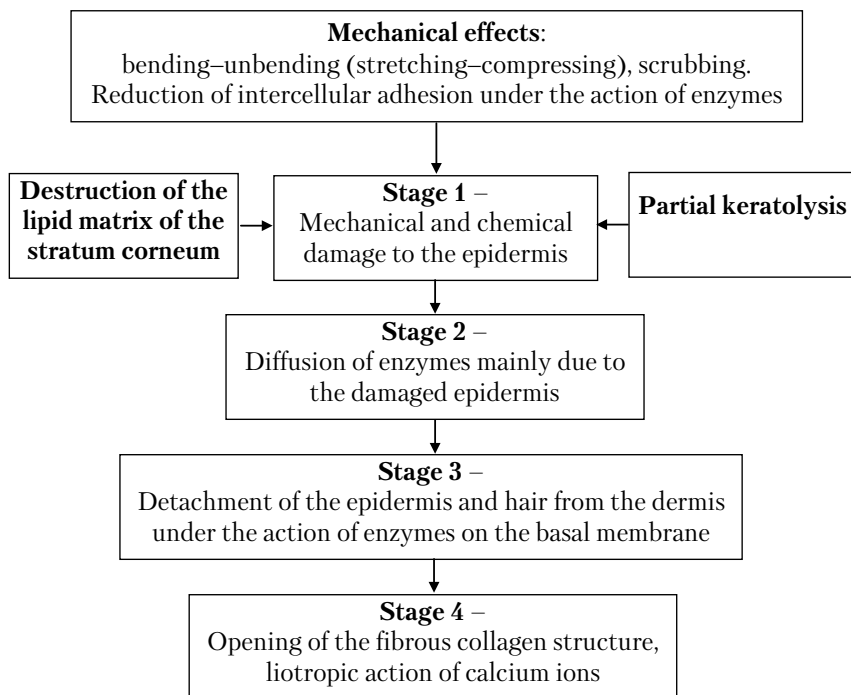


Fig. 2.6. Stages of dehairing and liming

and it helps to separate the epidermis from the dermis, facilitates the access of reagents to it with an insignificant activity of the enzyme towards collagen and the lyotropic effect of calcium ions on it.

Therefore, the slowest stage of dehairing with the utilization of hair is the destruction of intercellular lipid formations of the stratum corneum of the epidermis.

In developing a new technology for dehairing and liming, which make it possible to reduce dramatically the falling of products of the hide hair side destruction in industrial wastewater, it was assumed that the developed technology should meet the following requirements:

- to provide pure pelt with a moderate swelling and without hair remnants (scud), with the parameters of the process that should promote maximum weakening of the hair connection with the dermis;
- the length of the production cycle should not be significantly increased compared with the technology that involves the hair destruction;
- not to be material overintensive and ensure the minimum use of scarce chemical reagents;
- to ensure the efficient use of raw materials and a high quality of leather materials.

2.3.1. Dehairing and liming with the hair shaft immunization

To protect the hair from a destructive action of alkaline reagents, it is necessary to use pre-treatment with reagents that will facilitate the formation of alkali-resistant bonds in its structure due to changes in interfibrillary primary bonds, the hydrolysis of which is the basis of the hair dissolution. Structurating agents such as $Ca(OH)_2$ and aldehydes belong to the substances that may contribute to the formation of alkali-resistant bonds in the hair keratin, i.e., to immunize the hair shafts. In particular, $-S-S-$ bonds in keratin, the hydrolysis of which is at the basis of the dehairing process, can be substituted by $-S-$ bonds with the help of $Ca(OH)_2$. The compounds formed by the influence of $Ca(OH)_2$ have a high reactivity and can form chemical bonds with the

participation of $-S-O-Ca-S-$, $-S-Ca-S-$ calcium, they are resistant to alkaline reagents and sulfur compounds.

Moreover, additional immunization protection of the hair shaft against its destruction is needed for effective and rapid dehairing, which requires the use of high concentrations of Na_2S . Otherwise, the removed hair is greatly damaged, it will be fragmented with a reduced strength, and becomes rigid and fragile after neutralization and drying. At the same time, the undercoat is hydrolyzed and this leads to an increased content of keratin proteins in industrial wastewater, which, in turn, increases their toxicity and negative impact on the environment.

An insufficient degree of the hair shaft structuring by treatment with $Ca(OH)_2$ can not be eliminated by increasing the time of treatment after the diffusion of calcium ions to the hair roots and their subsequent immunization with the hair sacks. The result is incomplete hair removal and the appearance of defects on the outer layer of the dermis. Formaldehyde, which can be applied in tanning processes, was used to enhance the hair shaft immunization in the dehairing solution of the developed technology [34]. To estimate the time of its addition to $Ca(OH)_2$ solution, the study of the kinetics of calcium ions diffusion into the structure of the soaked dermis has been carried out.

$Ca(OH)_2$ diffusion was studied on the samples of average cowhide and heifer, selected from the least thick parts of the hides. For soaking of the samples, in order to eliminate the influence of $NaCl$ on the diffusion of calcium ions during the process, SAVENOL NWP non-ionic surfactant (Ukraine) was used as a catalyst instead of Na_2CO_3 . After reaching the 67 % moisture content in the dermis, the samples were washed with distilled water and placed in the solution of $Ca(OH)_2$ with a concentration of g/dm^3 : 5, 15, 25, 35 at the temperatures of, °C: 18–20 and 28–30. The depth of $Ca(OH)_2$ diffusion into the structure of the dermis was determined by the microscopic method after the coloring of the cut with phenolphthalein. The thickness of the dermis of the average cowhide and heifer at the standard point is respectively 3.93 and 3.15 mm, while the reticulate layer is 2.71 and 2.23 mm. Moreover, the reticulate layer of both types of raw materials is taken as 100 %.

The studies [24, 35–37] show that, at the temperatures of 19 and 29 °C (**Fig. 2.7**), the diffusion of calcium ions into the reticulate layer

of the dermis is characterized by a gradual deceleration of the process speed for 20 minutes followed by its significant decrease. At the same time, $Ca(OH)_2$ solution with a concentration of 5 g/dm^3 reaches the boundary between the papillary and reticulate layers, where the hair roots are, which corresponds to 90 % of the thickness of the reticulate layer of the cowhide, in 50–55 minutes.

An increase in $Ca(OH)_2$ concentration up to 35 g/dm^3 leads to deceleration of its diffusion, which results in a decrease in the penetration depth of the reagent to 70 %. These effects are caused by a significant hydration ability of calcium ions with the formation of complex intermolecular compounds with collagen. This can lead to an increase in the thickness of the structural elements, reduction and disappearance of interstructure gaps. In this case, the heterogeneous structure is converted into homogeneous.

Inceasing $Ca(OH)_2$ concentration in the liming solution, the form of kinetic curves does not virtually change, but the time when calcium ions achieve the hair roots increases up to 80 minutes at the peak concentration of the reagent. It is necessary to point out that the decrease in the solution temperature up to $19\text{ }^\circ\text{C}$ slightly increases the diffusion speed at the beginning of treatment. So, the depth of $Ca(OH)_2$ diffusion with the $10\text{ }^\circ\text{C}$ decrease in temperature increases in 10 minutes for a normal cow hide and heifer from 27–40 and 23–35 % to 30–45 and 29–40 respectively. It can cause the increase in $Ca(OH)_2$ solubility with the decrease in temperature and with the decrease in interaction intensity of calcium ions with carboxylic groups of collagen that will facilitate watering and complexation.

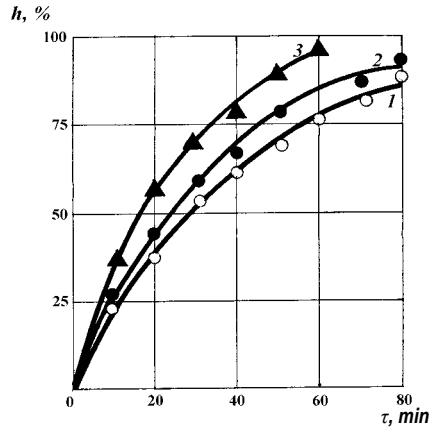


Fig. 2.7. Diffusion kinetics of $Ca(OH)_2$ into a reticulate layer of the dermis of a soaked skin at the temperature of $28\text{--}30\text{ }^\circ\text{C}$ and the concentration, g/dm^3 : 5 (1), 15 (2), 35 (3)

Thus, the studies of calcium hydroxide diffusion into the structure of the reticulate layer with its various consumption and temperature conditions have shown the highest speed of the process through the first 10–15 minutes. It has been determined that the time when the processing liquor of calcium hydroxide reaches the hair roots is 50–55 minutes with its peak concentration and the temperature of 28–30 °C. Taking into account the peculiarities of the above-mentioned interaction with an additional use of formaldehyde for the hair shaft immunization, it is necessary to dose it into the calcium solution, up to 50 minutes from the start of dehairing.

To determine the influence of formaldehyde on the dehairing of raw hides, the studies of the hair properties after the use of calcium and sulfide solution have been carried out [38]. In order to prevent a negative influence of $Ca(OH)_2$ and formaldehyde on the hair immunization, it is necessary to provide an appropriate degree of their interaction, especially of formaldehyde, with the membranes of keratine structure of hair covering. As formaldehyde causes collagen structuring that manifests itself in the increase of its shrinkage temperature (T_{sh}) from 73 to 89 °C with the concentration of 0.05 % and with the pH of 7.0 and 10.0 respectively, a rational consumption of formaldehyde in the technological solution must be identified.

On the basis of a priori information about the selected contents of technological solutions, in which, apart from $Ca(OH)_2$ and formaldehyde for the immunization of the hair shaft, Na_2S was used to accelerate the weakening of the bond between the immunized hair shaft and epidermis with the dermis. In this case, the consumption of chemical reagents is, % of raw materials: $Ca(OH)_2$ 60 % 0.5–3.5, formalin 40 % 0.032–0.08, Na_2S 65 % 1.2–1.8. Due to the fact that the weakening of the hair bonds with the dermis is performed using a solution at the pH of 11.3–11.7; as a result of the studies, a range of low Na_2S concentrations has been chosen and they do not lead to significant destruction of the hair shafts and, at the same time, provide an active action on its roots.

The analysis of the findings (**Table 2.8**) indicates that an increase in the concentration of formaldehyde is accompanied by an increase in the strength of the hair and its resistance to the alkali action. However, the period of weakening of the hair bond with the dermis slightly increases. At the same time, the increase in Na_2S significantly reduces

Table 2.8

**Consumption of chemical reagents at the dehairing stage
and the properties of the received hair**

Indicator	Consumption of reagents and the indicator values according to the variant				
	1	2	3	4	5
Consumption of, % of the raw material mass,					
formaldehyde	0.032	0.064	0.08	0.048	0.032
calcium hydroxide	3.5	1.5	0.5	0.5	0.5
sodium sulfide	1.2	1.2	1.2	1.6	1.8
Resistance of the hair to the alkali action, %	89.4	90.4	89.0	92.7	88.6
Strength of the hair, MPa	34.0	104.0	90.0	79.0	26.0
Time of weakening of the hair bond with the dermis, min.	90	115	120	38	20

this period, but the strength of the hair decreases. A complete weakening of the hair bond with the dermis occurs in 50–85 minutes and the hair is easily separated from the dermis in the dehairing solution. The strength of the hair is 35 and has 45 % of the strength of the raw and untreated and obtained after the liming by the SLP technology in the production of Russian leather respectively, with the time of a complete weakening of 36 hours.

Therefore, the study of the properties of the hair obtained after treatment with alkaline solutions adding formaldehyde has shown the effectiveness of its common use in lime and sulfide dehairing of skins and hides. The maximum strength of the hair has been identified at formaldehyde consumption of 0.064 %.

The technology of dehairing and liming using formaldehyde should provide for its minimal impact on the structure and properties of collagen in the dermis. Diffusion of formaldehyde into the structure of the dermis can lead to its interaction with collagen and other proteins that are part of the interfilament matrix and their structuring. This will prevent the removal of inter-fiber substance, which is a prerequisite

for the formation of the pelt, penetration of chemical reagents during further treatments. Along with the study of the hair, the properties of the received pelt have been determined (**Table 2.9**) by the method of the leather enterprise CJSC *Chinbar* after dehairing according to the above-mentioned variants.

According to the data, the properties of the pelt, unlike the indicators of the hair, do not vary much within the studied limits of the formaldehyde consumption. However, there is a tendency to increase the temperature of the pelt welding by 4 °C at the maximum use of formaldehyde – 0.08 %. At the same time, the enzymatic and thermal stability (ETS) of the collagen in the dermis and the concentration of protein substances in the spent solution increases. This effect may be due to the increased structure forming effect of the aldehyde, which, owing to the increased reactivity in the alkaline medium, is localized on the subdermal tissue. Due to the consolidation of the structural elements of the dermis, collagen resistance to the action of enzymes increases and

Table 2.9

Properties of the pelt and the spent liming solution

Indicator	The indicator values according to the variant					
	under study					OSL-S
	1	2	3	4	5	
Temperature of welding, °C	53	54	56	52	52	54
ETS, min.	54	54	57	55	54	55
Gelatin smelting, %	12.4	11.8	11.3	11.9	13.1	12.5
Concentration in the spent solution, g/dm ³ ,						
protein material	3.18	2.92	2.71	3.12	2.96	5.21
sodium sulfide	4.81	4.73	4.85	4.75	4.91	4.82
calcium hydroxide	11.4	11.9	11.4	11.3	11.2	12.5
the <i>pH</i> of the solution at the stage of						
immunization	12.5	12.5	12.3	12.3	12.3	—
dehairing	11.4	11.3	11.4	11.4	11.6	—
liming	13.4	13.2	13.4	13.3	13.6	13.5

the amount of smelted gelatin decreases slightly. With the increase in formaldehyde consumption, the content of protein substances in the spent solution is reduced by 1.8 times in relation to the standard technology of a one-stage liming (OSL-S) due to the preservation of keratin proteins in the hair, which are especially dangerous to the environment.

The study of elastic and plastic properties of the pelt has also shown a slight change in its composition and structure under the influence of formaldehyde in the amount up to 0.064 % when used during dehairing. Therefore, the conditionally elastic and conditionally plastic components of the deformation are within 53.8–58.3 and 17.2–18.1 % respectively. These values correspond to similar indices of the pelt obtained by the method of JSC *Chinbar*. All samples of the formed pelt after liming have a uniform degree of dermal liming value in layers with the degree of swelling of 25.1–26.8 % in the absence of the front surface cockling. Thus, the use of 0.064 % formaldehyde in dehairing and liming solutions has shown its prevailing influence on the hair properties and the absence of a negative influence on the collagen in the dermis.

To determine the specific effects of formaldehyde on the hair, a study has been carried out on its amino acid composition and on the interaction of formaldehyde with keratin by the method of IR spectroscopy and microscopy. The nature of the dependence of the above-mentioned investigated properties of the hair on the concentration of a dehairing solution may be explained by a change in the amino acid composition of the hair and its structure.

The amino acid composition of keratin was determined for the hair samples pre-immunized with $Ca(OH)_2$ (Variant 1), in the presence of formalin with the consumption of 0.064 % (Variant 2) treated by the technology of liming with the hair utilization at Na_2S concentration of 0.7–0.8 g/dm³ (Variant 3), without any treatment (Variant 4). The results of chromatographic studies of the hair that are given in **Table 2.10** [39] indicate the characteristic presence of sulfur-containing amino acids. The highest content of these amino acids is observed in the untreated hair and the lowest – in the hair treated by the method of a long-lasting liming with the hair preservation.

The treatment of the hair with formaldehyde and $Ca(OH)_2$ increases the content of these amino acids by 67.6 % compared with a long-lasting

Table 2.10

The content of the most important amino acid groups in the hair

Amino acid group	Amount, mol %, according to the variant			
	1	2	3	4
Diaminocarboxylic (<i>R, K</i>)	9.9	10.8	10.9	7.9
Aminodicarboxylic (<i>N, Q</i>)	16.8	14.4	15.9	17.7
Sulfur-containing (<i>C', M</i>)	19.3	20.2	12.0	22.8
With a nonpolar side residue (<i>A, V, L, I</i>)	18.9	19.0	21.8	18.5
Hydroxyacids (<i>S, T</i>)	16.4	14.8	17.4	14.7
Including:				
alanine	4.9	4.3	5.5	3.7
serine	9.7	8.4	9.8	9.4

treatment for 36 hours. (Variant 3). The treated hair of this variant in terms of the amount of sulfur-containing amino acids by 11,5 % is inferior to the native hair. This, obviously, can be explained by the fact that in the process of a long-lasting splitting of disulfide bonds of keratin by calcium hydroxide in the absence of formaldehyde, reactive hydrolysis products – the cysteine and sulfenic acid residues – can be converted in the alkaline media into the derivatives of serine and alanine, the formation of which is accompanied by the emission of sulfur. It follows that not all residues of cysteine and sulfonic acid, formed as a result of the reaction of hydrolysis of disulfide bonds, take part in the immunization of the hair shaft. At the same time, there is a replacement of disulfide bonds by lanthion bonds, which are resistant to the action of alkaline reagents.

In the absence in the system of structuring reagents that can interact with the active groups of side chains of keratin and products of splitting of disulfide bridges after an intense destruction of disulfide bonds in keratin, only their internal intermolecular redistribution occurs. However, this redistribution does not occur if new bonds are formed simultaneously with the destruction of the native ones. The presence in the keratin and hydroxide solution of calcium and formaldehyde, capable of a polyfunctional response with both active side chain groups and products of hydrolysis of disulfide bonds of keratin, prevents internal

molecular redistribution in the structure of keratin after the intense destruction of its disulfide and other inter- and intramolecular bonds.

Adding formalin to the immunization solution prevents the conversion of the reactive residues of cysteine and sulfonic acid into the derivatives of serine and alanine. This is probably due to the interaction of formaldehyde with active groups of these newly formed hydrolysis products of disulfide bonds and active groups of molecular chains of keratin, primarily nitrogen-containing.

The foregoing is confirmed by a higher content of amino acids, the molecules of which include sulfur, and a lower content of serine and alanine in the hair samples treated with formaldehyde solution compared to Variant 1 and Variant 3.

The possible formation of new additional bonds in the structure of the hair is also confirmed by a higher content of diaminocarboxylic acids of lysine and arginine in hydrolyzates of the hair treated with formaldehyde.

With the simultaneous use of $Ca(OH)_2$ and formaldehyde, cross-linking bonds can be formed. In addition, there can be formed $=CH-S-CH=$ lanthion bonds, the bonds of $-S-O-Ca-S-$, $-S-Ca-S-$ type, and with the participation of formaldehyde – the bonds of $-S-CH_2-S-$ type with the participation of $-SH$ groups of the native keratin, of $-S-CH_2-NH-$ and $-S-CH_2-N-$ type with the participation of $-SH$ groups, which are formed during the hydrolysis of disulphide bonds and $-NH_2-$ and $-NH-$ groups of keratin structure of the $-NH-CH_2-NH-$ type with the participation of $-NH_2-$ groups and other types.

The results of the study of the amino acid composition [40–43] of the worked liming solutions using formaldehyde after the immunization of the hair shaft with $Ca(OH)_2$ (**Table 2.11**), by Variant 1 and Variant 2, and the subsequent sulfide and calcium liming with the LQ of 1.5, indicate that the content of amino acids is sharply reduced compared with the technology of OSL, which involves the hair destruction. At the same time, the keratin of the hair is 6 % of the mass of raw materials, which completely fall into industrial effluents.

The relative concentration of amino acids after dehairing and liming by Variant 1 and Variant 2 in comparison with the OSL technology, respectively, is only 6.3 and 5.3 %. Moreover, the immunization of the

Table 2.11

**The content of the most important amino acid groups
in the spent liming solution**

Amino acid group	Amount, mg/100 cm ³ , according to the variant of treatment	
	1	2
Diaminocarboxylic (<i>R, K</i>)	56.6	31.5
Aminocarboxylic (<i>N, Q</i>)	63.9	57.2
Sulfur-containing (<i>C, M</i>)	35.5	27.7
With a nonpolar side residue (<i>A, V, L, I</i>)	60.8	55.0
Hydroxy acids (<i>S, T</i>)	35.7	40.6
Total amount	252.5	211.4

hair shaft adding formaldehyde reduces the concentration of amino acids in the spent solution by 12.0 % compared with the variant of lime immunization. The given data refer to 80 % of the keratin protein content in the spent solutions.

The analysis of the results obtained according to amino acid groups indicates deep chemical changes in the structure of the hair during alkaline treatment, with the hair shaft immunization by the second treatment variant being accompanied by a 1.8-fold decrease in the content of diaminocarboxylic acids and 10.5 % decrease of aminocarboxylic acids. This effect, caused by the interaction of formaldehyde with diaminocarboxylic acids, helps to stabilize properties of the hair

Thus, the analysis of the amino acid composition of the hair after the treatment of raw hides using technologies with the preservation of the hair whose shafts are immunized with calcium hydroxide, indicates its significant dependence on the type of alkaline treatment, especially in the technology with a relatively low concentration of sodium sulfide in the processing liquor and long-lasting liming. A combined calcium and sulfide treatment of the hair covering leads to 60 % increase in the content of sulfur-containing amino acids in the keratin hydrolyzate and reduction of alanine and serine by 23 and 15 % respectively. In addition, the variant of the hair shaft immunizing solely with calcium hydroxide is characterized by a 16 % higher content of diaminocarboxylic acids in the hair and 9 % less content of aminocarboxylic acids.

The identified nature of changes in the amino acid composition of the hair and spent liming solutions using structure forming agents indicates the formation of new intermolecular bonds in its structure, resistant to the action of alkaline reagents, and this shows the perspective of their use in technologies with the preservation of the hair. Reducing the content of products of keratin destruction by 15.8–18.9 times compared with the technology of full hair destruction indicates a high ecological efficiency of the developed technology of dehairing and liming.

In order to identify chemical changes in the keratin structure, the hair samples after alkaline treatments with $\text{Ca}(\text{OH})_2$ and Na_2S adding formaldehyde according to the relevant technologies [44] were analyzed using an IR spectroscopic method on a *Specord 75IR* spectrophotometer (Germany) using tablets with *KBr* and fine-cut hair at the ratio of 1/50. The results of the study are shown in **Fig. 2.8** and **2.9**.

Absorption bands at 470 and 610 cm^{-1} are characteristic for the native hair, corresponding to the valence vibrations of S-S and C-S bonds in the peptide chains. The intensive absorption band with three

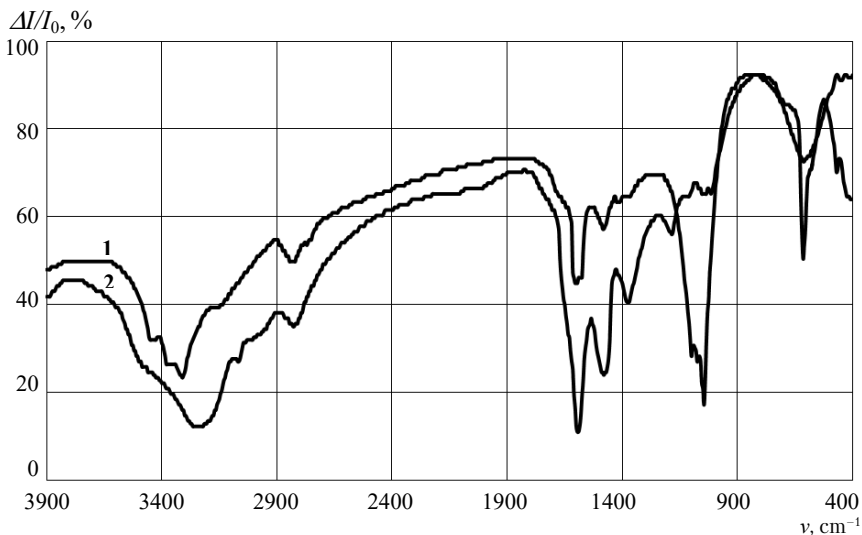


Fig. 2.8. IR-spectra of keratin:
1 – native, 2 – treated with $\text{Ca}(\text{OH})_2$

maxima at 1080, 1100, 1130 cm^{-1} can be attributed to the deformation oscillations of $-OH$ groups, the bonds of $C-N$, $N=N$, $C-C$ type, and $C-O-C$ ester groups.

Deformation vibrations of carboxyl groups are manifested only after the treatment with $Ca(OH)_2$ with a low intensive absorption band at the frequency of 1430 cm^{-1} , and deformation vibrations of amide II – with a band of 1510 cm^{-1} . Vibrations of amide I correspond to the absorption band at 1600–1720 cm^{-1} . For the valence vibrations of the $C-H$ methyl and methylene groups, the absorption bands are characteristic at 2800–2900 cm^{-1} , and the valence vibrations of the $N-H$ primary and secondary amides are characterized by absorption bands with a maximum at the bands of 3400, 3470 and 3520 cm^{-1} .

Treatment of the hair with $Ca(OH)_2$ leads to the hydrolysis of $-S-$ bonds and formation of new lanthanic bonds ($\equiv-S-C\equiv$) in the structure of keratin, resistant to the action of alkaline reagents. It is also necessary to expect the creation of bonds of $\equiv C-S-Ca-S-C\equiv$ type. As a result of the interaction of aldehydes and alcohols formed due to

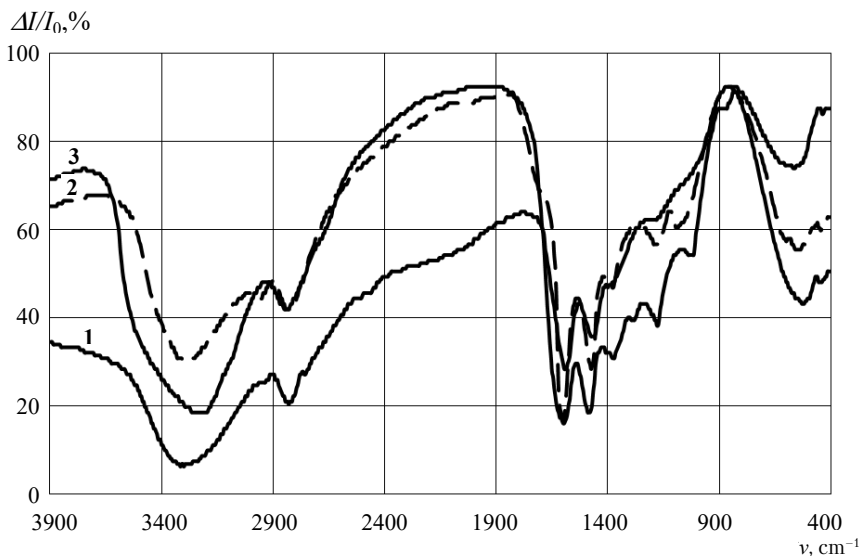


Fig. 2.9. Infrared spectra of keratin treated with $Ca(OH)_2$ and additionally with: 1 – formaldehyde, 2 – Na_2S , 3 – formaldehyde and Na_2S

the decomposition of sulfenic acids with sulfur liberation, it is possible to form alkali-resistant $-N=CH-$ bonds with amidogroups of adjacent chains of keratin.

As the interaction of $Ca(OH)_2$ with keratin results in the deamidization of carboxyl groups of monoamino dicarboxylic acid residues and facilitates the weakening and breaking of the native keratin inter- and intramolecular bonds, it is necessary to expect significant changes in the spectrum of keratin treated with $Ca(OH)_2$. Indeed, in the hair spectrum (**Fig. 2.6**, Curve 2), treated with $Ca(OH)_2$, there are a number of significant changes compared to the spectrum of the native hair. In this case, the intensity of the 470 cm^{-1} absorption band, which characterizes valence vibrations of disulfide bonds, is significantly reduced, and the 610 cm^{-1} absorption band, which characterizes the valence vibrations of the $\equiv C-S-$ bonds, extends and manifests itself in the spectrum with the frequency of 650 cm^{-1} , which corresponds to the vibrations of the $\equiv C-S-C\equiv$ groups of atoms.

The deamidization of carboxyl groups of dicarboxylic acids of the polypeptide chains of keratin under the action of calcium hydroxide and the possible destruction of intermolecular $-NH-CO-$ bonds in the side chains of keratin may indicate an increase in the intensity of the 1430 i 1510 cm^{-1} bands.

Under the influence of alkaline reagents, due to a significant destruction of disulfide and other bonds in keratin, there is an internal intermolecular redistribution that prevents the formation of a sufficient number of new transverse bonds. These effects are reflected by changes in the spectral regions at the frequencies of 3300 and 3500 cm^{-1} . The spread and increase of the intensity of the bands in these spectral regions with a high degree of probability may indicate a decrease in the density of the hair structure, which is explained by the formation of hydrogen bonds in the structure of keratin due to an intense alkaline effect, which results in an increase in the number of free functional OH , NH , NH_2 , CO groups.

The sharp reduction of intensive absorption bands in the spectral region of $1080-1130\text{ cm}^{-1}$ is primarily due to the destruction of the native bonds under an intensive alkaline action, which is accompanied by an internal intermolecular redistribution in the structure of keratin.

In the presence of formaldehyde, which can interact with different functional groups of polypeptide chains ($-SH$, $NH_2=NH$, $-OH$) with the formation of bonds of various types ($-S-CH_2-S-$, $-NH-CH_2-NH-$, $-CH_2-S-CH_2ONH-$, $-N=CH-$, etc.), internal redistribution of bonds does not occur.

Such changes correspond to the spectrum of the hair (**Fig. 2.7**, Curve 1); its shaft immunization was performed with $Ca(OH)_2$. At the same time, there is an extension of the absorption band at the frequency of 650 cm^{-1} , as well as a decrease in the intensity of absorption bands with maxima of 1430 , 1510 and 1630 cm^{-1} and a significant decrease in the intensity of the formed absorption band with a maximum of 3400 cm^{-1} . This may be the result of the formation of various types of keratin in the structure of keratin with the participation of formaldehyde and active keratin groups, peculiar to the structure of native keratin and formed as a result of the hydrolysis of disulphide and other intermolecular bonds under the action of calcium hydroxide. This contributes to the increase in the number of inter- and intra-molecular bonds, the result of which is the consolidation of keratin structural elements.

Under the influence of Na_2S , partial hydrolysis of the bonds specific to the native keratin and those formed during the immunization of the hair shaft may occur. This is confirmed by changes occurring in the spectrum (**Fig. 2.7**, Curve 2) in comparison with the spectrum (**Fig. 2.6**, Curve 2). First of all, the changes relate to the area of $450-600\text{ cm}^{-1}$ spectrum, where the bonds specific to the sulfur-containing amino acids of keratin are manifested. In this area of the spectrum, there is a low-intensity absorption band of a disulfide bond with a maximum of 470 cm^{-1} , and the intensity of the absorption band specific to the $C-S$ bond decreases, which may indicate that part of these bonds is destroyed under the action of a sodium sulfide solution with the sulfur liberation and the formation of alanine and serine derivatives. At the same time, there is an extension of the absorption band in the frequency range of $3300-3400\text{ cm}^{-1}$ and the shift of this band maximum to the long-wavelength region of the spectrum, which may indicate an increase in the number of intermolecular hydrogen bonds in the structure of keratin as a result of the change in the number of free groups capable of forming such bonds.

The analysis of the influence of Na_2S on the hair keratin, whose shaft was immunized with $Ca(OH)_2$ and formaldehyde (**Figure 2.7**, Curve 3), shows that the characteristic changes are similar to those observed after the hair treatment with $Ca(OH)_2$ and formaldehyde (Curve 1). The main differences are reflected in the area of the absorption spectrum, where vibrations of sulfur-containing groups occur. The presence of absorption bands with maxima at 470 and 540 cm^{-1} , indicating the presence of disulfide bonds in the structure of the hair, the formation of new $\equiv C-S-C\equiv$, $\equiv C-S-Ca-S-C\equiv$ bonds under the influence of $Ca(OH)_2$ and with $-S-CH_2-S-$, $-S-CH_2-NH-$, $-S-CH_2-N=$ formaldehyde, and their modification under the influence of Na_2S may indicate a complex process of self-organization of the keratin structure. A broad band of intermolecular bonds with the maximum of 3300 cm^{-1} may confirm this.

Thus, IR spectroscopic analysis of the hair after treatment with alkaline reagents of different chemical composition indicates significant chemical changes in its structure, manifested in a significant decrease in the intensity of the absorption band of 470 cm^{-1} and the appearance of a broad band with the maximum of 650 cm^{-1} , which corresponds to the destruction of disulfide bonds and the formation of new bonds under the influence of calcium hydroxide and formaldehyde. In addition, the structuring effect of formaldehyde on keratin is manifested in the reduction of the intensity of the bands belonging to carboxyl groups and the bands of amides I and amides II. The transformation of the bands in the region of 3300–3520 cm^{-1} may indicate a modification of intermolecular bonds involving the NH -groups of the keratin structure. A sharp decrease in the intensity of bands in the range of 1080–1130 cm^{-1} shows significant changes in the structure of keratin under the influence of alkaline treatment, indicating a deep destruction of native keratin.

The use of compounds that polifunctionally interact with the active groups of side radicals of keratin (amino, carboxylic, imidic, phenolic, sulfhydryl groups) and form chemical intermolecular bonds, can increase the resistance of the hair, especially its epidermis, to the action of strong alkaline reagents. As the microscopic examination shows, the native hair, degreased with nonionic surfactants, is characterized by the lack of damage to the facial layer after the alkaline treatment (**Fig. 2.10**). Cuticle scales tightly adhere to the hair shaft without detachment of

the cuticle from the cortical layer [45]. Treatment of the hair with Na_2S after immunization of the shaft with $\text{Ca}(\text{OH})_2$ leads to detachment of the cuticle layer from the cortical layer, and in some areas it is significantly damaged or completely absent. As the cuticle and especially its outer covering, the epicuticle, has an increased chemical resistance and protects the inner part of the hair from physical and chemical influences, the significant damage to this layer is crucial for the safety of the hair shaft, its completeness and strength.

Immunization of the hair shaft with $\text{Ca}(\text{OH})_2$ and formaldehyde gives an opportunity to substantially increase its protection against a negative effect of a dehairing reagent. This is confirmed by the image in the microphotograph of the hair shaft after this treatment, where there is a slight detachment of the cuticle layer scales from the hair shaft. Obviously, this time the cortical layer undergoes a much less destructive influence of Na_2S solution.

Therefore, the immunization of the hair shaft with calcium hydroxide and formaldehyde contributes to a more effective protection of

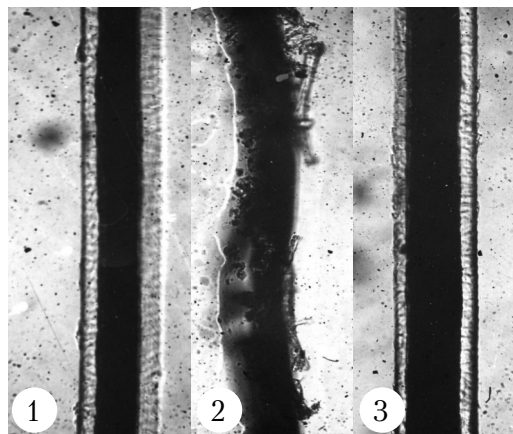


Fig. 2.10. The degreased hair (1), treated with sodium sulphide with pre-immunization of its shaft with calcium hydroxide (2) and the same if there is formaldehyde (3)

the hair from the action of a dehairing solution of sodium sulfide, preserving its structure and completeness of the shaft. The analysis of the results of structural investigations of the interaction of the hair keratin with the components of immunizing and dehairing solutions gives an opportunity, basically, to switch off an internal intermolecular redistribution in the structure of keratin and facilitates the formation of new additional, resistant to the action of the alkaline reagents, bonds in its structure. At the same

time, new bonds are formed with the participation of groups of different nature, specific to native keratin, as well as active groups, which are formed as a result of hydrolysis of disulfide bonds.

The results of the study of the amino acid composition of the hair show a higher resistance of the hair, immunized with calcium hydroxide and formaldehyde, to the action of sodium sulfide solution compared to the hair immunized only with calcium hydroxide. This is confirmed by a higher content of sulfur-containing, diaminocarboxylic acids, as well as by a slight decrease in the content of alanine and serine in the hair samples immunized with the addition of formaldehyde. Spectroscopy studies show the destruction of native disulfide bonds in the structure of the hair keratin and the formation of methylene intramolecular bridges with the participation of newly formed sulfide groups, amino and imino groups of keratin.

Studies of the amino acid composition of the spent solutions have found that the use of formaldehyde at the stage of the hair shaft immunization promotes a 19.0-fold decrease in the total content of amino acids in the spent solution compared with the standard technology of soaking and liming processes, as well as by 30 % of amino acids containing sulfur compared to the immunization of the hair shaft only with calcium hydroxide. This indicates the formation of additional, resistant to sodium sulfide, bonds in the structure of the hair with the participation of active groups of amino acids of the hair keratin and formaldehyde.

The results of microscopic studies of the hair condition after more effective protection of its structure from the hydrolyzing action of sodium sulfide when used at the stage of formaldehyde immunization, which is confirmed only by slight destructive changes in its outer covering – a cuticle.

The technology of a two-stage liming with the hair immunization involves the use of a suspended-type VULCAN drum of *Olcina* company (Spain) with a volume of 21 m³ and with a device for the hair utilization. The processes are carried out at a stable temperature of 26–28 °C and the speed of a drum rotation of 2.0–2.5 min⁻¹. The drum rotation is constant during washing, soaking, immunization and utilization of the hair.

The technology involves [45] preliminary washing of raw materials using 0.3 % sodium carbonate with 120 % water consumption and

subsequent discharge. A one-stage soaking is performed with the consumption of reagents, mass %: water – 80, nonionic surfactant – 0.2; sodium carbonate – 0.4; in one hour, an enzyme preparation is added – 0.3 and the treatment continues for 3 hours.

Immunization of the hair shaft and dehairing: mass %: calcium hydroxide – 1.0 and 40 % formalin – 0.05 are added in a soaking solution with an interval of 15 minutes; after 45 minutes of the treatment, the drum is filled with sodium sulfide – 1.0 and 1.5 hour later, the hair is utilized.

Liming of the pelt, mass %: water – 20, calcium hydroxide – 2, sodium sulfide – 1.0. The process lasts another 10 hours with a periodic rotation of the drum, min.: during the first hour – 30, the second – 10, then for 5 minutes of every hour and before the completion of the process – 30. The technology is completed by double-washing for 15 minutes with a total water consumption of 200 % and a gradual decrease in its temperature up to 20–22 °C.

Thus, the technology of a two-stage liming with the hair utilization has been developed, and it involves combining the processes of soaking and liming and the use of the hair stabilizer. The developed technology involves a time reduction of raw materials treatment by 2.2 times compared with the existing technology.

2.3.2. Non-sulphide dehairing and liming

One of the effective ways of developing the advanced technology is the use of natural environmentally safe chemical reagents. In particular, this may apply to hydrophilic aluminosilicates. Taking into account a high adsorption capacity of the lime solution, a highly dispersed mineral was used – natural kaolin [46–48]. The studied sorbent is obtained by modifying kaolinite clay of the Hlukhiv deposit after the release of mineral impurities – quartz, mica, granite, sulfur, etc. The used aluminosilicate has substantially higher hydrophilic and sorption properties in comparison with Hlukhiv kaolinite clay. Thus, at the *pH* of 7.0, the heat of wetting with water and the capacity of cation exchange of dehydrated samples of Hlukhiv kaolinite is 25 and 7 times higher,

respectively, at 37.5 J/g and 0.24 mg-eq/g. According to the chemical composition, the main component of kaolinite corresponds to the general formula of $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ with 1/2/2 ratio of components. The particles of Hlukhiv kaolinite have a plate-like shape measuring from 0.02 to 0.5 microns, consisting of 3–5 parallel scales.

During the development of a new non-calcareous dehairing and liming technology, using sodium hydroxide to obtain a uniformly limed pelt with a well-pilled structure without the cockling of its outer layer and, accordingly, without loosening and swelling of the skin, the process is important when a uniform and sufficient diffusion of alkaline reagents in the structure of the dermis throughout its entire thickness and area occurs. This eliminates the excessive swelling of the outer layers of the pelt and thereby facilitates the transition of destruction products of soft keratins and other non-collagen formations from the dermis into the processing liquor.

To determine the possibility of using kaolin as $NaOH$ sorbent, the study of sorption and desorption of alkaline solution with high-alumina silica has been carried out. The results of the experiments are shown in **Fig. 2.11**. As the data show, the $NaOH$ concentration in the solution due to its sorption on the surface and interlayer spaces decreases slightly over 10 hours with subsequent acceleration. Maximum absorption is observed after 24 hours. $NaOH$ desorption into water at the pH of 7.0 occurs at the rate reduced almost twice and reaches 89 % against the sorbed quantity. The regenerated sample of kaolin after washing with water and drying has practically the same sorption and desorption characteristics.

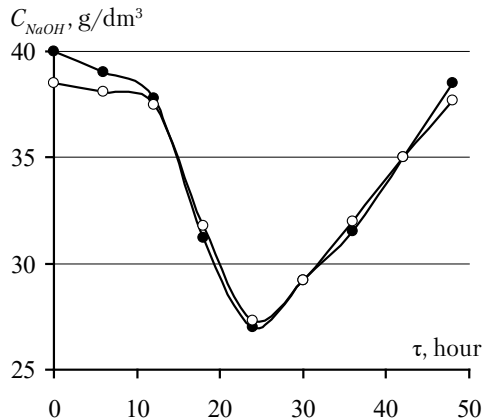


Fig. 2.11. Sorption and desorption kinetics of $NaOH$ with original (○) and regenerated kaolin (●)

A significant amount of adsorption is due to the mosaic surface of kaolinite particles, mainly by the presence of $\equiv SiO-H^+$ acid groups both as the ion capacity on basal surfaces, and on the lateral faces and edges of aluminosilicate crystals. It is known that Hlukhiv kaolinite is characterized by a higher degree of imperfection of the crystalline structure and is used as a sorbent and a catalyst.

Due to a high chemical activity of alkaline solutions during liming, for the regulation of their uniform diffusion and prevention of unwanted destructive processes in collagen of the dermis, the study of the liming effect using $NaOH$ on the amino acid composition of the pelt after the liming process was performed (**Table 2.12**) [3]. The samples of raw materials dehaired after soaking by the developed OSL technology were studied.

According to the first variant of the new technology, the treatment of the pelt was carried out with $NaOH$ solution at the concentration of 30 g/dm^3 at the temperature of $19-21 \text{ }^\circ\text{C}$ for 20 hours.

As there is already some damage to the hair at the concentration of 24 g/dm^3 , the effect of aluminosilicate sorbent on the amino acid composition of the collagen and the spent solution after the completion of the liming process was determined at the concentration of $NaOH$ of 20 g/dm^3 using kaolin in the amount of 10 g/dm^3 (Variant 2). The standard technology of calcium and sulphide liming was the reference variant Number 3.

According to the results, the content of amino acids in a limed sample, using kaolin and a reduced amount of alkali, is close to the variant with a higher consumption of alkali and the variant of the standard technology. The reduction of tyrosine residues in Variants 2 and 3 compared with the native collagen and Variant 1 indicates almost a two-fold decrease in the degree of hydrolysis of telopeptide endings of macromolecules with the use of kaolin. A characteristic increase in the content of dicarboxylic amino acids in all the variants of treatment compared to the native collagen can be attributed to the transformation of glutamine and asparagine under the action of alkali into the corresponding acids due to the destruction of inter- and intramolecular bonds. The total content of diamino acids, on which the strength of the attachment of the papillary and reticular layers depends, is slightly lower than that of the standard technology. In experimental Variant 2,

Table 2.12

**Amino acid composition of collagen of the cattle hide dermis
after liming**

Amino acid	Amount, mol %, according to the variant			Disagreement with the native collagen*
	1	2	3	
Alanine	12.81	12.72	10.57	+1.05. – 1.19
Arginine	4.39	3.58	4.87	+1.52. +0.23
Aspartic acid	4.98	5.38	6.53	–2.17. – 3.82
Asparagine	–	–	–	+ 1,66
Valine	1.94	2.49	2.02	+0.21. – 0.34
Glycine	30.54	30.12	28.40	+4.45. +2.31
Glutamic acid	8.08	8.08	9.40	–3.47. – 4.69
Glutamine	–	–	–	+ 2.74
Histidine	0.11	0.10	0.10	+0.35. +0.34
Hydroxylysine	0.40	0.55	0.40	+0.19. +0.04
Lysine	2.44	2.36	2.75	+0.48. +0.09
Hydroxyproline	7.98	7.90	10.58	+2.58. – 0.10
Proline	14.92	13.44	13.96	–1.96. – 3.44
Methionine	0.01	0.01	0.02	+0.61. +0.60
Isoleucine	1.24	1.51	0.91	+0.03. – 0.57
Leucine	2.97	3.69	3.35	–0.51. – 1.23
Serine	3.60	3.83	2.20	+1.13. – 0.50
Tyrosine	0.46	0.24	0.28	+0.21. – 0.01
Threonine	2.09	2.07	2.49	–0.47. – 0.89
Phenylalanyl	1.10	1.50	0.94	+0.27. – 0.29

Note. *Deviation of the native collagen amino acids from a limed semi-finished product

there is virtually no significant decrease in the content of diamino acids. At the same time, in comparison with the native collagen, there is a 1.7-fold decrease in the content of sulfur-containing (methionine) and carbocyclic (phenylalanine, tyrosine) amino acids and an increase in the number of amino acids with non-polar side radicals, indicating that the structure of the dermis is sufficiently “pilled”.

Therefore, due to the use of kaolin, it is possible to reduce the consumption of alkali for the liming of raw hides, with a slight change

in the amino acid composition of the dermis collagen compared with the standard technology. This is also proved by a reduced content of hydroxyproline in the dermis.

The study of the amino acid composition of the spent lime solutions (**Table 2.13**) established its correlation with the amino acid composition of the dermis of various treatment variants. The spent lime solution of the experimental Variant 1 contains by 7.3 % more amino acids than the standard technology, which may indicate an intense effect of alkali on the structure of the dermis and is accompanied by the destruction of collagen macromolecules with the release of interfibrillar proteins. The closeness of the content of these amino acids in the spent solutions of Variants 1 and 3 and their substantially lower content in Variant 2 indicates the mild effect of alkali in the presence of kaolin on destructive processes during liming.

The absence of significant destructive changes in the collagen of the dermis after liming is also confirmed by the results of the study of the change in the acid and alkaline capacity of the delimed pelt (**Table 2.14**). The experimental data indicate a high acid capacity of the sample of Variant 1 in comparison with other samples, indicating a greater splitting of collagen end groups. The electrochemical equivalent of collagen acquires the minimum value. By the ratio of alkaline and acid capacities, the samples of the second and third treatment variants are closer to the native collagen.

Table 2.13

**The content of the most important amino acid groups
in the spent lime solution**

Amino acid group	Amount, mg/100 cm ³ , according to the variant of treatment		
	1	2	3
Diaminocarboxylic (<i>R, K</i>)	9.1	11.8	31.4
Aminodicarboxylic (<i>N, Q</i>)	27.4	36.1	66.4
With a nonpolar side residue (<i>A, V, L, I</i>)	17.3	20.0	57.0
Imino acids (<i>P, P'</i>), including <i>P'</i>	20.3	5.9	14.6
Tyrosine	5.5	5.0	13.8
Total amount	80.7	78.9	183.2

Table 2.14

Determinations of alkali-acid capacity of the pelt

Variant of treatment	Capacity, meq/g		Electrochemical equivalent, meq		Ratio of alkali and acid capacity
	acid	alkali	acid	alkali	
1	2.49	1.13	402.0	885.0	0.45
2	1.95	0.78	513.0	1282.0	0.40
3	2.09	0.72	478.0	1389.0	0.34
Native collagen	0.82–0.92	0.25–0.34	1225–1090	4000–2967	0.30–0.37

Thus, the study of the amino acid composition of the pelt and the spent lime solutions, as well as the alkali-acid capacity of the limed pelt, indicates that liming with the alkaline solution with a high concentration of sodium hydroxide leads to significant changes in the collagen structure of the dermis and excessive removal of amino acids into the spent lime solution, which may be accompanied by the deterioration the pelt quality. The complex use of an aluminosilicate sorbent and sodium hydroxide makes it possible to “pill” the structure uniformly in order to carry out effective further technological processes.

To determine the minimum consumption of chemical reagents in the liming of hides, the properties of spent solutions have been studied (**Table 2.15**). According to the data of **Table 2.15**, the concentration of alkali in the studied ratios of alkali/kaolin in the spent solution depends on the initial concentration of alkali, and the increase in $NaOH$ concentration by 4 g/dm^3 is accompanied by its growth by 1.2 g/dm^3 in spent solutions. However, the pH of the spent solution in the presence of kaolin virtually remains equal to the pH when using standard technology. The decrease in the protein content of spent solutions when using alkaline-kaolin treatment of raw hides should be noted.

The diffusion of dehairing reagents occurs mainly through a thick layer of the dermis, which significantly increases duration of the dehairing process. To accelerate this process, a mixture of alkaline reagents, among which $NaOH$ and Na_2SO_3 are effective, can be used. In this case, lipids of the lipidic and corneous layer of the epidermis are, first of all,

Table 2.15

Characteristics of the spent lime solutions

Main characteristics	Initial concentration of $NaOH/kaolin$, g/dm ³					OSL-S
	16/0	16/5	20/0	20/5	20/10	
<i>pH</i> of the solution	13.1	13.0	13.4	13.3	13.2	13.2
Content of $NaOH$, g/dm ³	4.25	4.30	5.2	5.5	5.5	—
Residual kaolin, g/dm ³	0	4.0	0	3.7	8.8	—
Amount of protein, g/dm ³	11.25	11.10	11.58	11.50	11.34	12.3

subjected to destruction. The duration of this process is determined by the chemical activity and concentration of alkaline reagents.

A comparative analysis of the physico-chemical properties of the pelt and a chrome upper shoe semi-finished product (**Table 2.16**) has been carried out to determine the effectiveness of the liming process using an aluminosilicate sorbent. As we can see from **Table 2.16**, the concentration of $NaOH$ during liming with the preservation of the hair of 16–20 g/dm³ provides a sufficient liming value of the dermis. In this case, the concentration of kaolin in the solution, which provides a steady rate of the process, is not less than 5 g/dm³. With the specified parameters of treatment, the pelt is obtained without apparent defects, sufficient liming value and swelling.

Hydrothermal stability of the pelt, which characterizes its hydrothermal stability, is significantly decreased relative to the raw material and equals 64 °C. Moreover, this effect tends to decrease in the presence of kaolin. A smaller decrease of T_w during liming with alkali only indicates the uneven running, as $NaOH$ at its increased concentration is excessively absorbed by the facial layer, which complicates the further diffusion of the lime solution into the thickness of the dermis. It should be noted that the pelt of non-calcareous liming has slightly lower gelatin smelting and the values of EFS close to the values of the samples of standard technology.

Chrome semi-finished product has a welding temperature of more than 100 °C that meets the standard requirements. According to the physical and mechanical parameters, the semi-finished product obtained by the complex technology of kaolin use is not inferior to the

Table 2.16

Physical and chemical properties of the pelt and the semi-finished product after tanning received in different proportions of NaOH and kaolin

Indicator	Concentration of NaOH/kaolin, g/dm ³					OSL-S
	16/0	16/5	20/0	20/5	20/10	
T_w , °C, of the pelt	54.0	53.0	55.0	53.0	53.0	52.0
— of the tanned semi-finished product	103.0	105.0	103.0	107.0	105.0	107.0
EFS, min.	58.0	54.0	56.0	52.0	51.0	52.0
Smelting of gelatin S_g , %	6.2	6.9	6.4	6.8	7.2	9.2
Porosity of the semi-finished product, %	48.4	51.5	49.0	51.0	52.5	54.0
Volume yield, %	210.0	229.0	210.0	230.0	230.0	235.0
Ultimate tensile strength, MPa	16.9	18.0	17.0	18.5	18.8	19.0
Elongation, %, at break	65.0	69.0	67.0	73.5	75.5	87.0
under the strain of 9,8 MPa	38.0	41.0	39.0	45.0	40.5	48.0
Content in the skin ¹ , %, PS	80.5	79.8	81.0	79.4	79.2	79.5
of mineral substances	6.8	6.8	7.6	7.9	7.0	8.9
of substances extracted with organic solvents	7.5	7.8	8.2	7.9	7.8	7.5
Leather yield ² , %	75.4	81.0	76.0	82.0	84.0	86.0

Notes:

¹ — on a totally dry basis;

² — from watered raw materials

semi-finished product produced by the standard technology. Somewhat higher values of relative elongation at breakage and tension of 9.8 MPa are due to the absence of the structure orientation during the dilution of the semi-finished product in the laboratory. An increase in the porosity of the corresponding samples indicates a uniform process of liming of raw materials in the variants with kaolin. In general, the lower absolute values of the received pelt porosity and the smelting of gelatin, as compared to the reference variant, are due to the “softer” effect of alkaline reagents and, accordingly, a slightly less pilling of the fibrous structure compared with the action of the sulfide and lime solution.

Changes in the collagen structure, which are accompanied with NaOH during the liming, correlate with the output of the semi-finished product after tanning in terms of area size. Despite the fact that the use of kaolin for dehairing and liming contributes to a certain increase in the area size of the semi-finished product, but in absolute value, this indicator for experimental samples is smaller compared with the technology of one-stage liming. It should be noted that in cases without the use of kaolin, there are remnants of the hair roots, which is manifested as gneist in the hair follicles of the pelt.

The use of some salts in the soaking and liming processes makes it possible to implement the fibrous spiral structure of the dermis collagen more effectively as a result of the weakening of the intermolecular interactions of functional groups with further opening of its structure. In particular, the use of sodium carbonate during soaking of hides

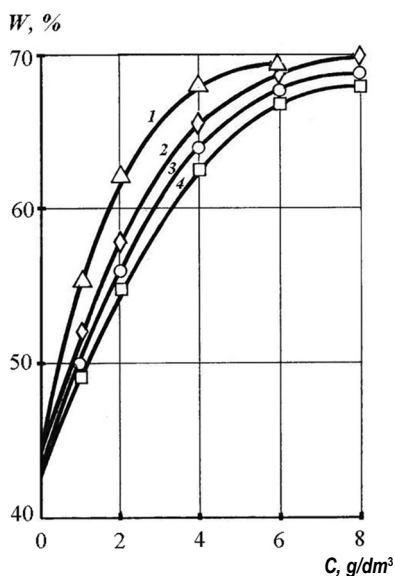


Fig. 2.12. Kinetics of the hide watering with the salt concentration of 10 g/dm^3 : Na_2SO_3 (1), Na_2CO_3 (2), $\text{Na}_2\text{S}_2\text{O}_3$ (3), Na_2SO_4 (4)

[23] indicates a faster restoration of their water balance. In order to increase the efficiency of the use of raw materials, intensify the dehairing effect and reduce the concentration of alkali during liming, the effect of sodium salts on the soaking process has been studied (Fig. 2.12).

It can be seen from the data that the degree of raw materials watering depends significantly on the chemical composition of salt. The raw materials in the presence of Na_2SO_3 are the most intensively watered in the first two hours with the subsequent slow-down of the process which virtually ends in 6 hours. In case of other salts, the process of the sample watering is slowed down only in 4 hours and finishes in 8–10 hours. Effectiveness of the influence of the salts, used during soaking, on the properties of the pelt

after kaolinite-alkali liming with $NaOH$ concentration of 16 g/dm^3 can be seen from **Table 2.17**.

The data analysis in **Table 2.17** shows that in the presence of alkaline with kaolin and Na_2SO_3 salt, the temperature of hydrothermal stability of the pelt decreases by $3\text{--}4 \text{ }^\circ\text{C}$, and this effect is less intense for other salts. $2.8\text{--}4.0 \%$ increase of gelatin melting is observed when using each of the studied salts; these values are placed at the level of the variant of the standard technology and they are somewhat lower than the variant involving the use of alkali and kaolin at the concentration of 20 and 10 g/dm^3 , respectively.

The most sensitive indicator of the pelt to the action of chemical ingredients of the processing liqor was the degree of its swelling, which reaches the maximum and minimum values for Na_2SO_3 and Na_2SO_4

Table 2.17

Physical and chemical properties of the pelt and the tanned semi-finished product obtained with the use of kaolin and sodium salts

Indicator	Salt, g/l									Reference technology
	Na_2CO_3			Na_2SO_3			$Na_2S_2O_3$			
Concentration of salt, g/dm^3	6	8	10	6	8	10	6	8	10	10
T_w , $^\circ\text{C}$, of the pelt	52	53	53	51	50	50	53	52	52	51.0
Degree of swelling, %	18	18	18	19	19	19	17	17	17	18.5
ETS, min.	56	54	53	55	55	54	56	56	54	56.0
S_g , %	11.3	10.9	11.0	10.9	11.0	11.4	10.4	10.2	10.3	12.1
Porosity, %	52.0	53.0	53.0	54.0	55.0	54.0	53.0	54.0	54.0	53.0
Volume yield, %	225	235	230	260	268	255	235	245	240	249.0
Ultimate tensile strength, MPa	20.2	20.5	20.6	20.8	21.4	20.6	20.0	20.7	19.9	18.6
Content in the hide, %, PS	79.9	80.0	79.7	77.2	78.8	78.3	78.7	78.3	78.1	77.0
of mineral substances	7.0	7.3	7.2	6.8	7.1	6.9	8.8	9.0	9.2	9.4
Leather yield, %	89.0	91.0	90.0	90.0	91.0	91.0	89.5	90.0	90.0	89.0

Note. The reference technology involves the use of $NaOH$ and kaolin with the concentration of 20 and 10 g/dm^3 , respectively

salts, respectively. Such a nature of the dependence of these data on the composition of the processing liquor indicates a deeper opening of the collagen structure when using the studied salts and, especially, Na_2SO_3 salt. These data are confirmed by the results of the porosity analysis of the pelt after delimiting and bating, the indicators of which are at the level of the reference variant and, accordingly, by the output of the semi-finished product in terms of area after tanning. At the same time, it is necessary to point out the insignificant dependence of other studied parameters on the concentration of salt. In terms of strength, the samples of semi-finished products with the use of salt have higher values than the reference variants and samples obtained without the use of salt. The correlation between the strength and porosity indices for the pelt variants formed with the use of Na_2SO_3 , $Na_2S_2O_3$ and Na_2CO_3 salts indicates a more homogeneous porous structure compared to the samples of the reference variant. When using Na_2SO_4 salt during liming, the pelt samples have lower porosity characteristics and, accordingly, the yield of leather semi-finished products in terms of area.

Thus, non-calcareous liming of raw materials with the use of sodium salts during soaking gives an opportunity to get the pelt with a moderate degree of swelling of 18.0–19.0 % and an increased yield of semi-finished products in terms of area in comparison with the standard technology. A possible mechanism of influence of the system of sodium hydroxide-kaolin in the presence of sodium salts is the ability of aluminosilicate sorbent to desorb the alkali and thereby regulate its interaction with the epidermis and dermis of raw materials and promote the effective implementation of the fibrous structure of the dermis when forming leather materials.

The technology of two-stage dehairing and liming of raw cattle hides involves the use of a highly dispersed aluminosilicate mineral, kaolin, as a sorbent and a regulator of the process of a lime solution diffusion into the structure of the dermis [47, 48]. The washing processes of the two-stage and soaking of wet-salted raw materials are carried out in VULKAN drum of *Olcina* company at the rotational speed of 3–4 min.⁻¹ and the temperature of 26–28 °C.

Washing occurs in the presence of 120 % of water and 0.3 % of sodium carbonate for 30 minutes.

The first *soaking* is carried out in a new solution with the consumption of, mass %: water – 80, nonionic surfactant – 0.2, sodium carbonate – 0.35; duration – 1 hour.

The second *soaking* involves a gradual dosing of chemical reagents, mass %: water – 80, sodium sulfide – 0.8, nonionic surfactant – 0.2. After 30 minutes of the rotation of the drum, 0.3 % enzyme preparation is added into the solution and the process continues for 2.5 hours. Then, 0.2 % sodium hydrosulphide is added and the drum rotates for another 1.0 hour.

Dehairing of raw materials is done in the spent solution adding 1.0 % urea and aqueous suspension of kaolin mass %: water with the temperature of 18 °C – 20, kaolin pre-saturated with 1,6 % *NaOH* – 0,65; the process is carried out at the temperature of the reaction system of 23–25 °C for 2.5 hours with the subsequent utilization of the hair.

Liming of raw materials is performed in the spent solution with the reinforcement by 0.4 % *NaOH* for 11.5 hours and a drum rotation mode, minutes: during the first hour – 30, the second hour – 10, then hourly for 5 minutes; before the process is completed – 30. The drum rotation speed should be 2.0–2.5 min.⁻¹.

Thus, the technology of non-calcareous two-stage dehairing and liming of raw cattle hides has been developed to provide the efficient use of raw materials and utilization of the hair. A complex application of sodium hydroxide and kaolin for dehairing and liming gives the grounds to consider the developed technology as environmentally safe.

2.3.3. Multipurpose dehairing and liming

The development of a versatile two-stage dehairing and liming technology with the hair utilization (TSL-U) requires an accelerated dehairing of raw materials. This is facilitated by the use of effective surface and biologically active substances. In addition, favorable conditions are created for the transportation of chemical reagents, a deep division of the fibrillar structure of collagen, increased mobility of structural elements of the dermis, the formation of plastic structure of the pelt and the efficient use of raw materials.

The basis of the developed versatile technology of dehairing and liming is a crucial importance of the gradual sequence of chemical reagents dosing for accelerated dehairing and liming of raw materials [49–52]. Amino calcium sulfide dehairing was carried out in a technological solution after the second soaking of raw materials containing enzyme preparation Basozym S-20 of BASF company (Germany) and 0.2 % of sodium hydrogen by raw material weight in the alkali medium. In this process, the treatment with $Ca(OH)_2$ suspension is performed in two stages, adding amines at the first stage and sodium sulfides at the second one.

Soaking of raw materials in the alkali medium with the enzyme preparation and the gradual addition of $Ca(OH)_2$ suspension with amines within the limits studied (**Table 2.18**) promotes the liberation of intercellular pathways of reagent diffusion from the lipids to the hair follicle and basement membrane, destruction of intercellular bonds and the hair and epidermis separation from the dermis, which increases the strength of the hair compared to the lime and formaldehyde immunization of the hair shaft [41].

The consumption of chemical reagents according to the treatment Variant 4 does not provide separation of the hair and epidermis from the dermis, and the implementation of the technology by Variant 5 leads to the loss of the hair resistance to the action of alkali and reduction of its strength.

The results of raw materials treatment in Variants 1–3 give an opportunity to carry out a technological process with the hair utilization with increased characteristics of the hair resistance to the action of alkali and its strength in 1.5–1.9 times compared with the technology of lime and formaldehyde immunization of the hair shaft (**Table 2.18**). In this case, the most rational treatment is the first variant, because it gives an opportunity to get stronger and more resistant to alkali hair with a slightly lower consumption of chemical reagents.

The results of the study of the properties of the pelt received from white and black areas of black and white hides (Variants 1 and 2, respectively), treated with a technological solution of the composition according to the first variant, are given in **Table 2.19**. The selected samples belong to the butt area of an average cow hide. The given data

Table 2.18

Consumption of chemical reagents and properties of the hair

Process: reagent, % by weight of raw materials. Indicator	Variant of treatment				
	1	2	3	4	5
Soaking:					
sodium carbonate	0.25	0.50	0.55	0.40	0.60
enzyme preparation Basozym S-20	0.25	0.30	0.35	0.20	0.40
savenol NWP surfactant	0.15	0.20	0.25	0.10	0.30
Dehairing:					
calcium hydroxide (1 stage)	0.25	0.30	0.35	0.20	0.40
with amine based preparation Mollescal-LS	0.9	1.0	1.1	0.7	1.3
calcium hydroxide (2 stage)	0.9	1.0	1.1	0.7	1.3
sodium hydrosulfide	0.6	0.7	0.8	0.5	0.9
sodium sulfide	0.55	0.60	0.65	0.50	0.70
Resistance of the hair to the alkali action, %	96.5	95.0	94.0	97.0	91.5
Strength of the hair, MPa	156	150	130	160	100
Period of the hair connection weakening with the dermis, min.	140	120	95	360	90

indicate a deeper division of the structure elements of white sections of the pelt. This is indicated by slightly lower values of the pelt welding temperature, the ETS indicator and higher porosity indicators with practically identical nitrogen and oxyproline content in the pelt.

Compared to the standard technology, which is characterized by a considerable duration and significantly higher content of environmentally harmful substances in the spent solution, the developed technology makes it possible to receive the pelt with a lower degree of swelling and higher porosity.

Larger differences are observed for the pelt samples obtained by the developed and standard technologies of SLP. Reducing the T_w of the pelt samples obtained from black areas of hides, treated with the previously used technology, may indicate the influence of alkaline medium and temperature of the process on the swelling and structural state of the pelt obtained by a versatile technology. This is confirmed by a decrease

Table 2.19

Physical and chemical characteristics of the limed pelt from the raw materials with black and white coloration of the hair coat

Indicator	Variant of SLP technology		
	developed		OSL-S
	1	2	
Duration of dehairing and liming, hour	18.0	18.0	44.5
Temperature of the process, °C	26–28	26–28	20–22
Temperature of welding, °C	53	55	52
Degree of swelling, %	19.0	18.0	25.0
Porosity, %	58	56	53
ETS, min.	54	57	58
Smelting of gelatin, %	1.8	1.7	1.8
Content, %, of total nitrogen	18.40	18.38	18.05
oxyproline	12.78	12.76	12.66
hexose	0.42	0.44	0.48
Concentration of, g/dm ³ ,			
sulfides	4.5	4.7	8.0
calcium hydroxide	3.9	4.1	16.0
keratin in the spent solution	0.3	0.6	19.0

in porosity and an increase in the ETS indicator of the samples obtained by the technology of one-stage liming, showing a somewhat less “pilling” of the microfibrillar structure of the dermis collagen.

The given data also indicate the ecological advantages of the developed technology. Thus, in spent solutions, in comparison with the standard technology, the content of sulfides, especially calcium hydroxide that is deposited in communications and takes them out of operation, is significantly reduced.

Therefore, the study of the influence of the composition of soaking and lime processing liquors on the physical and chemical properties of the hair and the pelt has shown a slight difference in the values of certain indicators of white and black areas of raw hides when treated by the developed versatile technology, which has a shorter duration of processes than the standard one. The developed technology with the hair utilization makes it possible, in comparison with the standard technology, to effectively carry

out dehairing and liming processes of raw stock, with more than two-fold reduction of the treatment duration, significantly lower content of toxic substances in the spent solutions. Preservation of the hair allows almost completely eliminating the presence of keratin in industrial effluents.

In order to effectively implement the versatile technology of two-stage liming with the hair utilization [53] in the industry, it has been optimized. To test the experiment, 20 experimental batches with 8 samples in each of 150×160 mm in size, with the thickness of 3.0–3.5 mm, obtained from the butt topographic sections of two wet-salted steerhides. At the same time, the samples were packed in lots using the asymmetric fringe method [54, 55]. The subcutaneous tissue of the studied hides was removed on a shaving machine and the treatment of all samples was completed with chrome tanning according to the existing technology at the leather enterprise, CJSC *Chinbar*. After laying and sammying, the samples were splitted in 1.5 mm thickness each and brought to the finished material by the production technology of the elastic skin [56].

To limit the number of factors in optimizing dehairing and liming processes, the influence of sulfide and sodium hydrosulphide ratio on the efficiency of dehairing by the second variant of treatment has been investigated [57, 58]. The received data [28] suggest the expediency of using sulfides in the ratio of 1/1 (**Table 2.20**). An increase in sodium sulfide consumption causes excessive swelling, which inevitably leads to the loss of skin area, and its reduction – to incomplete dehairing and insufficient swelling.

Optimization of chemical and technological processes with several output variables starts with solving a problem with one criterion

Table 2.20

Influence of sodium hydrogen sulfide on dehairing and liming of cattle hides

Ratio of Na_2S : $NaHS$ with S^{2-}	Degree of swelling, %	Dehairing
1/0	27.0	complete
0.75/0.25	24.0	complete
0.5/0.5	21.0	complete
0.25/0.75	17.0	incomplete

and corresponding restrictions. For this purpose, depending on the geometry of the response surface and the nature of the restrictions for optimization, it is recommended to use the methods of indeterminate Lagrange multipliers, linear and nonlinear programming, ridge analysis, and others. However, some difficulties arise in search of the conditional extremum, for example, on the basis of indeterminate Lagrange multipliers concerning the necessity to solve a system of nonlinear equations.

One of the most rational ways to solve the problem of a technological process optimization, which has basically several output variables, is the use of a multi-criteria approach based on the calculation of a general desirability function on the basis of the obtained mathematical models [58]. This approach makes it possible to determine the optimal mode of the investigated process, taking into account the requirements for the used output variables. In this case, the generally recognized optimization criterion is calculated on the basis of the Harrington function Y^* . In general, the optimization task involves finding such values of the technological process parameters, which would correspond to the compromise and desirable values of the output variables:

$$Y^* = F[y_j(x_i)], \quad (i = 1, 2, \dots, k; j = 1, 2, \dots, m),$$

where F – the Harrington function, k – number of functions, m – number of dependent variables.

To obtain mathematical models of dehairing and liming processes with technological factors influencing this process, the following has been selected:

X_1 – total consumption of sulfides in equal proportions of sulfide and sodium hydrosulphide in terms of S^{2-} anion, % of raw material weight;

X_2 – consumption of calcium hydroxide in terms of Ca^{2+} cation, % of raw material weight;

X_3 – duration of liming, hours.

The effectiveness of the process was determined by:

y_1 – the consumption of raw materials per 1 m² of a skin, kg/m²;

y_2 – degree of the pelt swelling, % of green raw material weight;

y_3 – elongation under stress 9.8 MPa, %.

The multicriterial optimization of the liming process of raw hides involves, first of all, the performing of a complete factor experiment of 2^3 type, completing it to a rotatable Box and Hunter design of the second order with 6 experimental points in the center of the design and a star shoulder of 1.682, and performing a statistical analysis of the mathematical models of the following type

$$\hat{y} = b_0 + \sum_{i=1}^k b_i x_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^k b_{ij} x_i x_j + \sum_{i=1}^k b_{ii} x_i^2 \quad (2.1)$$

using the developed program (site <http://mnk-online.narod.ru>). The search for the liming process optimum was carried out by a scanning method using the desirability function.

To obtain regression equations of $\hat{y}_j = f(x_i)$ dependence for $i = 3$, the zero level of the selected factors and their variation interval have been established (**Table 2.21**). The results of the experiment by the central composite rotatable design (CCRD) are shown in **Table 2.22**.

Table 2.21

Experimental design parameters

Name	Natural values of the factors		
	X_1	X_2	X_3
Zero level	0.74	1.19	12
Variable interval	0.2	0.22	4

After processing the experimental data with a confidence probability of 0.95, adequate mathematical models of the liming process of raw cattle hides have been obtained:

$$\hat{y}_1 = 6.51346 - 6.727833 \cdot 10^{-2} x_1 - 0.1053295 x_2 - 0.116352 x_3 + (2.2) \\ + 0.127792 x_1^2 + 0.0480732 x_2^2 + 0.1012196 x_3^2;$$

$$\hat{y}_2 = 20.89248 + 2.647162 x_1 + 1.714939 x_2 + 2.817191 x_3 + (2.3) \\ + 0.3600024 x_1^2 + 0.3600043 x_2^2 - 0.525766 x_3^2;$$

$$\hat{y}_3 = 34.45781 + 3.825634 x_1 + 5.074461 x_2 + 5.150681 x_3 - (2.4) \\ - 3.56452 x_1^2 - 2.324439 x_2^2 - 3.210208 x_3^2,$$

where \hat{y}_j – predicted values of the output variable by j model.

As the received models contain quadratic effects and can not have one solution, it is advisable to compare \hat{y}_{min} single-factor and \hat{y}_{max} functions constructed in two experimental variants. To do this, at the calculated \hat{y}_{min} point with $x_{1min}, \dots, x_{imin}, \dots, x_{nmin}$ coordinates, one factor was consistently taken as a variable, and the rest ones as

Table 2.22

Design of the experiment and the received output variables

Number*	Values of the process factors						Output variable		
	coded x_i			natural X_i					
	x_1	x_2	x_3	X_1	X_2	X_3	y_1	y_2	y_1
1	-1	-1	-1	0.54	0.97	8	7.21	14	12
2	+1	-1	-1	0.94	0.97	8	6.93	19	18
3	-1	+1	-1	0.54	1.41	8	6.78	17	21
4	+1	+1	-1	0.94	1.41	8	6.71	23	27
5	-1	-1	+1	0.54	0.97	16	6.98	20	20
6	+1	-1	+1	0.94	0.97	16	6.67	25	26
7	-1	+1	+1	0.54	1.41	16	6.72	24	29
8	+1	+1	+1	0.94	1.41	16	6.63	29	38
9	-1.682	0	0	0.4036	1.19	12	6.87	17	19
10	+1.682	0	0	1.0764	1.19	12	6.77	26	34
11	0	-1.682	0	0.74	0.81996	12	6.74	19	21
12	0	+1.682	0	0.74	1.56004	12	6.45	24	39
13	0	0	-1.682	0.74	1.19	5.272	7.03	15	17
14	0	0	+1.682	0.74	1.19	18.728	6.46	23	38
15	0	0	0	0.74	1.19	12	6.57	20.5	34
16	0	0	0	0.74	1.19	12	6.44	21.5	35
17	0	0	0	0.74	1.19	12	6.5	21	37
18	0	0	0	0.74	1.19	12	6.45	20	35
19	0	0	0	0.74	1.19	12	6.55	21.5	32
20	0	0	0	0.74	1.19	12	6.59	21	33

Note. * Experimental point

constant; the same at the calculated \hat{y}_{max} point. In this case, the ranking is carried out at the largest Δy scale of one-factor dependencies within the studied area of the factor space in both zones.

After a successive tabulation of one-factor dependencies at the calculated points of the minimum and maximum values of the output variable with fixation of the remaining parameters at the corresponding extreme levels, we obtain graphs in $y_j - x_i$ coordinates (**Fig. 2.13**).

As it can be seen from **Fig. 2.13**, under the conditions of the experiment both in the zone of minimum and in the zone of maximum, the greatest influence on the output variables is exerted by the duration of liming; the least impact on the consumption of raw materials and the degree of swelling – the consumption of calcium hydroxide, and on the elongation of the skin under stress of 9.8 MPa – the consumption of sodium sulfides.

The evaluation of the simultaneous influence of the investigated factors on the output variable is carried out on the basis of general models of the second order, from which we obtain quasi-one-factor dependencies on the x_i type

$$W_i = (b_i + b_{ij}x_j)x_i + b_{ii}x_i^2, \quad (2.5)$$

that is, each received “cut” from the complete polynomial model contains only effects with the index for the factor being analyzed. In this case, it is reasonable to exert the influence of each factor by a comparative analysis of one-factor $W_i = f(x_i)$ dependencies, stabilizing the remaining factors at the lower, zero and upper levels. So, for the output y_1 variable we will have:

$$W_1 = -6.727833 \cdot 10^{-2}x_1 + 0.127792x_1^2 \quad (2.6)$$

$$W_2 = -0.1053295x_2 + 0.0480732x_2^2 \quad (2.7)$$

$$W_3 = -0.116352x_3 + 0.1012196x_3^2. \quad (2.8)$$

By the results of the dependency tabulation (2.6–2.8) in increments of $\Delta x = 0.2$ in the range of $-1.68 \leq x_i \leq +1.68$, the graphic dependencies have been built (**Fig. 2.14**).

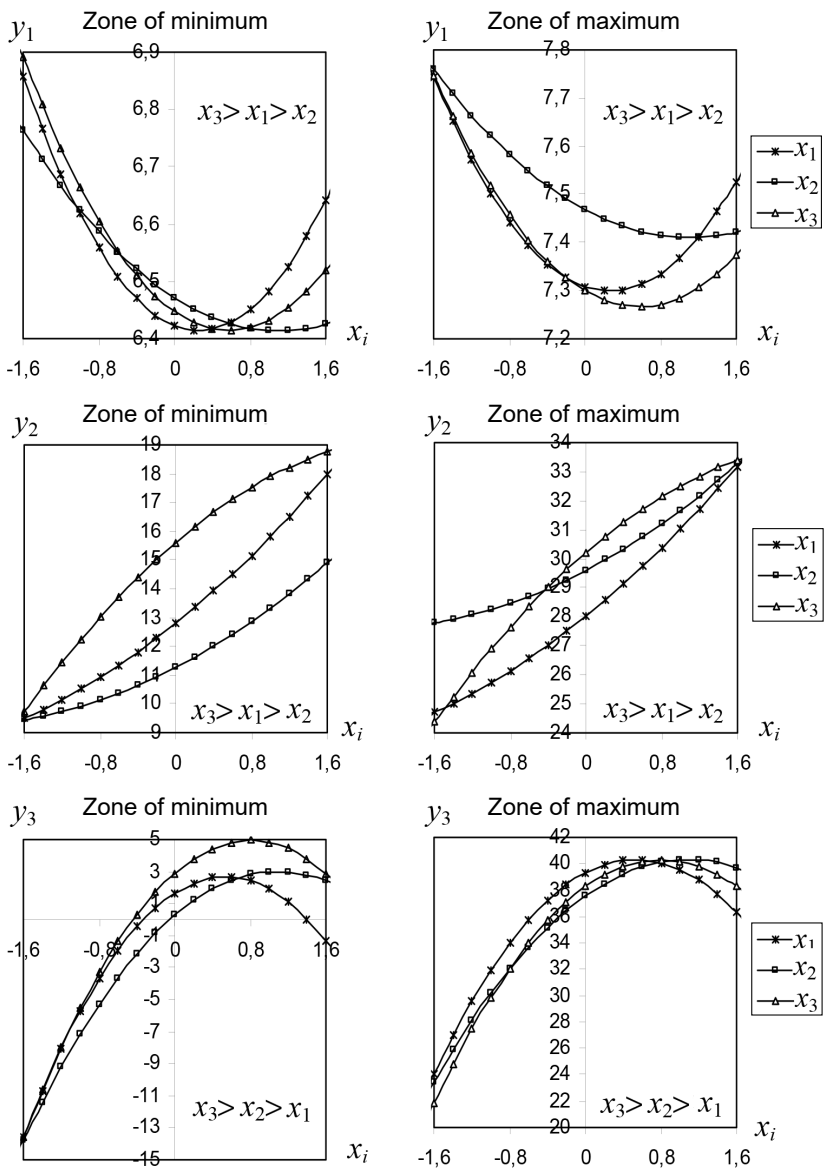


Fig. 2.13. Ranking of factors according to the influence degree on the output variable

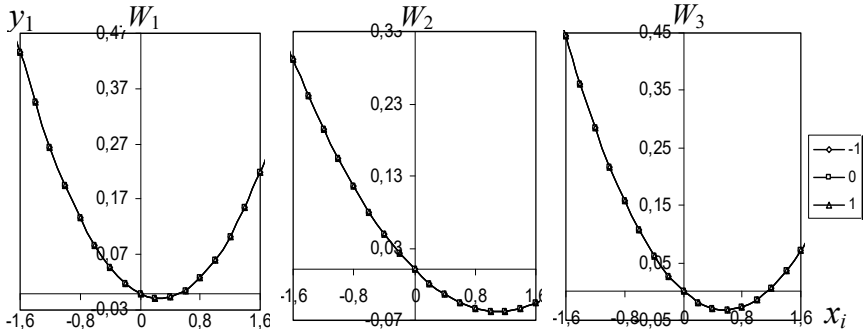


Fig. 2.14. The degree of influence of each factor on the output variable

Analysis of the given information shows that all factors independently of each other obviously affect the consumption of raw materials, and in order to reduce their consumption per unit of the skin area, the process must be conducted in the positive region of the factor space.

To determine the optimum liming process parameters based on the technological requirements to output variables, the optimization search has been conducted using a generalized desirability function [59] obtained by regression equations in a coded form. According to this approach, for the optimal process control vector the limits on output variables that match the worst and the best values have been identified: $y_1 - 6.58$ and 6.47 kg of raw materials/ m^2 of the skin, $y_2 - 21.5$ and 20.5 % by weight of raw materials, $y_3 - 32$ and 37 % of the initial length of samples. The optimal liming process parameters under study, obtained by determining the maximum for the generalized desirability function by scanning with 0.01 search precision in the range of $-1.68-1.68+$ by all the factors. The value of the desirability function D at the optimal point is 0.6216541 , the number of calculations of the function values is 37933056 .

By stabilizing one factor at the optimum level and output variables in the range of their technological values from the minimum to the maximum, one can obtain a compromise area, and building the isolines of the desirability function – an optimal area of the process. For example, stabilizing the x_3 factor at the optimal level of $6.000126 \cdot 10^{-2}$, an optimal area for the process of liming has been obtained (**Fig. 2.15**).

$x_3 = -6,000126E-02$

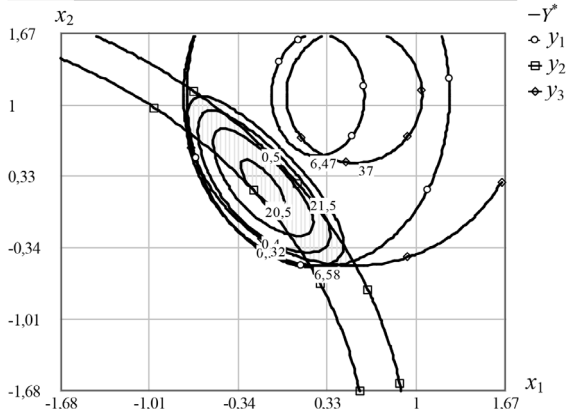


Fig. 2.15. The optimum area of the liming process

The vector of the technological process control is located at the point with the coordinates: $X_1 = 0.71$ and $X_2 = 1.25$ % of the raw material weight, respectively for the ions S^{2-} and Ca^{2+} , $X_3 = 11.76$ hours. In this case, the output variables have the values: $y_1 = 6.51$ kg of raw materials/m² of the skin; $y_2 = 20.8$ %

of the green raw material weight; $y_3 = 34.6$ % of the initial length of the sample under stress of 9.8 MPa. The obtained optimization results indicate that the raw material consumption can be reduced by 4.7 %.

Thus, the method of multicriteria optimization using a computer program, tested on the labor-intensive versatile technology of the raw hide liming, makes it possible to establish accurately the values of this process parameters. According to the developed method, the least amount of raw cattle hide consumption with a moderate swelling of the pelt and rational elongation under stress of 9.8 MPa is achieved with the consumption of 70 % of hydrosulfide and 72 % of sodium sulfide, 70 % of calcium hydroxide – hydrated lime, according to the % of the raw material weight: 0.89; 1.19; 3.30 and the duration of the dehairing and liming process of 12.0 hours.

The developed versatile technology of dehairing and liming of raw cattle hides of wet-salted curing [38] involves the carrying out of soaking and liming processes in VULKAN drum at a constant speed of 6–7 min⁻¹ for washing and soaking in two stages at the temperature of 26–28 °C.

Washing of raw materials is carried out with the consumption, mass %: water – 100 and Na_2CO_3 – 0.25 for 30 min. After pouring out the spent solution, the following is added into the drum, the mass %:

water – 80, nonionic surfactant Eusapon W – 0.15, sodium carbonate – 0.1 and the process lasts 1 hour. The solution is poured out.

Soaking 2 is performed with sequential addition of reagents, mass %: water – 80, Na_2CO_3 – 0.4; non-ionic surfactant – 0.2; after 30 minutes the enzyme preparation Basozim S-20 is added – 0.3, and after 2,5 hours $NaHS$ – 0.2. The process lasts for another 1 hour.

Dehairing is performed in the spent solution with a gradual addition, mass %: $Ca(OH)_2$ – 0.3; amine based preparation Mollescal-LS – 1.0; in 1 hour the content of $Ca(OH)_2$ is increased to 1.3; $NaHS$ – to 0.9 and Na_2S is added – 0.6; in 1 hour the hair is utilized through the drum sieve. The rotation speed of the drum is 2.0–2.5 min^{-1} periodic, min.: at first – 30, after 0.5 hours – 10 and when utilizing the hair – 30.

Liming is carried out after bringing the temperature of the solution to 28–29 °C with water consumption of 20 wt. % and subsequent addition of Na_2S and $Ca(OH)_2$ into the drum, respectively, 0.6 and 2.0 wt. %. The total duration of the liming process is 10 hours. The mode of the drum rotation is periodic, min.: during the first hour – 30, the second – 10, in the subsequent hours – 5, before the completion of the process – 30.

The received pelt is washed twice with a water consumption of 100 wt. % with a gradual decrease in the temperature to 20–22 °C at the end of processing. The duration of each washing is 15 minutes. The drum rotation is continuous with the speed of 2.0–2.5 min^{-1} .

The received pelt is sent to further processing according to the appropriate technique.

Thus, a versatile technology of two-stage liming of raw cattle hides with the hair utilization has been developed and it involves a gradual increase in the concentration of chemical reagents in the processing liquor, combining the stages of technological treatment and the controlled influence of physical and chemical factors on the structure of the dermis collagen. The developed technology contributes to the production of the pelt of a moderate swelling with the efficient use of raw materials and production of the Wet-blue semi-finished product [60] for a wide range of leather elastic materials.

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Questions for self-control

1. Factors that affect the effectiveness of fur and leather production.
2. Peculiarities of the interaction of aqueous reagent solutions with rawhides.
3. Consequences of adding salts into alkali solutions during the treatment of various skins and hides.
4. Influence of some oxidants of various chemical compositions on the destruction of disulphate bonds in keratin.
5. Dehairing of rawhides using enzyme preparations.
6. One-stage dehairing and liming of rawhides.
7. Influence of the process temperature and consumption of sodium carbonate on the kinetics of soaking in terms of moisture content in the middle layer of the dermis.
8. Liquid coefficient as one of the main technological parameters of the influence on rawhides during their treatment.
9. Results of the study of a complex of the pelt deformation properties.
10. Analysis of gelatin smelting process in carbonate-sulphide liming depending on the temperature and water ratio.
11. Thermal indicators of the dermis samples at different stages of rawhide treatment.
12. Two-stage dehairing and liming with the hair utilization.
13. Dehairing and liming with the immunization of the hair shaft.
14. Influence of formaldehyde on rawhide dehairing.
15. Study of the elastic and plastic properties of the pelt.
16. Analysis of the amino acid composition of the hair after rawhide treatment according to the technology of its saving.
17. Influence of sodium sulphide on the hair keratin, the shaft of which is immunized with calcium hydroxide and formaldehyde.
18. Non-sulphide dehairing and liming of rawhides.
19. The use of kaoline as a factor regulating the consumption of alkali for rawhide liming.
20. Determination of minimum consumption of chemical reagents in rawhide liming.
21. Dependence of rawhide watering degree on the chemical composition of the salt used in soaking and liming processes.
22. Washing, the first and second soaking, dehairing and liming as the processes of two-stage dehairing and liming of rawhides.

23. Multipurpose two-stage dehairing and liming of rawhides.

24. Influence of soaking and liming solutions composition on physical and chemical properties of the pelt and hair.

25. Optimization of chemical and technological processes using a two-stage liming of rawhides with the hair utilization.

26. Determination of the optimum parametres of the rawhide liming process.

27. The developed versatile technology of dehairing and liming of raw cattle hides of wet-salted curing using VULKAN drum: washing, soaking, dehairing, liming.

3. TECHNOLOGY OF THE LEATHER SEMI-FINISHED PRODUCT TANNING

While tanning collagen of the dermis, its chemical structuring and stabilization of the capillary and porous structure, created at the stage of pre-tanning colloids and chemical processes, take place. For this purpose, a wide range of chemical reagents and materials, including chromium compounds, polyphenols, modified aluminosilicates, etc., are used in the technology of tanning. All the developed technologies of tanning and filling have been tested and implemented at the leather enterprise CJSC *Chinbar*.

3.1. Efficiency of using the main chromium sulfate of anionic form

In the process of leather elastic materials manufacturing, the most common technology of tanning involves the use of chromium compounds. About 90 % of the world's total leather volume is produced by this technology. The results of the study of the influence of liming and tanning conditions on the properties of the received semi-finished product are given in **Table 3.1**.

The basic chromium sulfate (BCS) $Cr_2(SO_4)_n(OH)_{6-2n}$ (TU2141-033-541386-2003) of cationic form in the dissolved state with basicity of 33 % and the content of Cr_2O_3 of 21 g/dm² was in the experiments [2]. To compare the influence on the process of activating the structure of leather raw materials, a sample of a non-limed hide containing 30 % of the blocked carboxyl groups in the form of amide in collagen of the dermis. As it can be seen from the data, the content of chromium oxide (III) in the dermis after its tanning reaches an extreme value at the duration of liming for 16 days, followed by a 0.4–0.9 % decrease in 28-day liming depending on

Table 3.1

**The influence of raw material liming on the fixation
of chromium compounds and hydrothermal stability
of the semi-finished product**

State of raw materials	Tanning of the semi-finished product, hours					
	2		6		24	
	Con- tent ¹ of Cr_2O_3 , %	Reduc- tion ² , %	Con- tent of Cr_2O_3 , %	Reduc- tion, %	Con- tent of Cr_2O_3 , %	Reduc- tion, %
Middle layer of the dermis before liming	3.8	43	4.6	38	6.0	5
One-day liming	4.2	33	4.8	20	6.2	0
The same after the number of days:						
2	4.4	34	5.1	8	6.7	0
7	5.1	25	5.9	15	7.2	0
16	5.8	46	6.2	18	7.8	0
28	4.9	59	5.8	45	7.0	22

Note.

¹ – from the weight of the pelt;

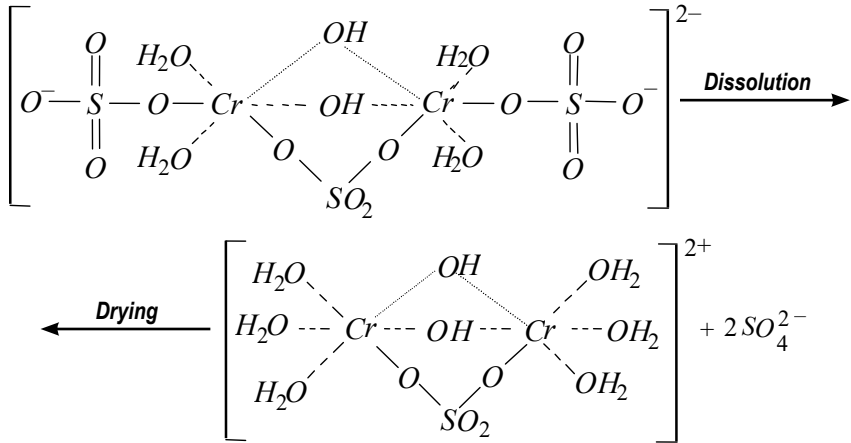
² – reduction of the area after three minutes of boiling.

the duration of tanning. At the same time, the minimum reduction I the area of the tanned semi-finished product during boiling is achieved by 2- and 7-day liming and the duration of tanning 2 and 6 hours, respectively.

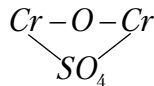
The boiling test is done for the samples of 24-hour tanning after 1–16-day liming. The intensification of the interaction of the dermis collagen with BCS occurs by releasing carboxyl groups during liming due to the detachment of the amide group ammonia [3]. The strong weakening of the intermolecular interaction in the structured collagen leads to the dissolution of deep collagen hydrolysis products with the content of a large number of carboxyl groups.

When structuring collagen of the dermis, it is reasonable to use complex chromium compounds of the anionic initial form with a molecular

size of about 0.7 nm [3, 4], which corresponds to their binuclear composition. In contrast to the previously used cationic BCS form for tanning of the dermis collagen, anionic complexes provide an acceleration of the structuring process of the leather semi-finished product due to a gradual transition to the cationic form [5] with the dissolution of hydroxo sulfatochromium complexes (HSCCs):



As the results of the dissolution process of BCS in water have shown, there is a significant decrease in the pH of the solution, especially intensive during the first 10 min. (**Fig. 3.1**) [5, 6]. Moreover, this effect is more clearly manifested at the higher temperature of the experiment. In this case, the transition of sulfato groups from the internal sphere of complexes of anionic forms into the external one after their displacement by water molecules occurs. As a result, a cationic form of HSCCs with a decrease in their activity at the reduction of the *pH* is formed. At the higher *pH*, the HSCC nuclearity increases due to the process of chromium complexes combining with the interaction of hydroxyl groups with their subsequent condensation [5] and the formation of bonds involving sulfato groups.



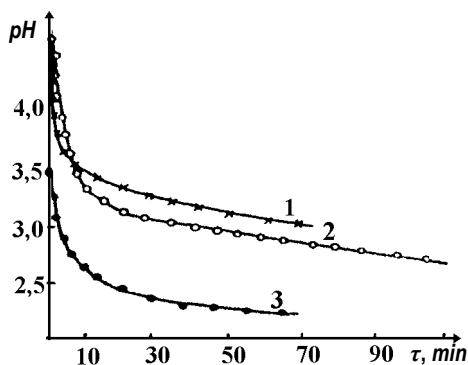


Fig. 3.1. Kinetics of the pH change at the dissolution of BCS with the concentration of, g/dm^3 : 40 (1) and 10 (2, 3) at the temperature of, $^{\circ}C$: 20 (1, 2) and 37 (3)

The interaction of HSCCs with collagen occurs predominantly with ionized carboxylic groups, as determined by many long-lasting studies on modified pelt powder [7]. In this case, one molecule of HSCC is capable of connecting two adjacent macromolecules of collagen microfibrils with a covalent bond (**Fig. 3.2**).

It can be seen from **Fig. 3.2** that the interaction of ionized carboxyl groups of collagen with cationic HSCCs occurs with their simultaneous combination of the salt formation

reaction between the cation of the dinuclear chromium complex (III) and ionized carboxyl groups of protein. As in a collagen macromolecule, carboxyl groups are often positioned in the same plane and sequentially one after another, belonging to polypeptide chains of adjacent macromolecules, after the interaction with them, HSCCs, which are located in parallel to them, with the increase in the pH of the medium,

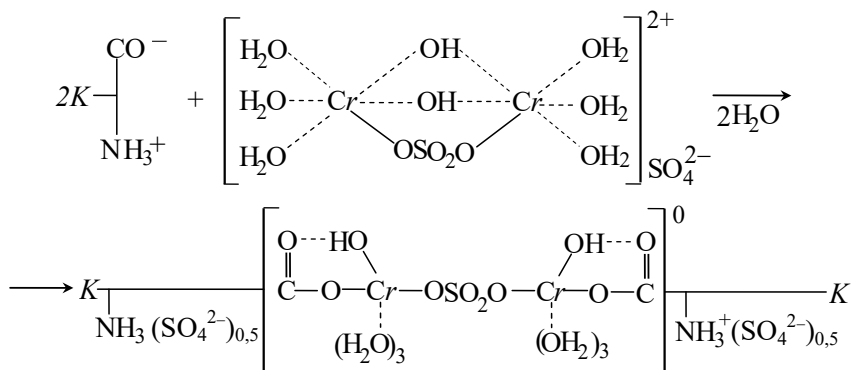


Fig. 3.2. The scheme of collagen interaction (K) with BCSC

combine hydroxyl groups, forming voluminous tetranuclear complexes [8] (**Fig. 3.3**), which greatly increases the strength of intermolecular bonds.

The structure of bridge bonds can be also linear tetranuclear, which depends on the location of hydroxyl groups of collagen and the presence of a free chromium atom in the binuclear complex that did not interact with the carboxyl group. This kind of interaction takes place in case of cationic complexes that are able to coordinate an oppositely charged carboxyl group of collagen in the internal sphere. A part of the HSCC is usually deposited between the fibrils.

The results of the use of the anionic form of the BCS of different basicity, given in **Table 3.2**, indicate a more effective interaction with collagen of the acid-salt treated pelt. In this case, the content of Cr_2O_3 in the leather semi-finished product with the BCS consumption of 1.2 % is over 3.5 %, and the hydrothermal resistance of the dermis collagen after the semi-finished product shaving is more than 100 °C in tanning of cattle hides with the thickness of 2.8–3.0 mm.

As it can be seen from **Table 3.2**, using the HSCCs of a cationic form for obtaining skins with the hydrothermal resistance, which would meet the standard requirements, it is necessary to spend far more BCS. It is not used efficiently, judging by the content of Cr_2O_3 in the finished dry leather. In case of anionic complexes, the interaction between the

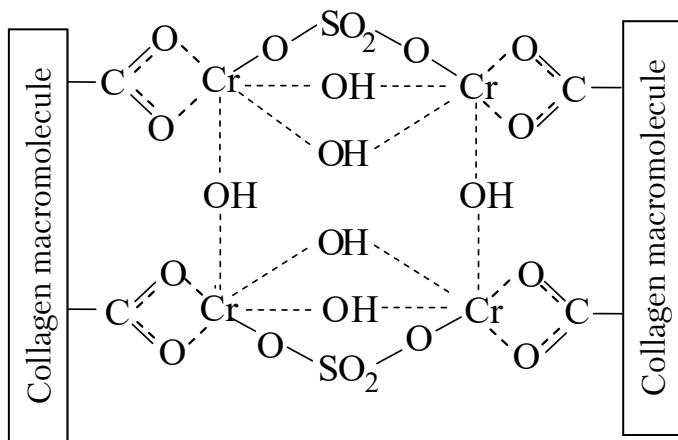


Fig. 3.3. The scheme of interaction of a double spatial HSCC with collagen

Table 3.2

**Change in the collagen hydrothermal resistance
under the BCS effect**

Consumption of the BCS		Content of Cr_2O_3 , % of a solid residual	Hydrothermal resistance of collagen, °C		
Cr_2O_3 , % of the pelt weight	of basicity, %		after tanning	after 12 hours	after shaving
1.1	34.0	3.47	101.0	105.0	102.0
1.2	42.0	3.78	104.0	107.0	104.0
1.3	26.0	4.89	106.0	113.0	108.0
2.0 ¹	40.0	4.06	99.0	103.0	98.0

Note. ¹ The variant corresponds to the use of a cationic form of the BCS

chromium atom and ionized carboxyl groups occurs during their transformation into the cationic form. This facilitates a deeper diffusion of anionic complexes into interfibrillar gaps and more uniform distribution of bridge bonds in the collagen depth. The activity of HSCCs of the anionic form is also confirmed by the data presented in **Table 3.3**.

According to **Table 3.3**, the use of anionic complexes made it possible to apply HSCCs more efficiently, which is confirmed by a significant increase in the degree of their absorption and thermal stability of collagen. With the increase in the consumption of cationic HSCCs, as provided by the standard technology, a large part of them is used inefficiently due to the formation of bridge bonds with carboxyl groups of surface layers of collagen fibrils deposition of the structuring agent excess on their surface. This causes an unequal distribution of HSCCs in the collagen structure. Removing moisture from collagen, structured in this way, a significant reduction of its area is observed due to the contingency of microfiber molecules and the formation of strong ionic bonds between charged side radicals of macromolecules. Thus, by using collagen of the anionic form of chromium complexes, which are predominantly of the dinuclear form, it is possible to increase their diffusion ability, intensify the process, reduce the consumption of the main chromium sulfate by 1.5 times, and increase the uniformity of

Table 3.3

The influence of HSCCs on the dermis collagen structuring

Indicator	Type of treatment with structuring					
	Anionic and cationic			Cationic		
	1	2	3	1	2	3
Consumption of, % of the pelt weight						
HSCC	1.1	1.1	1.1	1.1	1.7	1.7
Electrolyte-resistant grease	–	0.4	0.6	–	–	0.6
Absorption of HSCC by the pelt, %	99.7	99.2	99.0	96.0	92.0	90.0
Temperature of welding, °C	101.0	106.0	103.0	97.0	109.0	107.0
Volume yield, cm ³ /100 of collagen	220	246	250	180	205	230
Reduction of the area, %	10.7	3.3	3.9	14.0	11.5	9.0

tanning in the thickwise direction. The resulting effects contribute to a more rational use of leather raw materials.

Thus, the main chromium sulfate (III) interacts under the principle of systematic entry into the macromolecular structure of collagen. In addition, at the first stage, its ionized carboxyl groups primarily enter the near sphere of dinuclear chromium complexes, which occur at this stage most often. With a higher consumption of the main chromium sulfate and the increase in the basicity at the second stage of collagen structure stabilization, its carboxyl groups, which are located at greater distances from one another, interact with the subsequent increase in the temperature of welding. As a result, the transformation of chromium complexes from linear dinuclear into polynuclear volumetric structures with additional hydroxyl bonds between them is not to be avoided.

3.2. Anionic and cationic chrome tanning of the semi-finished product

Due to the research carried out into the structure of chromium complexes (III) and the mechanism of the chrome tanning, it is possible

to reduce the consumption of chromium compounds by their use in the anionic initial form and the concentrated state at the first stage of tanning. The technology of anionic and cationic tanning of the pelt is based on the ability of the HSCC sulfate-ion to migrate into the outer sphere of chromium complexes (III) with the dissolution of the BCS in the technological solution, immobilized with the pelt [6], which is confirmed by the theoretical studies [9]. This technology involves the preliminary treatment of the pelt with electrolyte resistant greasing emulsion. Due to its high surface activity, it easily diffuses into inter-structural gaps in the dermis, temporarily blocks carboxyl groups of collagen, which in turn accelerates the diffusion of chromium complexes.

In connection with the demand for the Wet-blue semi-finished product to obtain leather materials of different thickness from it, there is an objective need to develop new resource-saving ecologically oriented technologies. To a large extent, this is due to the structural disorder during the treatment of raw materials with different thickness and the duration and labour intensity of tanning.

The developed technology of tanning of the pelt with a high degree of HSCC absorption involves the use of the pelt from cattle hides with the thickness of over 3.2 mm, obtained according to the existing technology at the leather enterprise CJSC *Chinbar*. Samples of the pelt with the area of 25 dm², after its fleshing, delimiting and bating, are treated with a solution of sodium chloride at the concentration of 250 g/dm³ taking 4 % of sodium chloride of the pelt weight for 10 minutes in a drum of 10 dm³ volume at the temperature of 24–25 °C and the rotation speed of 10 min⁻¹. Then, the formic and sulphuric acids are added, respectively, by 85 % in the amount of 0.25 and 100 % – 0,5 % of the pelt weight, diluted with water in the ratio of 1/10, at intervals of 10 min. After acid-salt treatment, the propylation of the outer layers of the pelt cut should not be less than 60 % of its thickness. In this case, the acid content in the spent pickle solution in terms of sulfur acid should not be more than 0.2 g/dm³, and its specific density is – less than 1.035 kg/m³.

The spent acid-salt solution is drained and to increase the equal distribution of chromium complexes (III) in the thickness of the dermis, an electrolyte-resistant emulsion is used along with a pickling to block ionized carboxyl groups of collagen located on the surface of microfibrils

and then BCSs with the appropriate basicity are dosed. After one-hour rotation in a drum, the pelt is checked for the BCS diffusion depth by the colour of the cut. With its complete dyeing, magnesium oxide is added into a drum in two doses with an interval of 0.5 hour. At the end of the tanning process, the temperature of welding is determined, with the pH of the spent technological solution being 3.9–4.2. The duration of the pickling and tanning processes is 9–11 hours. Experiments of the second order CCRD [10, 11] have been carried out to optimize the pelt tanning and their plan is given in a coded form in **Table 3.3**. Mathematical models of the type (2.1) are calculated according to the program posted at the site <http://mnk-online.narod.ru>.

To receive mathematical models of this process, a full factor experiment of 2^3 type was initially implemented, in which the factors that significantly affect the tanning process were the consumption of the BCS against Cr_2O_3 and electrolyte-resistant emulsion, respectively, X_1 and X_3 , % of the pelt weight and the BCS basicity – X_2 , %. At the same time, on the basis of previous experiments, the X_1, X_2, X_3 values change on two levels with the corresponding interval of 0.3, 8.0, 0.3 and the position of the design centre at the point of the factor space of 1.2; 34.0; 0.5. For ecological and technological reasons, the absorption of chromium complexes (III) by the pelt during tanning was taken as the output variables – y_1 , % Cr_2O_3 of the initial amount; the temperature of welding – y_2 , °C; volume yield of the semi-finished product – y_3 , $cm^3/100$ g of the pelt substance; reduction of the tanned and dried Wet-blue area with respect to the area of the pelt – y_4 , %.

After the implementation of this factor experiment, linear mathematical models for each output variable were received and they turned out to be inadequate. Therefore, for the further research of anionic and cationic tanning process, we moved to the CCRD, when the equal predictable ability of the model in all the points, equidistant from the centre of the design by the circle with the same radius. According to the design of the experiment, the output variables were obtained at the experimental points 1–20 in the natural values (**Table 3.4**).

After the statistical analysis of the experimental data with a confidence probability of 0.95, mathematical models were received and they adequately describe the tanning process of the pelt:

Table 3.4

Research results of the pelt tanning process according to CCRD

Output variable	Experimental point									
	1	2	3	4	5	6	7	8	9	10
y_1	85.6	98.9	83.0	97.6	81.5	95.2	79.0	92.1	78.5	99.2
y_2	109	91	107	93	103	88	104	90	109	84
y_3	247	182	229	193	224	172	223	167	237	178
y_4	-10.2	-11.7	-6.9	-7.8	-12.1	-12.8	-8.7	-10.8	-4.3	-14.3

Table 3.4, cont.

Output variable	Experimental point									
	11	12	13	14	15	16	17	18	19	20
y_1	99.3	93.5	98.7	92.1	97.4	98.9	98.7	97.1	99.3	98.2
y_2	102	103	107	103	106	107	106	105	106	107
y_3	226	217	248	198	232	239	238	236	231	237
y_4	-7.4	-8.9	-4.3	-9.9	-3.7	-5.1	-3.9	-3.5	-3.8	-4.9

$$\hat{y}_1 = 98.40497 - 6.557516x_1 + 1.410355x_2 + 2.080501x_3 - 4.213231x_1^2 - 1.538193x_2^2 - 1.8925x_3^2;$$

$$\hat{y}_2 = 106.2637 + 7.548662x_1 + 1.591814x_3 - 4.039975x_1^2 - 1.914109x_2^2 - 1.028337x_3^2;$$

$$\hat{y}_3 = 235.8863 + 22.5815x_1 + 10.91991x_3 - 12.36966x_1^2 - 7.409307x_2^2 - 6.877843x_3^2;$$

$$\hat{y}_4 = -4.093616 + 1.612336x_1 - 0.738743x_2 + 1.26114x_3 - 2.182103x_1^2 - 1.774649x_2^2 - 1.402626x_3^2.$$

To determine the degree of influence of each of the factors on the output variable, they were ranked in the minimum and maximum zones. Since the mathematical models were received as a result of processing the second order rotatable design, in the range of the factor changes $-1.68 \leq x_i \leq +1.68$, the y_{min} and y_{max} coordinates are determined by the scanning method. At the calculation points of minimum and maximum values of the output variable, one-factor dependences $y = f(x_i)$ are

successively tabulated, fixing others at the corresponding experimental levels. The obtained results are presented graphically in the $y-x_i$ coordinates, which for y_1 are shown in **Fig. 3.4**.

As it can be seen from **Fig. 3.4**, all the output variables are the most affected by the initial consumption of BCSs, both in the minimum and maximum zones. At the same time, the influence of the factors on the absorption of a chrome tanning agent by the pelt and the temperature of welding is manifested differently here. Thus, the consumption of the BCS in the minimum zone exceeds the influence of the basicity of chromium complexes (III) on its absorption by the pelt and the consumption of electrolyte-resistant greasing emulsion by 3.8 and 3.0 times, respectively, and in the maximum zone — by 3.0 and 2.5 times. The same decisive influence is exerted by the consumption of the BCS on the temperature of welding, but the excess of other factors, being analyzed, during the transition from the zone of minimum to the zone of maximum increases from 4 to 5 times. This corresponds to an increase in the concentration of dinuclear chromium complexes (III) in the interstructure gaps at the first stage of tanning with the subsequent formation of a greater number of three-level bonds at the second stage of tanning.

As it should be expected, the consumption of electrolyte-resistant greasing emulsion produces a great effect on the formation of the volume yield and reduction in the area of the tanned semi-finished product after

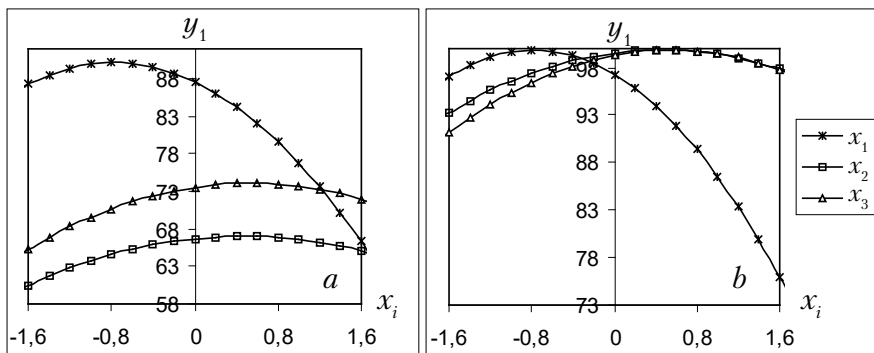


Fig. 3.4. Ranking of the factors by the degree of the influence on the output variable y_1 in the minimum (a) and maximum (b) zones

drying relative to the area of the limed pelt. Thus, this factor by the influence on the volume yield is only twice lower as for the consumption of a chrome tanning agent both in the zone of minimum and in the zone of maximum. The reduction in the area is equally affected by both the basicity of the BCS and the consumption of greasing emulsion, which is by 1.3 times less than that of a chrome tanning agent.

To describe the influence of each factor on the output variables, the previously obtained quasi-one-factor dependence was used (2.5). Thus, for the evaluation of the influence of x_1, x_2, x_3 factors on the y_1 output variable, the obtained dependence acquires the corresponding form

$$W_1 = -6.557516 \cdot x_1 - 4.213231 \cdot x;$$

$$W_2 = 1.410355 \cdot x_2 - 1.538193 \cdot x;$$

$$W_3 = 2.080501 \cdot x_3 - 1.8925 \cdot x.$$

In order to obtain all the factors, other than x_p , on the basis of the equations of graphic dependences, which are used to interpret the results of the research, $\text{крим } x_i$, it is necessary to fix, respectively, at the levels of $-1.68, 0, +1.68$, and tabulate x_i in this interval with the quantization step of $\Delta x_i = 0,2$. The results received for y_1 are shown in **Fig. 3.5**.

Analysis of the information shown in **Fig. 3.5** and other dependences, give grounds to draw conclusions about the studied process. Each of the factors affects the output variable independently of others, because in all the figures the effect on the lower, zero and upper levels is represented by only one curve. The overlap of the curve indicates

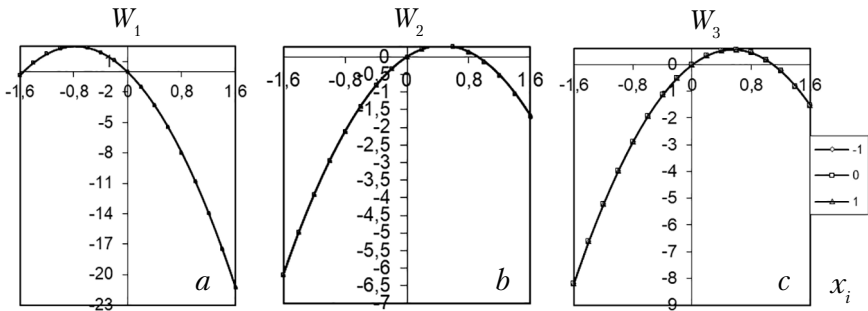


Fig. 3.5. The degree of influence of x_1 (a), x_2 (b), x_3 (c) factors on the output variable y_1

the ambiguity of the influence of the factors being analyzed on the output variable. To obtain maximum absorption of BCS, its initial x_1 concentration must be reduced, which is contrary to the other output variables. To improve the value of the output variable, apart from y_1 , x_2 factor must be placed in the centre of the design, which is further confirmed by the results of the multicriteria optimization, performed using the desirability function. At the same time, x_3 must to be given a value in the positive zone.

Therefore, it follows from the physical and chemical analysis of graphic dependences, received on the basis of mathematical models, that all the analyzed factors are important for the formation of the porous structure of the skin and for the effective use of a chrome tanning agent and electrolyte-resistant ester. For the purpose of a rational influence on the formation of the skin structure and the use of raw materials, it is necessary to optimize the tanning process of the pelt.

As the obtained models adequately describe the tanning process, the search for a compromise sphere using a multicriteria optimization according to the received mathematical models gives a possibility to identify the optimal parameters of the process taking into the account the requirements for all output variables. A generalized optimization criterion is calculated by the Harrington function [10]. The following data were taken for y_1 – y_4 as the best values of output variables in relation to the used approach: the BCS – 99.3 % Cr_2O_3 , 106 °C, 240 cm³/100 g, – 3.7 %. Accordingly, the worst values in the same units are the following: 98.0, 103, 229, – 7.4. The search for a compromise point is based on the restrictions in a coded form for all the factors: $-1 \leq x_i \leq +1$, $i = 1, 2, 3$ or in natural values: X_1 is located in the range of 0.9–1.5 % Cr_2O_3 , X_2 – 26.0–42.0 %, X_3 – 0.2–0.8 %. The optimization was carried out by scanning with specification of the coordinates of the optimum point by the Gauss-Seidel method.

The following location of the optimum point in the factor space was obtained: $X_1 = 1.2$ % Cr_2O_3 , $X_2 = 34.17$ %, $X_3 = 0.68$ % of the ester. The values of the output variables, calculated at the optimum point by the models, are the following: $y_1 = 99.27$ % Cr_2O_3 , $y_2 = 106.6$ °C, $y_3 = 239.6$ cm³/100 g, $y_4 = -4.05$ %. For comparison, the output variables of the tanning process of the pelt were determined based on the check variant, where the previously existing technology is taken as $X_1 = 2.2$ %,

$X_2 = 40.5$, $X_3 = 0$, since it does not involve the use of a greasing reagent. The consumption of sodium chloride and sulphuric acid is 6.0 and 1.0 % of the pelt weight. The duration of pickling and tanning is 16–19 hours. In this case, $y_1 = 74.3$ % Cr_2O_3 , $y_2 = 104.0$ °C, $y_3 = 203.0$ cm³/100 g, $y_4 = -11.6$ % were obtained. The advantage of the developed technology is the significant reduction in the consumption of chemical materials, with 25 % higher absorption of a tanning agent and 7.5 % less reduction in the area of the semi-finished product obtained by control treatment.

A compromise zone with $x_2 = 0$, obtained in a coded form, is shown in **Fig. 3.6**. Determination of the area of admissible parameters of the tanning process of the pelt is carried out for x_2 fixed factor at the levels close to the optimal in the range of 30–35 %. Under such conditions, the placement and size of a compromise area do not change significantly. With the consumption of the BCS – % Cr_2O_3 : $1.15 < X_1 < 1.23$ and the ester, % $0.4 < X_3 < 0.68$, the absorption of a tanning agent is located in the range of 98–99 %, the temperature of welding – 103–107 °C, the volume yield – 228–240 cm³/100 g, the reduction in the pelt area – 5.0–3.7 %.

As at this stage of a technological process, the calculation of chemical materials is done depending on the pelt weight and it exceeds the weight

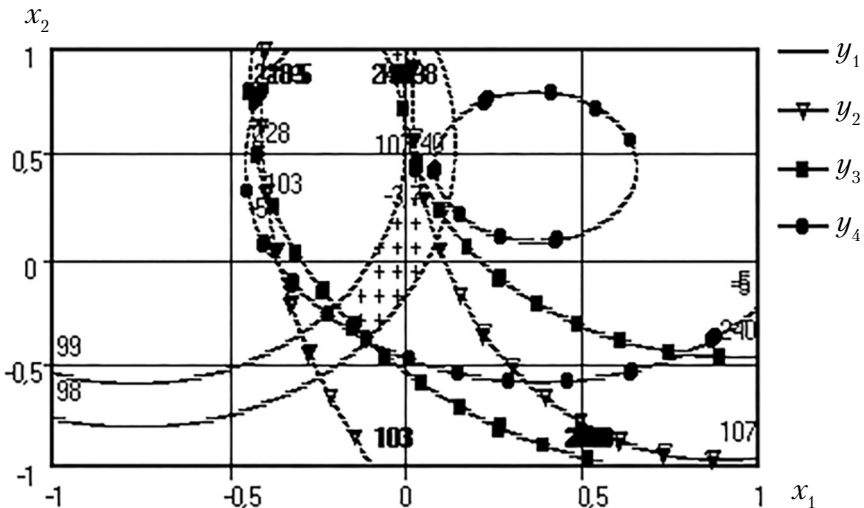


Fig. 3.6. A compromise area of the pelt tanning in coded coordinates

of the shaven semi-finished product by 2.5–3.5 times, which depends on the thickness of the finished leather, from the economic considerations, the preference is given to the minimum value of x_3 factor.

Therefore, the developed low-waste technology of the pelt tanning with the use of the main chromium sulfate makes it possible to reduce its consumption. Compared with the current technology – by 45 % with the five-fold reduction in water consumption, two-fold – in acid consumption and over thirty-fold reduction in the mass of chromium compounds in spent solutions with a significant increase in the efficiency of its use and a reduction in the duration of the process by 40–60 %. Due to the mathematical planning of the experiment for studying the tanning process of the pelt, a multicriteria optimization and construction of a compromise area, one can determine practical intervals of variation of the essential technological parameters and receive the Wet-blue semi-finished product with the increased output volume and area of the pelt with the temperature of welding that corresponds to the standard requirements.

3.3. Modification of montmorillonite with chromium compounds

Taking into account the toxicity of chromium compounds [12], systematic scientific and technological research has been carried out for a long time in order to replace their use with more environmentally friendly ones. Despite a large number of papers on this issue, due to a wide range of leather materials, such research is of interest at this time. The development and use of materials that combine the properties of fillers and structuring agents will be promising. [13–15]. This may apply to the materials based on highly hydrophilic aluminosilicates that have significant dispersion ability in aqueous media. The use of such bifunctional materials will probably be effective in the technology of leather materials treatment.

Modification of montmorillonite with the main chromium compounds (III) is promising for the development of a number of valuable

materials (adsorbents, fillers, pigment concentrates, tanners, etc.) and the creation of nanotechnologies on their basis [16–20]. Due to the effect of recharging the surface of montmorillonite particles as a result of the absorption of positively charged hydrochromium complexes [21–25], the adsorption capacity of highly dispersed minerals to organic substances that dissociate according to the anionic type – syntants, surfactants, dyes, etc. – can sharply increase [26, 27].

The choice of chromium compounds (III) for the modification and recharge of montmorillonite surface is caused by more characteristic properties of salts of transition metals, including aluminum, iron, titanium, zirconium, etc. According to the surface recharge, the action of inorganic compounds is manifested in two properties:

- the ability of the metal ion to form complexes that include two or more central atoms and stable complexes with anions of organic acids, as well as with acid residues of polypeptide chains of the dermis collagen;
- the change in the *pH* value (**Table 3.5**).

According to the data in **Table 3.5**, it is reasonable to choose the *pH* range for the effective complex formation and the processes of recharging mineral particles characteristic for chromium compounds (III), taking into account the *pH* intervals of technological processes of the leather semi-finished product liquid finishing [28]. They also

Table 3.5

The *pH* value of metal hydroxide formation

Metal hydroxide	The <i>pH</i> value of			
	the beginning of setting-out with the concentration, mole/dm ³		a complete setting-out	the beginning of dissolution
	1.0	0.01		
$TiO(OH)_2$	0	0.5	2.0	–
$ZrO(OH)_2$	1.3	2.2	3.7	–
$Fe(OH)_3$	1.5	2.3	4.1	13–14
$Al(OH)_3$	3.3	4.0	5.2	7.8
$Cr(OH)_3$	4.0	4.9	6.8	12

have the greatest ability to hydrolyze and form complexes obtaining reactive-capable polynuclear positively charged hydrocomplexes with a high absorbing activity.

In general, the advantages of chromium compounds for recharging and obtaining polyfunctional materials for the liquid finishing of leather semi-finished products are determined by:

- a high ability to form complexes and polynuclear hydrocomplexes;
- a significant thermodynamic stability of *Cr* (III) ions in octahedral coordination;
- the most favourable *pH* interval for the optimal complex formation;
- the maximum stability of chromium complexes bonds with adsorbed compounds of the anionic type on the surface of minerals;
- an optimal size of complex hydroxychromium ions and their multinuclear variety;
- the availability of chromium compounds.

Considering the information on the mechanisms of the structuring action of chromium compounds [2, 29], it is reasonable to study the conditions for recharging a mineral particle and stability of the obtained dispersions and determine the mechanism of the influence of chromium compounds (III) on the structural and electro-surface properties of montmorillonite dispersions as a promising basic material for obtaining polyfunctional compositions for the leather semi-finished product liquid finishing. Chromium nitrate and the MCC were used to study the changes in the structural and electro-surface properties of montmorillonite, due to its modification with chromium compounds, and the dispersion properties. Taking into account that Na^+ ions the most easily displace other cations from the exchange positions, the chosen method of hydroxychromation involved transferring the natural mineral from Ca^{2+}/Mg^{2+} - into Na^+ -form, and then the ion exchange of Na^+ -ions with *Cr* (III) ions by processing Na^+ -form with 0,1 M of the solution of chromium compounds [28, 30]. The method of preparation of hydroxychromium dispersions of montmorillonite involves the preliminary preparation of solutions of polynuclear hydroxychromium compounds with chromium of different basicity taking into account *OH/Cr* ratio – 0:1; 5:1; 1:1; 1.5:1; 2:1. To do this, 0,1 M volume of

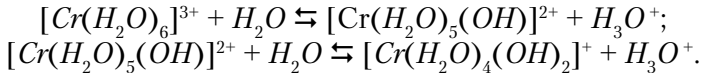
NaOH solution is slowly added to 100 ml of 0,1 M $Cr(NO_3)_3$ solution constantly stirring and bring the volume to 300 ml with distilled water. To achieve the balance, this solution is allowed to stand for 10 days at room temperature. The received solutions of chromium compounds are used to modify montmorillonite. For this purpose, 100 ml of 5 % montmorillonite suspension is mixed with 100 ml of the corresponding chromium solution. The obtained montmorillonite suspension with the *pH* of 4.5–5.5 is periodically stirred and allowed to stand for 24 hours. Then, by means of centrifugation or filtration, the precipitate is separated from the solution and the next 100 ml of the corresponding concentration of chromium solution is added.

In order to achieve the completeness of the exchange reaction, the third processing with the chromium solution is carried out after 24-hour shaking and decantation of the system. The precipitate is separated, washed 1–2 times with distilled water and stored as a suspension for further research. The colloidal and chemical properties of modified Na^+ -montmorillonite, in particular the *pH*, ζ -potential, surface-charge tension of mineral particles and adsorption of chromium polyhydroxycations have been determined [25]. In a similar way, the dispersion of chromium hydroxo complex montmorillonite (CHCM) is prepared by mixing 5 g of peptized Na^+ -montmorillonite with the main chromium sulfate with the consumption of 10–15 % Cr_2O_3 of the dry mineral weight. It has been found that the interaction of highly dispersed minerals with chromium compounds (III) is accompanied by charge effects. This affects the electro-kinetic properties of MMT dispersions, their aggregate stability and makes it possible to establish the mechanism for the modification of minerals.

Fig 3.7 gives the concentration dependences of ζ -potential of Cherkassy *Na*-MMT in the solutions of a single-charged electrolyte *NaCl*, two-charged – *CaCl*₂ and three-charged – $Cr(NO_3)_3$ (at *pH* of 4.2 and 5.5). A comparative analysis of these dependences shows a regular decrease of a negative value of ζ -potential with an increase in the concentration of electrolytes and counterion charge, which confirms a well-known Schulze-Hardy rule [31]. As it can be seen, unlike *NaCl* and *CaCl*₂, at $Cr(NO_3)_3$ concentration of $2,4 \cdot 10^{-3}$ mole/dm³ and the *pH* of ~ 4,2 – ζ -potential decreases up to zero, passes an isoelectric

points and changes its sign for a positive one. At a higher $pH \sim 5.5$, the dependence of ζ -potential on $Cr(NO_3)_3$ concentration (**Fig. 3.7**, Curve 4) is characterized by a sharp decrease of its value at $\sim 2,4$ mole/dm³. In this case, the effect of recharging montmorillonite particles dramatically increases and ζ -potential reaches higher positive values, and then gradually decreases with the increase of $Cr(NO_3)_3$ concentration.

As it is known [32–34], chromium (III) salts tend to hydrolyze in aqueous solutions forming hydroxo complex compounds. In particular, chromium nitrate hydrolysis $[Cr(H_2O)_6]^{3+} + 3NO_3^-$ in the aqueous solution occurs in two stages:



Taking into account the fact that the pH of the beginning of $Cr(OH)_3$ formation is ~ 4.0 – 4.9 for 0.1 – 1.0 M of solutions [35], it can

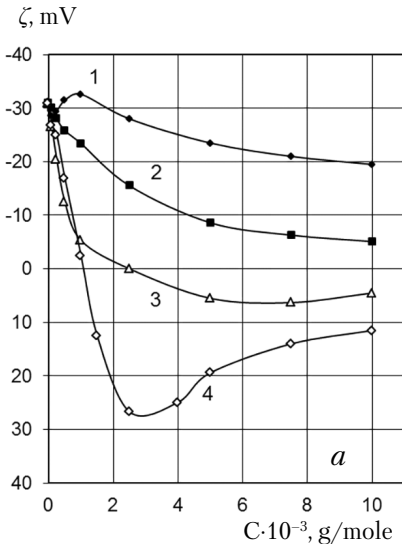


Fig. 3.7. Dependence of ζ -potential of Na-MMT dispersions on the solution concentration: 1 – $NaCl$, 2 – $CaCl_2$, 3 – $Cr(NO_3)_3$ at the pH 4.2, 4 – $Cr(NO_3)_3$ at the pH 5.5

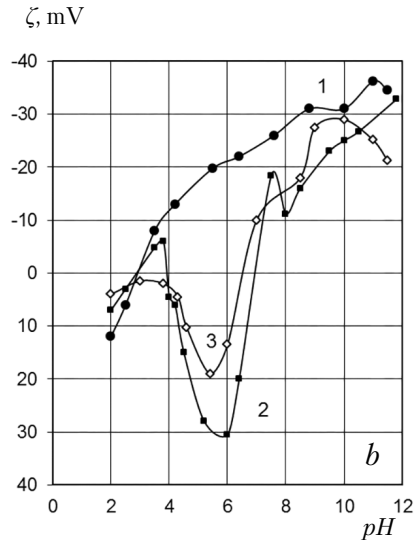


Fig. 3.8. Dependence of ζ -potential of Na-MMT dispersions on the pH of the medium у розчинах: 1 – $NaCl$, 2 – $Cr(NO_3)_3$, 3 – OCH за іонної сили фонового електроліту $1 \cdot 10^{-2}$

be argued that *Na*-MMT dispersions with chromium nitrate (**Fig. 3.7**, Curves 3 and 4) in the solution contain a sufficient amount of hydroxo-complex chromium ions of $[Cr_n(OH)_m(H_2O)_x]^{(3n-m)+}$ type. Thus, it can be expected that the *Na*-MMT surface recharge is not due to Cr^{3+} -ions, but to hydroxocomplex ions, which have high polarizability and adsorption capacity [36–39].

In order to establish a mechanism for *Na*-MMT recharging in $Cr(NO_3)_3$ solutions and the main chromium sulfate, the dependences of the stability of the CHCM dispersions and their ζ -potential on the *pH* of the medium under conditions of a constant ionic force of the background electrolyte at the concentration of 0.01 M (**Fig. 3.8**) of *NaCl* solution have been investigated.

In the absence of $Cr(NO_3)_3$ (**Fig. 3.8**, Curve 1), the dependence of $\zeta = f(pH)$ is characterized by the IEP at the *pH* of ~ 3.0 , above which *Na*-MMT particles are negatively charged. After adding $Cr(NO_3)_3$ (Curve 2) or the BCS (Curve 3) to *Na*-MMT dispersion, the dependences of ζ -potential on the *pH* of the medium become more complex. Within the *pH* values of 2.0–12.0, there are three zones of the dispersion stability, which alternate with three zones of coagulation. Within their limits, ζ -potential changes its sign three times. In the acid area with the *pH* of 2.0–3.0, *Na*-MMT particles are charged positively due to a weak-dissociation of its surface *AlOH*-groups of the basic type. At the same time, ζ -potential is not high and Al^{3+} coions, undergoing electrostatic repulsion of the surface, are allocated predominantly in the diffuse part of the double electric layer (DEL).

Within the *pH* values of 3.0–3.8 due to the dissociation of acid *SiOH*-groups, ζ -potential of montmorillonite, despite the presence of Cr^{3+} counterions in the solution, becomes negative. This suggests that Cr^{3+} ions cannot cause montmorillonite recharging and they are allocated predominantly in the diffusion part of the DEL. Thus, to the *pH* ~ 3.8 , the potential determining ions are H^+ i OH^- , and the exchange of $Cr^{3+} \rightleftharpoons H^+$ i $Cr^{3+} \rightleftharpoons Na^+$ only causes the compression of the DEL, the decrease in the ζ -potential and the destabilization of the systems.

Therefore, the change in the charge of the sign is caused by some other reasons. As the *pH* is reaching 4.0, the $-\zeta$ -potential of montmorillonite drops sharply by the absolute value and becomes positive again.

This corresponds to the alternation of the coagulation zone at the IEP with the stability zone of the positively charged dispersion (**Fig. 3.9**).

The *pH* range of 4.0–6.0 is characterized by a rapid, gradual increase in the positive ζ -potential and stability of the dispersion. At the same time, the IEP coincides with the *pH* of the beginning of chromium hydroxide precipitation, and the stability zone of a positively charged dispersion expands to the *pH* of a complete precipitation of $Cr(OH)_3$ at the *pH* 6.8. Obviously, this coincidence is not accidental, given that the state of chromium ions in the solution sharply changes

due to the hydrolysis process and complex formation at the *pH* 4.0–6.0. Indeed, as shown in the works [38–40], apart from hydrolysis, in the solutions of $Cr(III)$ salts there occurs complex formation, as well as processes of condensation and polymerization, which lead to the formation of polynuclear chromic compounds. These processes are accompanied not only by the

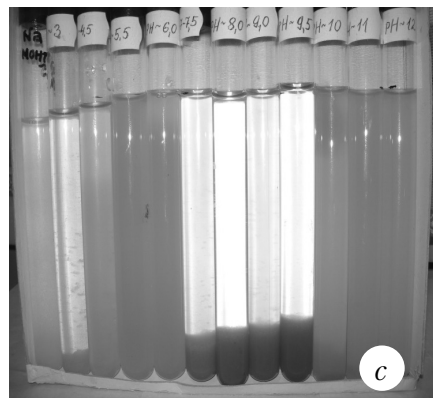
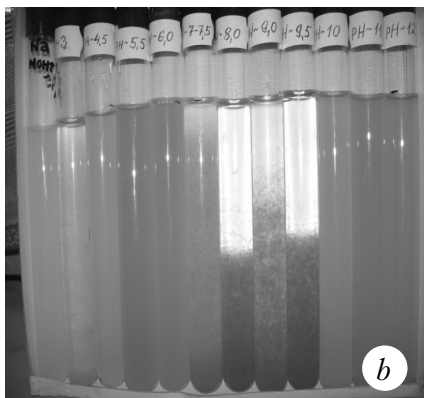
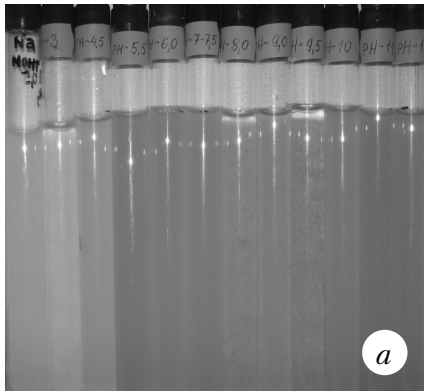
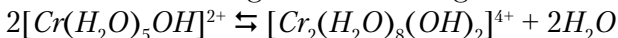
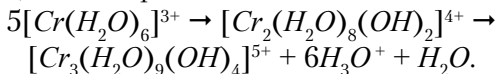


Fig. 3.9. Coagulation and stability zones during the interaction of Na-MMT dispersions with $Cr(NO_3)_3$ solutions (*a*), after sedimentation for 3 (*b*) and 4 hours (*c*) at various *pH* media

change in the charge of hydroxocomplex ions and by the coloring of the solution, but also by an increase in their molecular weight. According to the source [38], the process of dimerization of hydroxypentahaccharomyous ions occurs according to the following scheme:



with the hydrolysis constant of $K_2 = 10^4$ mole/dm³. Further polymerisation and hydrolysis, which proceed very slowly at room temperature, are also possible, for example:



As noted in the work [40], the replacement of water molecules in the internal coordination field of the hydrated metal with a hydroxyl ion dramatically increases the ability to adsorb this ion on the surfaces of dispersion particles of different chemical compositions. This is due to the increasing polarization of complex ions and the decrease in their hydration. The ion-exchange adsorption of such polymeric complex ions, in particular chromium ones [20, 36], supplemented by specific adsorption, may exceed the capacity of mineral exchange by several times.

Therefore, the most likely reason for changing the montmorillonite charge sign and the emergence of the stability interval of a positively charged dispersoid solution is the supra equivalent specific adsorption of polymerized ionic forms of chromium from the solution. In this case, the gradual growth of a positive ζ -potential of montmorillonite particles with the increase in the pH (**Fig. 3.8**) can be explained by the gradual adsorption of monomeric and dimer forms of hydroxocomplex chromium ions in accordance with the increase of their basicity.

The further process of the ζ -potential dependences on the pH of dispersions in solutions of chromium compounds is likely to determine the nature of the dissociation of the surface groups of montmorillonite and the transformation of adsorbed polymerized hydrolysis products [25, 32–34]. Thus, the further addition of alkali and the increase of the pH cause a decrease in the positive ζ -potential up to zero and the next third recharging of the montmorillonite surface at the pH 6.8–7.0. This is accompanied by a new coagulation zone and a dispersion stability zone (c) with a negative charge sign, although the dissolution of chromium hydroxide, according to the reference data [35], starts at the $pH \sim 12.0$.

Polynuclear chromium complexes are stable in the pH range of 4.5–6.5, presumably, because in this case recharging is associated with the decomposition and desorption of polymer chromium complexes. The recharge of the MMT surface is also facilitated by the consistent dissociation of $SiOH$ - and $AlOH$ -groups, which increases the negative charge of montmorillonite particles. At the same time, the processes of further transformation of adsorbed hydrolysis products are caused by this. In the pH range of 7.0–10.0, the depolymerization of $Cr_n(OH)_m$ is likely to dominate. Starting from the $pH \sim 8.0$, the process is enhanced by the formation of $[Cr(OH)_6]^{3-}$ and $[CrO_4]^{2-}$ anions. This is facilitated by a sharp jump of $-\zeta$ -potential. The dissociation of $Al-OH$ -groups, which finishes at the $pH \sim 11.0$, also affects. The result of such processes is the emergence of a zone with maximum stability of negatively charged dispersion (c).

It is also known [32–35] that increasing the pH and the basicity of the solution, $Cr(NO_3)_3$ OH^- -ions can locate in the inner sphere of complex chromium ions with a change in the charge sign. As a result, the adsorption of formed negatively charged complex chromium ions on a positively charged surface of montmorillonite may also be one of the reasons for the third recharge of particles and an increase of $-\zeta$ -potential to the $pH \sim 11.0$. The next decrease of $-\zeta$ -potential is undoubtedly caused by the growth of the ionic strength of the solution by OH^- -ions and the compression of the DEL. The data correspond to the change in the stability of dispersions (**Fig. 3.8**).

At the same time, due to the general similarity of the ζ -potential dependences on the pH of the medium in the investigated solutions of chromium compounds (**Fig. 3.8**, Curves 2, 3), the characteristic peculiarity of the ζ -potential dependence on the pH of the medium for the BCS is the presence of a small positive charge on dispersion particles in the acidic pH zone of ~ 3.0 – 4.0 . This is likely due to the fact that even without adding the alkali, BCS solutions are already partially hydrolyzed, and because of the presence of organic and inorganic reducing agents in its composition, complex chromium ions are unevenly charged.

Thus, the fact that in the same pH range of 4–6, along with the hydrolysis of $Cr(III)$ compounds, there is a recharge of the MMT surface and a new stability zone of positively charged dispersions appears,

indicating a close connection of these processes with the complex formation of Cr^{3+} ions in solutions.

Therefore, the optimal conditions for the modification of MMT by $Cr(III)$ compounds are realized in the pH range of 4–6, within which the surface of mineral particles acquires a maximum positive charge due to the adsorption of hydroxochromium cations [22–25]. In order to obtain information on changes in the structure and electro-surface properties of montmorillonite within this pH range, the adsorption of chromium hydrolysis products, depending on the basicity of $Cr(NO_3)_3$ solutions, has been studied and the X-ray analysis of modified montmorillonite samples has been performed [25, 28].

As seen from **Fig. 3.10**, in the absence of alkali and the basicity of $OH^-/Cr^{3+} = 0$, the adsorption of Cr^{3+} cations does not exceed Na -MMT exchange capacity of 0.81 mg-eq/g. Increasing the degree of $Cr(NO_3)_3$ solution basicity from 0 to 0.1, chromium adsorption on Na -MMT significantly increases, which is due to the appearance of its polynuclear forms – dimers, tetramers, etc. in the solution [32]. A further increase in the ratio of OH^-/Cr^{3+} is accompanied by a slow, linear increase in the adsorption of polynuclear varieties of chromium. This is due to a gradual increase in their molecular weight and size. It is probably the adsorption of polynuclear chromium of a polymolecular nature. However, by means of the linear zone extrapolation, the amount of adsorption, which corresponds to the monomolecular surface filling (1.93 mg-eq/g), can be approximately estimated. Due to the adding of this number of graft polyoxochromium cations to the amount of Na^+ ions that had the ion exchange reaction with them (0.72 mg-eq/g), it was determined that one chromium polyhydroxylation on the surface of montmorillonite consists of ~3 chromium ions: $n_{Cr} = 1.93 / 0.72 \approx 3$, although more or less degree of polymerization is probable.

Fig. 3.10 shows that increasing basicity, the adsorption of polymer chromium complexes on Na -MMT reaches high values, which in 2–5 times exceed the capacity of the cation exchange of the mineral ($E = 0.72$ mg-eq/g). This is in good agreement with the data of other works [16, 17]. However, it should be taken into account that such interaction of neutralizing ion exchange nature and the excessive positive charge, which occurs on the surface of particles, only create unequivocally sorbed chromium polyhydroxy cations.

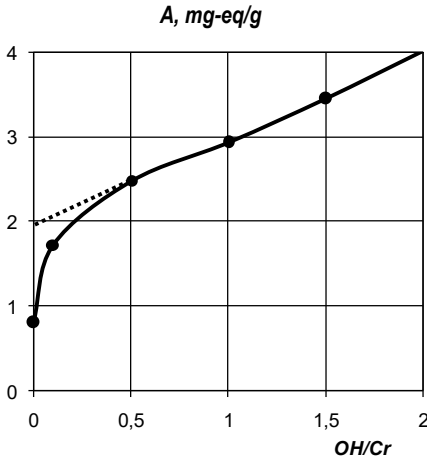


Fig. 3.10. Dependence of hydroxochromium complexes adsorption on Na-MMT on the solution basicity $Cr(NO_3)_3$

It is difficult to accurately calculate the magnitude of this charge due to the fact that the exact composition and the charge of adsorbed polyhydroxy cations is unknown. However, it can easily be verified that the surface charge formed as a result of their adsorption is very large and reaches tens and hundreds $\mu C/cm^2$.

Let us calculate the surface charge density σ for CHCM with 1.0 basicity, remembering that supraequivalent adsorption of chromium polyhydroxy cations corresponds to the range of $2.94 - 0.72 = 2.22$ mg-eq/g, and the specific surface area of the initial Na-MMT $S_{sp} = 520$ m²/g.

As a minimum charge of polyhydroxy cations, let us take $z = 1$, $\sigma = z \cdot a \cdot F / S_{sp} = 1 \cdot (2.22 \cdot 10^{-3}) \cdot (9.65 \cdot 10^4) / 520 = 0.412$ C/m² = 41.2 $\mu C/cm^2$ (Table 3.6). If we take the maximum charge of chromium polyhydroxy cations as $z = 4$, then $\sigma = 164.8$ $\mu C/cm^2$, in fact such a large electric charge is distributed volumetrically in the surface layer consisting of polyhydroxochromium cations with the thickness of about 1nm.

The main characteristics of CHCM obtained under different conditions [25] are given in Table 3.6. According to it, montmorillonite particles, modified by the main compounds of Cr(III), acquire a high positive charge, potential and developed surface. This allows for a significant adsorption and their strong fixation on the surface of anionic dyes, tanning agents, surfactants, etc.

Adsorption of polynuclear complex chromium ions on montmorillonite, which changes the charge and the nature of its surface, greatly affects the rheological behavior of mineral dispersions. Analysis of the curves of MMT dispersion flow in $Cr(NO_3)_3$ and BCS solutions and $\eta = f(\tau_r)$ dependences makes it possible to determine that an increase in

Table 3.6

The main colloidal and chemical characteristics of CHCM

Modifica- tor	Basicity, OH^-/Cr^{3+}	Adsorption of chromium complexes, mg-eq/g	Surface charge, C/m ²	S_{sp} , m ² /g	pH	K_{sp} , 10^{-3} Sim/cm	ζ , mB
$Cr(NO_3)_3$	0.1	1.73	0.187	95	4.5	0.15	11.0
	0.5	2.49	0.328	140	4.6	0.125	16.4
	1.0	2.94	0.412	190	4.7	0.22	20.5
	1.5	3.46	0.508	235	5.0	0.14	25.9
	2.0	4.02	0.612	260	5.3	0.12	30.3
BCS	1.5	3.42	0.501	256	4.9	0.14	23.6

the concentration of chromium compounds causes significant dilution of dispersions. This is confirmed by a sharp decrease in viscosity of dispersions with an increase in the concentration of chromium compounds (**Fig. 3.11**). The diluting effect in both cases occurs due to the supraequivalent adsorption of polynuclear chromium complexes and the acquisition of a high density positive charge (at the level of hundreds of $\mu C/cm^2$) by dispersed particles of MMT, the mutual repulsion between which leads to a complete peptization of the system.

The results of studies into the influence of BCS consumption on the modification of MMT dispersions by evaluating the nature of the dependences of kinematic viscosity and the pH level [41] are given in **Fig. 3.12** and **3.13**. The curves of the dependences of the kinematic viscosity of dispersions, taking into account the type of their modification by alkaline peptizators – sodium carbonate (SC) or sodium polyphosphate (PPh), against the consumption of the main chromium sulfate in terms of Cr_2O_3 (**Fig. 3.12**) are identical. For Na -MMT_{sc} dispersion, there is a slight increase in a kinematic viscosity at the consumption of Cr_2O_3 in the range of 0–3 % of the mineral weight. The increase in the consumption of Cr_2O_3 up to 5–6 % of its weight will cause a sharp drop in the dispersion viscosity of montmorillonite.

In contrast to Na -MMT_{sc} dispersion, with the modification of the BCS for the dispersion of Na -MMT_{pPh} (**Fig. 3.12**), a gradual decrease in

the viscosity at the consumption of Cr_2O_3 within 0–7.5 % of the mineral weight is observed. At the same time, the lowest level of viscosity for Na - MMT_{pph} dispersion is 1.62 cP, whereas for Na - MMT_{sc} – 2.53 cP. This may be due to the effect of the alkaline peptizer type on the dispersion level of montmorillonite particles. Sodium polyphosphates have a strong dispersant effect on montmorillonite dispersions in comparison with sodium carbonate, the influence of which is largely manifested as structure formation [42].

The diluting effect (**Fig. 3.12** and **3.13**) occurs as a result of the supraequivalent adsorption of polynuclear chromium complexes with a full recharge of the surface of montmorillonite particles from anion to cation and the acquisition of a high positive charge density at the level of hundreds of $\mu C/cm^2$ [25]. This manifests itself in the mutual repulsion between the mineral particles of the dispersion, which causes an increase in the peptization of the system [43]. With an increase in

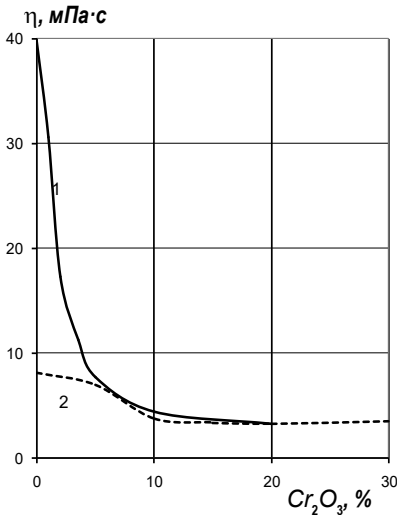


Fig. 3.11. The dependence of the plastic viscosity of 10% Na - MMT dispersion on the consumption of $Cr(NO_3)_3$ (1) and 6% Na - MMT dispersion of in the presence of BCS (2)

Cr_2O_3 consumption up to 10 % of the mineral mass, both for the dispersion of Na - MMT_{sc} and for Na - MMT_{pph} ,

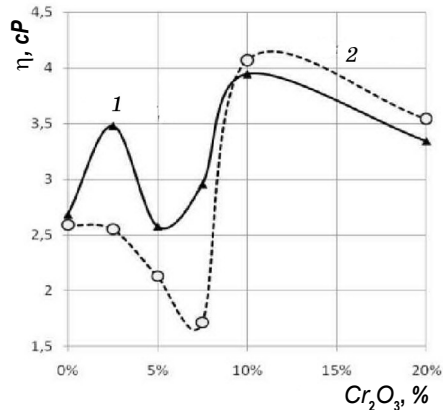


Fig. 3.12. Dependence of a kinematic viscosity on the consumption of the BCS (2) for dispersions:

- 1 – Na - MMT_{sc} ,
- 2 – Na - MMT_{pph}

there is a zone of the second extreme growth of the kinematic viscosity of modified dispersions. It should be noted that for Na -MMT_{sc} (**Fig. 3.13a**) and Na -MMT_{pph} (**Fig. 3.13b**) dispersions, due to their modification by chromium compounds, it is possible to obtain a stable pH level.

In general, the analysis of viscosity dependences on the consumption of the BCS indicates the maximum dispersions of montmorillonite at the consumption of chromium compounds of 5–7.5 % Cr_2O_3 of the mineral weight, which is the result of the peptization of mineral dispersions. In this case, the modified dispersions are characterized by a stable pH level in the range of 3–4 at the corresponding consumption of chromium compounds.

Modification of montmorillonite dispersions by chromium compounds not only changes the kinematic viscosity of dispersions, but also manifests itself in the nature of adsorption (**Fig. 3.14**). It can be seen from **Fig. 3.14** that in solutions with the concentration of Cr_2O_3 up to 10 g/dm³, there is a rapid increase in adsorption of HSCCs on the surface of montmorillonite. The nature of chromium compounds adsorption on the

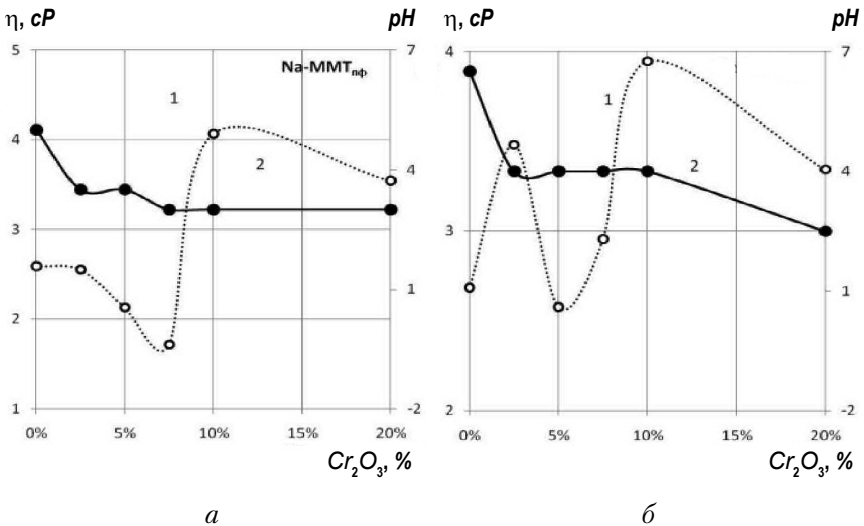


Fig. 3.13. Dependences of the kinematic viscosity (1) and pH (2) on the consumption of chromium compounds for processing montmorillonite dispersions, modified by sodium carbonate (a) and sodium polyphosphate

Na-MMT surface corresponds to the Langmuir curve. Consequently, adsorption of HSCC molecules on the surface of montmorillonite particles occurs due to the electrostatic interaction of chromium cations with the surface of the mineral, saturation of its surface, charge neutralization of the surface of montmorillonite, and subsequent polymolecular adsorption of chromium compounds by the Van der Waals forces. Further increase in the concentration of chromium compounds in the solution up to 20–40 g/dm³ results in a slight decrease in adsorption, which could lead to the “competition” of the same charges of hydroxochromium complexes on the surface of modified montmorillonite and its dispersions. The highest level of adsorption of hydroxochromium complexes is observed in solutions with Cr₂O₃ concentration of 10–20 g/dm³, which corresponds to 10–15 % of the material mass. The stability of montmorillonite dispersions modified by hydroxochromium complexes at different *pH* levels causes a high level of chemical interaction between active mineral centers and the BCS [44]. The obtained results indicate that Cr-MMT exhibits high stability in a wide *pH* range. There is an insignificant level of desorption at the *pH* 2.5 and 12. At the same time, at the high *pH*, it is likely that the chromium compounds are hydrolyzed, which

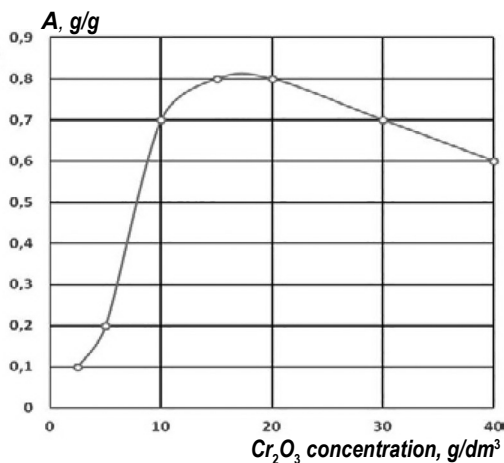


Fig. 3.14. Dependence of chromium compound adsorption on the Na-MMT surface on Cr₂O₃ concentration

is confirmed by changing the color of the dispersion.

Therefore, during experimental study of the colloidal and chemical properties of modified montmorillonite dispersions by the indicators of kinematic viscosity, the *pH* and adsorption modifier levels, it has been determined that obtaining the maximum diluted dispersions of montmorillonite is possible due to the consumption of chromium compounds (III) in the

range of 5–7.5 % Cr_2O_3 of the mineral weight. This is the result of the peptization of mineral dispersions. At the same time, modified dispersions are characterized by a stable pH level in the range of 3–4 at the corresponding consumption of chromium compounds. Because of modification of montmorillonite dispersions, a high level of adsorption of hydroxochromium complexes on the surface of mineral particles can be observed at the concentrations in the range of 10–15 % Cr_2O_3 .

The most important result of the simultaneous entry of different sized monomer and polymer hydroxochromium cations in the interplanar space of montmorillonite is its structure turbostraticity during the heat treatment and the weakening of the bonds between its adjacent silicate layers, as well as the preservation of the ability to coordinate organic ligands by interlayer complex chromium ions even after significant heat treatment [28, 30, 45]. This is confirmed by a sharp increase in the available surface of montmorillonite from 60 to 160–280 m^2/g [36, 37], as well as the fact that HSCC samples, heated to 300 °C and above, swell like Na^+ - and Ca^{2+}/Mg^{2+} -forms of montmorillonite in ethylene glycol (**Table 3.7**). In general, the process demonstrates the growth of chemical affinity and the possibility of subsequent modification of such montmorillonite by both anionic and non-ionic ligand-containing organic compounds, in particular, surfactants, dyes, etc.

Therefore, due to the modification of highly dispersed aluminosilicate, it is possible to purposefully regulate its dispersion and the sign of the particle surface charge in accordance with the requirements determined by the state of the leather semi-finished product, its structural

Table 3.7

**The value of the basal interplanar distance d_{001} , Å,
for various forms of montmorillonite**

Physical state of montmorillonite	Form of montmorillonite		
	Ca^{2+}/Mg^{2+}	Na^+	Cr^{3+}
air-dry	14.77	12.8	14.35
treated with ethylene glycol	17.03	17.10	17.25
heated to 300 °C and treated with ethylene glycol	17.10	17.10	16.96

and charge characteristics and the purpose of the technological process. For liquid treatment processes, it has been proposed to obtain aggregation-resistant anionic mineral dispersions by the influence of alkaline peptizers to increase the mineral particles dispersion and equalize its surface electrical charge of minerals.

The mechanism of alkaline peptizers action consists in the ion exchange of Ca^{2+} , Mg^{2+} into Na^+ -ions, which promotes the structure formation of dispersions, and the adsorption of carbonate anions and phosphates on positively charged edges of crystals and the dissociation of surface groups cause peptization of the dispersion. Sodium pyrophosphate is found to be the most potent dispersant, especially for minerals with imperfect crystalline structure. Cherkassy montmorillonite, whose particle size in modified suspensions is 53.8 nm, has a high dispersion. This ensures its application for the liquid finishing processes of the leather semi-finished product.

The influence of montmorillonite modification with $Cr(III)$ compounds on the structural and electrosphere properties of its dispersions has been investigated and the mechanism of hydroxochromazing of the mineral surface has been established. It has been proved that recharging of the montmorillonite surface is caused by hydroxocomplex chromium ions, which have high polarization and adsorption capacity. With the increase in the level of basicity of chromium compounds solutions, the adsorption of polynuclear complexes of chromium on montmorillonite by 2–5 times exceeds the capacity of the mineral cation exchange. The charge of 41.2–164.8 $\mu C/cm^2$, which arises as a result of the supra-equivalent adsorption of chromium polycations, has been revealed on the surface of montmorillonite particles by computation.

3.4. Chromium and montmorillonite semi-finished product tanning

Polyfunctional properties of the structuring agent and the filler are combined in montmorillonite modified with chromium complexes. They led to its application in the technology of leather elastic materials

production. The promise of such technology is also associated with a reduction in the consumption of toxic materials. According to the technology of montmorillonite tanning, the pickled semi-finished product from the grasser skin (the pelt) is obtained by the technology [46], being treated according to 4 Variants (**Table 3.8**). The pelt tanning is carried out with the main chromium sulphate (BCS) adding montmorillonite hydrophilized and modified with BCS at the LQ of 0.8. Before tanning, the pelt was treated with a solution, % of the mass of the pelt: sodium chloride – 6, formic acid – 0.2, duration 10 minutes. The reference variant was 4r with the consumption of 2 % chromium oxide (III). After tanning, two samples from each group were selected to determine hydrothermal stability. Technological solutions after tanning were analyzed for the residual concentration of chromium oxide (III) and the *pH* value.

After the tanned samples laying within 24 hours, they were neutralized with sodium bicarbonate and sodium formate of 0.8 and 0.5 % respectively. After that, the fatliquoring with the *Provel BA* preparation was performed in terms of a technical product of *Zschimmer & Schwarz* company (Germany) with its consumption of 6 % of the sammied mass of the semi-finished product. The *pH* of the fatliquor was corrected by acetic acid, which at the end of fatliquoring reached the value of 5.4.

Table 3.8

Variants of the pelt tanning

Variant	Cr_2O_3 , % of the pelt mass		MM, % of the pelt mass	pH after 12 hours of tanning	Increase in basicity			
	in BCS	in MM			Na_2CO_3 , %	pH in 40 minutes	Na_2CO_3 , %	pH in 2 hours
1	0.9	0.1	1	3.6	0.2	3.9	0.2	4.2
2	0.8	0.2	2	3.6	0.2	4.0	0.2	4.2
3	0.7	0.3	3	3.8	0.2	4.1	0.2	4.2
4r	2.0	0	0	2.8	0.3	3.8	0.3	4.2

The samples of experimental variants were slippery and plastic, and the samples of the reference variant were darker and rough on the front side.

The obtained samples after washing and sammying were dried in a free state at the temperatures of 20–23 °C. After tempering to 30–32 %, bating and staking, additional drying in a free state to the humidity of 14–16 %, the samples were ironed at the temperature of 70–80 °C. At the same time, the samples of experimental variants had a smooth and lighter front surface and were well staked. The control samples were more difficult to smoothen and flatten; they differed by more shrinkage from the experimental ones.

Stabilization and formation of the collagen structure of the dermis at the stage of tanning largely determines the chemical composition of the functional systems that were used [47]. At the same time, both the chemical composition and the physical and chemical properties of leather semi-finished products change considerably. This, in particular, is confirmed by the use of a mixture of montmorillonite, modified with hydroxosulphate chromium complexes, and the main chromium sulfate.

As the results of the study show [48] (**Table 3.9**), an increase in the content of modified BCS of montmorillonite in the leather semi-finished product is accompanied by an extreme dependence of chromium oxide (III) content in its structure. This points to the effective influence of

Table 3.9

The chemical composition of samples after chrome and montmorillonite tanning

Indicator	Variant			
	1	2	3	4r
The content in the skin of, % of moisture	13.7	12.7	12.4	12.9
chromium oxide*	2.1	2.5	2.4	4.3
mineral substances*	5.6	6.7	7.8	5.7
substances that are extracted with organic solvents (SEOS)*	6.6	6.5	6.3	6.8
protein substance	73.9	73.9	72.7	74.3
The content of Cr_2O_3 in the spent solution, g/dm ³	2.1	1.4	1.5	6.5

Note. Marked indicators * are calculated for a completely dry mass of the substance

MMT on the interaction of chromium complexes with active groups of collagen macromolecules. The effect can be explained by the structurally plasticizing action of hydrophilic aluminosilicate on the availability of ionized carboxyl groups of collagen prior to the interaction with HSCC, the content of which in the tanning system decreases. At the same time, the hydroxyl groups of montmorillonite, situated in the internal sphere of HSCC, displace more active ionized carboxyl groups of collagen. After reaching the Cr_2O_3 : MMT = 1:2 ratio, the efficiency of HSCC in the system is sharply reduced. At the same time, with an increase in the content of minerals in the structure of the semi-finished product, there is a decrease of the protein content in it. The advantage of the developed technology over the control one is a significant reduction in the content of chromium oxide (III) in the spent solutions.

It is efficient to use a co-modified HSCC of montmorillonite and BCS for structuring and stabilizing collagen of the dermis compared to a typical use of chromium compounds. Even with a two-fold decrease in the consumption of tanning substances in the first case, there are quite high values of the hydrothermal stability of the semi-finished product, which reach 94 °C in the tanning system of the second variant of the semi-finished product treatment (**Table 3.10**).

The study of the physical and mechanical properties of the semi-finished product obtained by the developed technologies indicates the achievement of extreme values by the indicators of the semi-finished product strength and the strength of its outer layer, which are higher by 16 and 31 % respectively compared with the reference variant. At the same time, the deformation characteristics of the studied samples have lower values and they grow increasing the content of modified montmorillonite. This is explained by less shrinkage due to the plasticizing effect of modified montmorillonite.

The depth of diffusion of modified montmorillonite microparticles in intermicrofibrillary gaps promotes effective splitting of collagen structure and its preservation after the removal of moisture. This is accompanied by an increase in the volume yield of the semi-finished product and the achievement of an extreme value of the area. The effect occurs due to the structural peculiarities of the dermis collagen associated with the inclination angle of fibers against the skin surface.

Table 3.10

**Physical and chemical properties of the leather material samples
of chromium and montmorillonite tanning**

Indicator	Variant			
	1	2	3	4r
Hydrothermal stability, °C	92.0	94.0	88.0	100.0
Ultimate tensile strength during stretching, MPa	24.0	29.0	27.0	25.0
Outer layer strength, MPa	16.0	21.0	19.0	16.0
Elongation under stress of 9.8 MPa, %	18.0	24.0	26.0	29.0
Relative elongation at rupture, %	44.0	52.0	54.0	58.0
Relative final elongation, %	11.5	12.0	11.0	14.0
Relative elastic elongation, %	32.5	41.0	43.0	44.0
Relative specific mass, g/cm ³	0.638	0.627	0.610	0.685
Volume yield, cm ³ /100 g PS	215.0	218.0	226.0	194.0
Area yield, %	102.0	105.2	103.1	100.0

Therefore, the combined use of montmorillonite, modified with monohydroxosulfate and chromic complexes, and hydroxosulfatochromium complexes contributed to the obtaining a chromium semi-finished product with a reduced by 1.7–2.0 times content of chromium oxide (III) as a two-fold reduction in the consumption of the chromium tanning agent. The use of montmorillonite modified with chromium hydroxosulfate complexes makes it possible to effectively influence the interaction of chromium compounds with functional groups of collagen due to its reactive plasticization action. By a complex of basic physical and mechanical characteristics, the obtained leather semi-finished product prevails over the control samples. The developed technology can be considered to be more environmentally friendly due to a 3.2–4.6 times reduction of chromium oxide (III) in the spent solutions.

3.5. Retanning and filling of the semi-finished product using the dispersion of montmorillonite

The process of modifying collagen of the dermis with aluminosilicate materials was studied by determining the structural features and physical and chemical properties of the chromesemi-finished product. At the same time, a comparative analysis of the obtained variants for the treatment of semi-finished products with the control technology was done [46]. Due to the application of the aluminosilicate mineral dispersion (**Table 3.11**), the filling of the leather semi-finished product [49] resulted in an increase in the output of the thickness, area, volume yield and reduction of the apparent specific mass of skins (**Table 3.12**).

The research was carried out on the samples of the chromesemi-finished product from sheepskin as the most labile structure. In each group, there were 8 samples of 50×120 mm size and of 1.1–1.2 mm thickness. Modification of aluminosilicate was performed by treating its aqueous dispersions at the concentration of 100 g/dm³ with sodium polyphosphate with the consumption of 12 % of a dry mineral weight.

The filling of the semi-finished product was combined with the retannage with the synthetic tanning agent BNS and the acrylic tergotan PMB filler of *Clariant* company (Austria). Further processing for the experimental groups was carried out using unmodified and modified dispersions of minerals, followed by the fixing treatment with alumina potassium alum and sodium formate with the consumption of

Table 3.11

Treatment variants during filling the semi-finished product

Variant of treatment	1	2	3r
Aluminosilicate dispersion, % of the semi-product mass	MMT		Tanicor AFP
natural	2.5	—	2.5*
Na ⁺ -form	—	2.5	

Note. In the treatment variants, the BTS syntane was used, in terms of tanning substances and Tergotan PMB acrylic filler, used — on a dry substance in the amount of 2.0 and 1.5 %; * — a mineral filler

1.5 and 0.3 %, respectively, of the weight of the shaven semi-finished product. The control group was treated using tanicor AFP mineral filler of *Clariant*. After conducting experimental and control treatments, all

Table 3.12

Indicators of the dermis formation

Indicator	Variant of treatment with MMT dispersion		
	natural	Na-form	Tanicor AFP
Leather yield, % of the semi-finished product, in terms of:			
– thickness	107	110	105.1
– area	103	105.6	101.8
Virtual specific mass, g/cm ³	0.533	0.47	0.485
Volume yield, cm ³ /100 g of protein	306	341	324
Moisture, %	12.9	12.1	12.1
Mass fraction, % on a dry substance:			
– protein	70.4	71.0	72.4
– mineral	8.5	7.5	7.4
– SEOS	5.2	5.1	4.9
Ultimate tensile strength under tension, MPa	19.0	21.0	18.1
Elongation, %:			
– at 10 MPa	26.4	30.6	27.0
– at break	43.2	44.4	40.6
– final	6.0	6.0	5.9
Temperature of welding, °C	119		
Deformation ¹ , %:			
– total	20.9	24.7	21.0
– instant elastic	79.4	75.3	79.5
– elastic aftereffect	14.8	12.0	14.3
– final	5.8	12.7	6.2

Note. ¹ – compression deformation under stress of 1 kg/cm²

the samples were fatliquored, sammied, dried at room temperature in a free state, tempered, allowed to lay for 12 hours, conditioned and used for further research.

For the development of the technology of retanning and filling of leather materials, a planed semi-finished product of the chrome tanning method of 1.5–1.6 mm thick, obtained from raw cattle hides, lightweight steerhides, using the current technique of the leather CJSC *Chinbar*. To analyze the forming ability of highly dispersed mineral fillers (for control), a control sample of chrome semi-finished product without a mineral filler was used. The second sample belonged to the semi-finished product obtained by filling with the dispersion of montmorillonite [50].

Electron microscopic studies of the facial surface and cross cut of the hides (**Fig. 3.15, 3.16**) made it possible to establish and analyze the peculiarities of the formation of the volume of the dermis with highly dispersed minerals [13, 50, 51]. The face of the control sample (**Fig. 3.15a**) is characterized by an increased density of the structural elements. At the same time, there is a partial violation of the upper layer homogeneity, which leads to a decrease in the quality of the finished leather grain.

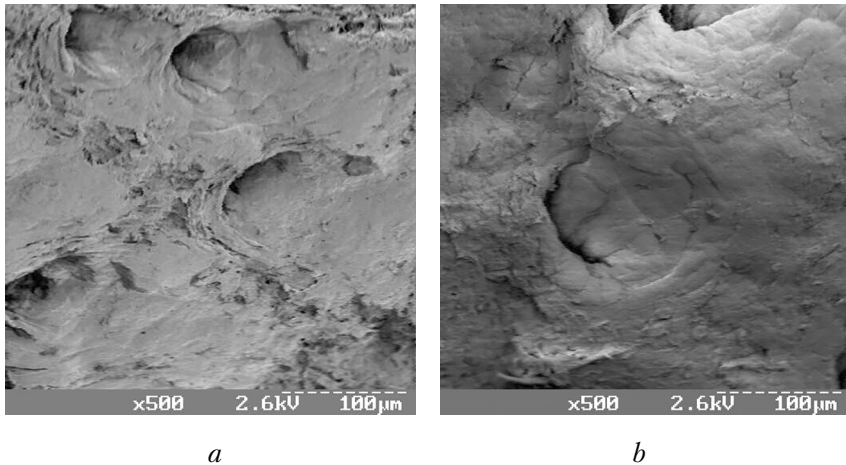


Fig. 3.15. Submicroscopic images of the face surface of the hide samples: filled without the use of a mineral filler (*a*), using the dispersion of montmorillonite (*b*)

As a result of the use of montmorillonite dispersion for filling (**Fig. 3.15b**), the face surface of the samples is significantly different and is characterized by the voluminosity and uniformity of the filler location. Organoleptically, the facial surface of these samples is pleasant to touch and has a good surface characteristic. The structural state changes of the facial surface is due to the diffusion of particles of montmorillonite dispersion and their sorption in the outer layers of the dermis, which compacts the papillary layer and increases the quality of the finished hide.

Submicroscopic images of the internal structure state of the dermis of the leather semi-finished product (**Fig. 3.16**) show that, in the absence of mineral filler, the degree of its formaton is not sufficient. In this case, collagen fibers are tightly packed (**Fig. 3.16a**) in bundles, and interstructural spaces are quite big. Probably, retanning the semi-finished with chrome and vegetable tanners is dominated by the fixation of the microstructure of the dermis, and the removal of moisture from the semi-finished product causes additional bonding of the fixed elements of the collagen structure.

The nature of the structural changes using the dispersion of montmorillonite for filling (**Fig. 3.16b**) differs significantly from the previous samples. It should be noted a good separation of collagen bundles into

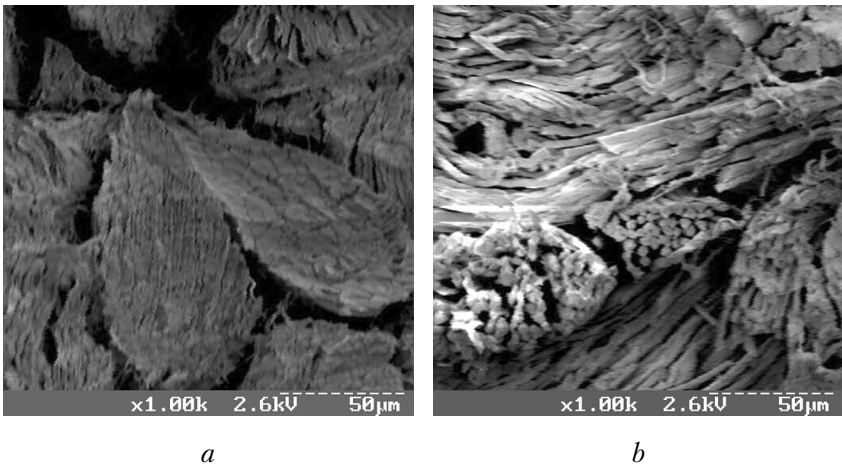


Fig. 3.16. Submicroscopic images of the transverse section of the hide samples: filled without the use of a mineral filler (*a*), using the dispersion of montmorillonite (*b*)

separate fibers and the uniform dispersion of the structure of the dermis. Analyzing the results of electron microscopic studies, it has been found that there is a shielding effect of the structural elements of the dermis with the montmorillonite particles and the preservation of the dermis microstructure in a mobile state. In addition, collagen fibers preserve elasticity and mobility to one another.

The most positive effect on structural changes in the dermis is observed as a result of the application of montmorillonite dispersion for the aluminosilicate filling of the semi-finished product [51, 52]. This may be caused by a more uniform diffusion of the filler in the dermis volume and the sorption of its particles on the surface of elemental collagen fibers. It has been confirmed by the results of the energy-dispersion analysis and the elemental composition of the leather semi-finished product filled with the dispersion of montmorillonite. The presence of a mineral filler and its distribution in the structure of the dermis is expressed by the percentage content of chemical elements (**Table 3.13**).

As it can be seen from **Table 3.13**, the chemical elements in the volume of the dermis are distributed unevenly. At the same time, the outer layers are enriched with *Al*, *Si*, *P*, elements, with the exception of sulfur. The *Al* content is almost twice more than the *Si* content due to the peculiarities of the samples processing after the fixing treatment with aluminum potassium alums. The reduced sulfur content in the outer layers is caused by the displacement and transition into a solution of sulfogroups of chromium complexes as a result of interaction with the active centers of montmorillonite, mainly from the outer layers of the chromesemi-finished product.

Table 3.13

Elemental composition of the semi-finished product filled with the dispersion of montmorillonite

Layer of the hide	Chemical element, %							Total
	Al	Si	P	S	Cl	Ca	Cr	
Facial	0.397	0.215	0.037	0.037	0	0.016	1.451	2.153
Middle	0.172	0.093	0.012	0.172	0	0.008	1.221	1.678
Flesh	0.391	0.204	0.075	0.074	0	0.018	1.274	2.036

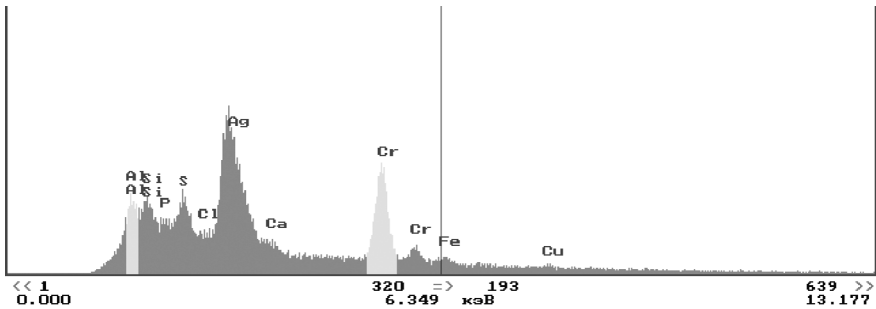


Fig. 3.17. Energy dispersive spectrogram of the semi-finished product filled with montmorillonite dispersion

Graphic representation of the elemental composition of the semi-finished product filled with montmorillonite is shown in **Fig. 3.17**. It should be noted that the presence of a significant amount of silver on the spectrogram is caused by the features of the preparation of semi-finished samples for the energy-dispersion study.

Consequently, as a result of electron microscopy studies, it has been determined that the semi-finished product is characterized by the effective separation of the structure of the dermis at the level of elementary fibers and fibrils when using montmorillonite dispersions modified with sodium polyphosphate. The high efficiency of modified montmorillonite as a filler of the skin is caused by the preservation of the degree of separation of structural elements achieved in the preparatory physical and chemical processes due to the active fixation of highly dispersed particles of aluminosilicate and their shielding of structural elements of the dermis collagen.

The development of mineral filling technology combined with the processes of retanning and filling with organic compounds in the production of elastic shoe upper leather involves optimizing the consumption of modified dispersion of montmorillonite [53]. The study was carried out in 6 groups of the samples obtained by the current technology of chromeshoe upper leather production at the leather enterprise CJSC *Chinbar* from the butt part of a lightweight cow hide. Each group contained 5 samples of 150×150 mm thickness of the semi-finished product after shaving to

a thickness of 1.5–1.6 mm. Treatment of the samples after washing and retanning with chromium compounds, neutralization and washing was performed according to the given parameters (**Table 3.14**). The variant of filling the semi-finished product without using the montmorillonite dispersion was considered as a control one (6k). After filling and drying, the samples of the semi-finished product were tempered, broken manually by stretching, and dried at the temperature of 40 °C. After 24 hours of laying, the samples were covered with a coat paint using the standard method of finishing in the production of the chromeupper shoe leather.

The obtained results, shown in **Tables 3.15** and **3.16**, indicate an increase in the area, thickness and volume yield at the consumption of

Table 3.14

Parameters of filling and retanning of the semi-finished product

Process / chemical material	Consumption, % of the semi-product weight	Duration of treatment, min.	Temperature, °C	Note
Filling and retanning: water, acrylic polymer, fatliquoring compounds, synthetic tanning agent, vegetable tanning agent, MMD	100.0 6.0 2.0 10.0 4.0 0–8*	 40 20 60 30 40	 30	Two-stage dosing with the period of, min. 20 30
Fixing treatment: sodium formate alumina potassium alums	0.4 2.5	30	30	<i>pH</i> of the spent solution 4.4
Washing: water	150.0	15	55	
Fatliquoring: water fatliquoring compounds ammonia	100.0 6.0 0.3	60	55	<i>pH</i> of fatli- quor emulsion 7.8–8.0
Fixing treatment: formic acid	1.0	10	40	<i>pH</i> of the spent solution 3.8–4.0
Washing: water	150.0	10	25	

Note. * Consumption of MMD: 1, 2, 4, 6, 8, 0 % by the treatment variants 1–6.

Table 3.15

Indicators of the structure formation of leather semi-finished products

Indicator	Consumption of MMD, %					
	1	2	3	4	5	6k
Yield of the semi-finished product, % of the reference variant: – n terms of thickness – in terms of area	102.3 102.8	103.6 104.8	104.5 105.7	103.7 104.9	103.1 104.7	100.0 100.0
Volume yield, cm ³ /100 g of protein	265.0	274.0	276.0	275.0	277.0	250.0
Virtual specific gravity, g/cm ³	0.570	0.572	0.573	0.575	0.579	0.568
Temperature of welding, °C	109	111	111	110	110	109

Table 3.16

Elemental composition and physico-mechanical characteristics of the leather material

Indicator	Consumption of MMD, %					
	1	2	3	4	5	6k
Content of, % on absolutely dry substance: – moisture – the pelt substance – mineral substances – chromium oxide – SEOS	12.9 74.9 4.8 8.7 6.8	13.0 73.4 4.7 9.3 6.8	12.7 72.7 4.6 10.1 6.7	12.8 72.3 4.3 11.3 6.8	12.8 71.5 4.2 11.8 6.8	12.9 76.8 4.8 7.7 6.6
Stiffness on PZHU-12M, N	0.23	0.218	0.215	0.226	0.246	0.28
Ultimate tensile strength under tension, MPa	14.1	14.0	13.8	13.6	12.4	12.8
Elongation, %: – under stress of 9,8 MPa – while tearing	22.0 34.6	21.7 33.0	20.3 32.4	20.1 31.7	20.6 30.3	21.0 30.0
Total deformation, %	44.6	43.4	42.4	41.7	40.3	40.0

montmorillonite dispersion by 2–4 % of the weight of the shaven semi-finished product in terms of a dry mineral residue [54]. Within the use of a mineral filler, its effect on reducing the stiffness index is clearly shown, which indicates an increase in the softness of the finished leather. At the same time, the strength of the leather semi-finished product slightly increases, which may be caused by the orderliness of the collagen structure due to the shielding of its elements by mineral particles. Consequently, the fixed particles of modified montmorillonite supplement the shielding of the structural elements of the semi-finished product, which is caused by fatliquoring compounds. An additional factor in the positive effect of fixed particles of the mineral on the structure formation of the semi-finished product is the prevention of adhesion of structural elements during drying of the skin by blocking the polar groups of a fixed acrylic filler.

Although a further increase in the consumption of a mineral filler leads to some growth in the number of minerals fixed in the structure of the skin, it is not accompanied by an increase in volume yield and output of the leather semi-finished product area. At the consumption of montmorillonite over 4 % of its mass, the yield of volume and area does not increase. In general, increased output of the area and thickness of the leather material at 2–4 % consumption of montmorillonite indicates a qualitative formation of the structure of the dermis collagen. As a result of the conducted studies, an elastic leather with an increased by 4.8–5.7 % thickness was obtained compared to the treatment variant that does not involve the use of montmorillonite for filling.

The introduction of MMD during retanning and filling of the leather semi-finished product greatly affects the indicators of the structure formation, operational and hygienic properties of the finished leather. It also allows you to adjust and optimize the consumption of acrylic polymers, vegetable and synthetic tanning materials as components of a combined treatment. The goal of such optimization is to develop new methods for improving and unifying the technology of natural leather production and providing it with the necessary functional properties, along with the reduction of consumption or exclusion of expensive materials and the solution to environmental issues of leather production.

In the process of developing the technology of retanning and filling of leather semi-finished products, the influence of other materials on

the quality of the finished leather has been established. To optimize the composition of retanning and filling materials, 10 groups of chrome semi-finished product samples from a lightweight steerhide were assembled by the asymmetric fringe method.

The treatment of chrome semi-finished products was carried out according to the method of coloring and fatliquoring processes of upper shoe leather production [46] from the raw cattle hides of CJSC *Chinbar* leather enterprise. Filling involved the treatment with acrylic polymers tergotan PMB, synthetic tergotan RS and sandotan VX of *Clariant* company (Austria), quebracho and MMD of vegetable tanning agents. After the process of filling and retanning of experimental batches, the fixing treatment of the semi-finished product with alumina potassium alums and sodium formate was performed. To do this, 1.5 % of alumina potassium alums and 0.3 % of sodium formate of the shaven semi-finished product mass were put into the spent liquor. Tanicor AFP mineral filler of *Clariant* company was used in the reference variant 10k. The emulsion fatliquoring was made with a fatliquoring emulsion obtained by emulsifying the provol VA material of the company *Zschimmer & Schwarz GMBH & Co* (Germany) with 8 % consumption of the shaven semi-finished product mass.

After the experimental batches treatment with the optimization of the composition of the materials for filling the chrome semi-finished product, the samples were dried in a free state, tempered to 26 %, three times treated at the staking machine, dried in a free state. Then, after conditioning and necessary measurements, the formation of the structure, physical and mechanical, chemical and hygienic properties of the leather semi-finished product were determined. Variants of treatments, covering various consumption of retanning and filling materials, as well as indicators of properties of the obtained leather are presented in **Table 3.17**.

The data analysis shows a significant contribution of each composition reagent to retanning and filling, which manifests itself in certain indicators of the leather semi-finished product. In particular, analyzing the formation of the dermis structure, there is a clear tendency to increase the yield of the area and thickness of the semi-finished product, increasing the volume yield when applying tannins and mineral filler

Table 3.17

Consumption of reagents and properties of leather materials

Reagent	Composition variant									
	1	2	3	4	5	6	7	8	9	10R
Acrylic polymer	6.0	8.0	6.0	2.0	—	—	3.0	6.0	—	6.0
Synthetic tanning agent	—	6.0	—	10.0	—	10.0	10.0	6.0	8.0	12.0
Tannins	7.0	—	—	—	7.0	—	7.0	4.0	3.5	6.0
MMD	—	—	3.0	5.0	4.0	5.0	4.0	3.0	5.0	3.5 ¹
Indicators of the leather structure formation										
Yield of the semi-finished product, %:										
– in terms of area	93.6	91.5	92.4	93.5	97.4	94.0	95.5	98.1	98.6	94.7
– in terms of thickness	109.7	107.4	105.8	106.8	106.4	102.8	106.4	111.2	105.7	104.9
Volume yield, cm ³ /100 g of protein	250.3	243.1	245.1	244.6	275.2	241.7	246.3	286.1	276.4	246.7
Virtual specific gravity, g/cm ³	0.647	0.649	0.643	0.644	0.610	0.641	0.620	0.602	0.612	0.645
Physical and mechanical properties										
Ultimate tensile strength under tension, 10 MPa	1.63	1.59	1.72	1.83	1.71	1.77	1.74	1.91	1.82	1.80
Elongation, %:										
– at 10 MPa	29.1	32.6	32.5	33.3	28.9	27.4	27.9	27.5	27.0	30.5
– at break	46.0	46.7	49.0	48.6	46.2	48.5	45.8	43.5	44.1	45.4
Hygienic properties										
Air permeability, cm ³ /(cm ² ·hour)	775	645	782	843	973	947	986	1008	974	754
Vapour permeability, mg/cm ² per hour	183	1.74	2.11	2.34	2.82	2.45	2.34	2.39	2.44	2.28
Water tolerance, %	9.7	8.9	9.2	10.0	10.9	10.6	10.2	10.4	9.9	14.4
Chemical composition										
Moisture content, %	15.9	15.5	15.3	14.6	14.9	14.5	14.9	15.0	14.9	14.4
Content of Cr ₂ O ₃ , % ²	4.1	4.1	4.0	4.5	4.1	4.0	4.2	4.2	4.0	4.1
Pelt substance, % ²	72.8	75.5	73.8	74.3	69.0	75.0	70.5	68.9	68.9	73.5
SEOS, % ²	6.6	6.8	6.7	6.8	7.2	6.9	7.0	6.8	7.2	6.9

Note. ¹ – mineral filler Tanicor AFP, ² – in terms of dry protein

MDM (Variants 5–8), especially at its consumption within 3–4 % of the semi-finished product mass. The maximum values of the output of leather area and thickness are characteristic of Variant 8, and the treatment of its samples involves the use of the entire complex of retanning and filling materials. At the same time, their consumption has been lowered compared to the reference variant of the treatment according to the existing technological scheme.

At the same time, every material in the composition played an important role in retanning and filling, as evidenced by some indicators of leather semi-finished products. Removal of acrylic filler from the composition or reducing its consumption (Variants 5–7) in the presence of MMD causes an increase in the output of leather area and volume yield. By Variant 2, which involves an increase in the consumption of acrylic filler without the use of a mineral component, a leather semi-finished product with the lowest yield of area and volume has been received.

The treatment of the samples from Variants 3 and 4 involved the combined filling of semi-finished products with acrylic and mineral compounds, and these variants show a higher efficiency of forming the structure of the semi-finished product. The use of a complex filler of a highly dispersed mineral in the composition significantly changes the mechanism of filling with acrylic polymers. The adsorption centers of the dispersion particles of montmorillonite with a high sorption surface prevents the premature aggregation of the primary particles of the acrylic dispersion and thus contribute to the diffusion and uniform distribution of the fillers in the structure of the dermis. At the same time, the penetration of nanoparticles into inter microfibrillary gaps reduces the ability of the collagen structure to agglutinate when the semi-finished product is being dried. This ensures increased softness and plasticity of the finished leather and increases its output in terms of area. Such filling mechanism explains the growth of hygienic and physico-mechanical properties of the finished leather (**Table 3.18**).

A positive role of synthetic tanning materials (Variants 4–8) is more manifested in terms of physical and mechanical properties: the tensile strengths during stretching are slightly higher for the samples treated with synthetic tanning agents. The introduction of a mineral filler into the retanning and filling composition greatly improves

Table 3.18

Physical and chemical properties of leather materials

№	Indicator	Technology	
		developed	existing
1	Thickness, mm	1.62	1.58
2	Ultimate tensile strength under tension, 10 MPa	2.21	2.04
3	Elongation, %: – under stress of 10 MPa – with occurrence of cracks in the grain – of breaks	39.20 52.60 60.70	36.20 49.40 57.50
4	Stiffness on PZHU-12M, N	0.228	0.254
5	Content of, % on absolutely dry substance: – mineral substances – chrome oxide – aluminium oxide – SEOS – pelt substance – water elutriating substances – non-organic water elutriating substances	8.02 4.80 0.50 7.81 65.40 0.19 0.12	7.41 4.65 – 6.53 67.10 0.34 0.21
6	Temperature of welding, °C	109	108
7	Vapour permeability, % – mg/cm ² per hour	24.5 1.78	22.4 1.56
8	Water vapour absorption per hour, %	0.56	0.48
9	Hygroscopic property, %	14.4	13.9
10	Water yielding capacity, %	12.4	11.6
11	Resistance of a protective film to: – multiple bending, points – wet friction, rotations	4 535	4 506
12	Adhesion of a protective film, N/m, in the state: – dry – wet	345 217	310 189
13	Consumption of raw materials, % of standardized value	89.6	94.7

the hygienic properties of the finished leather, their air permeability, vapour permeability and water yielding capacity. The basis of such changes is the peculiarities of the influence of modified dispersions of montmorillonite on the formation of the dermis structure and the interaction on the various levels of its organization. The polydisperse nature and anisometric form of mineral particles in dispersions can shield the surface of structural elements, reduce the ability to agglutinate during drying and increase their mobility during kneading and stretching, which is especially important in the production of elastic leather. This effect partially eliminates the effect of acrylic fillers, which largely align the structural heterogeneity of the semi-finished product on its hide sections, but reduce the softness and elasticity of the leather semi-finished product.

Retanning and filling by the standard technology (Variant 10R), compared with the experimental treatment of leather semi-finished products, leads to a partial reduction in porosity and air permeability of leather semi-finished products. This can be attributed to the “overload” of the collagen structure of the dermis with retanning and filling materials with the existing treatment, the use of which in large numbers is necessary to achieve high service characteristics of finished leather. The presence of MMD during the treatment of leather semi-finished products by organizing the structure of the dermis makes it possible to qualitatively shape the structure of the leather and adjust its functional properties, giving ready-made leather increased physico-mechanical and hygienic properties, indicators of the formation of the dermis volume, etc. In addition, the indicators of chemical analysis are not significantly different with the change in the consumption of chemical materials.

According to the analysis of performed studies on the optimization of the composition of the retanning and filling materials for the treatment of leather semi-finished products, the eighth variant is the best, which involves the use of 6 % acrylic polymer, synthetic and vegetable tanning agent, 6 and 4 % respectively, and the consumption of the mineral filler coincide with the results of previous studies and make up 3 %. The technology of retanning and filling of leather semi-finished products using modified dispersions of montmorillonite is based on the obtaining of the optimal consumption of materials. It involves their introduction at

the stage of processing with tannin, synthetic and acrylic compounds, it was tested in the conditions of the leather enterprise of CJSC *Chinbar*.

For liquid finishing processes, including filling the leather semi-finished product with a modified dispersion of montmorillonite; two batches of chrome semi-finished products made of a lightweight steerhide, with a thickness of 1.5–1.6 mm after shaving, were assembled. Each of them contained 50 raw hides. The treatment of the semi-finished product, before tanning, was carried out on whole hides using the current technology, and the technologies were combined before the neutralization process. Further processes of retanning and filling, dyeing and fatliquoring were carried out separately for the experimental and control lots according to the technological scheme, close to the scheme of production of upper shoe elastic leather from the raw cattle hides, functioning at CJSC *Chinbar*.

To fill the experimental lot, a modified dispersion of montmorillonite was used which was obtained by adding 10 % of sodium polyphosphate mineral mass to a water dispersion of montmorillonite at the concentration of 100 g/dm³ after it was pre-soaked for two hours at the temperature of 50 °C. For maximum dispersion of the mineral, stirring was performed on a mechanical stirrer at 1500 min.⁻¹ for 30–40 minutes. Then, the modified dispersion of montmorillonite was added to the suspended drum through a hollow axis. The schemes of further treatments of the experimental lot and indicators of finished leather are presented in **Fig. 3.18** and in **Table 3.18**, respectively. Subsequent dry-tempering and finishing processes of the semi-finished product were performed identically for the experimental and control lots according to the existing technological scheme [46].

Experimental skins, obtained by the current technology, have slightly higher indicators of physical and mechanical tests and hygienic properties (**Table 3.18**). These skins have a greater thickness due to more efficient filling, higher indicators of ultimate tensile strength and elongation with the occurrence of cracks and breaks. The experimental skins have almost 10.2 % lower stiffness index, which provides a higher elasticity and softness of the finished leather by the developed technology.

The resulting effects are probably due to the peculiarities of the influence of mineral filling on the structure formation of the dermis,

which also affects the parameters of hygienic properties. The interaction of mineral particles with structural elements of the dermis organizes its structure and forms the volume. The presence of mineral polydisperse particles with their structure and high specific surface positively affects air permeability, water vapour absorption, hygroscopicity and water yielding capacity of finished leather. According to an organoleptic assessment, experimental skins are characterized by good filling, volumetric surface characteristic and distinct grainy texture of the face.

Experimental skins hardly differ in the chemical composition except for 7.6 % slightly larger mineral content and hydrothermal resistance. They also have 10.3–12.9 % higher adhesion of coating to the skin in both wet and dry state. Probably, due to the appearance of additional adsorption centers on the face layer and improving the fixation of the coating to the skin. The level of resistance of the coating film to wet friction of the experimental skins increased by 5.4 % confirms this thesis. The quality grade of experimental skins by 0.3 % exceeds the quality grade of the skins of the existing finishing, obtained by the available technology.

Thus, the developed technology of mineral filling of leather semi-finished products reduces the cost of synthetic tanning agents and tannins

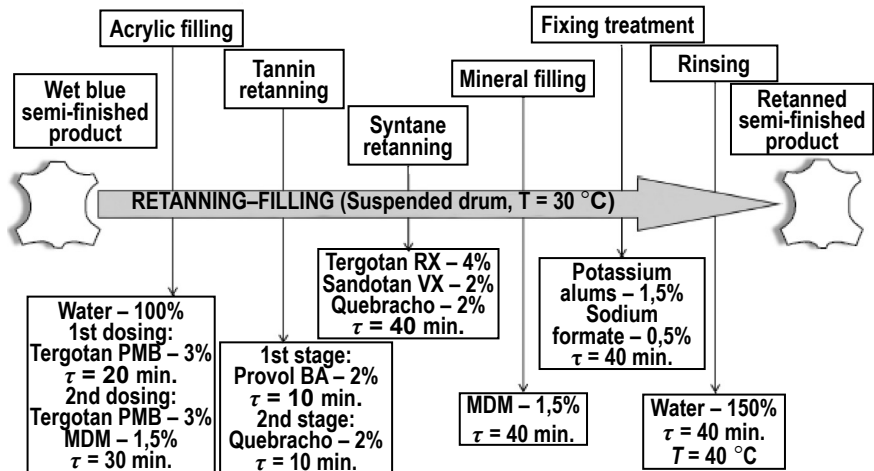
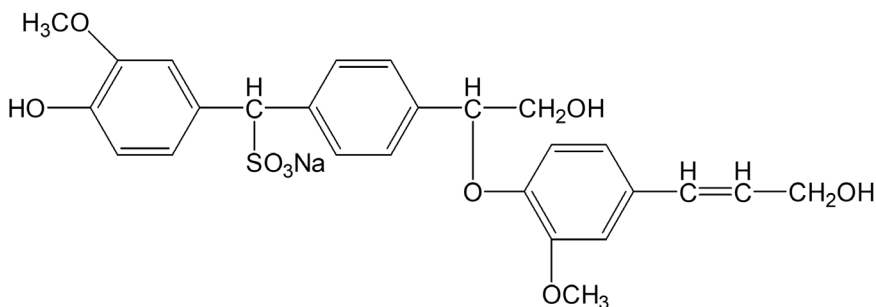


Fig. 3.18. Flow chart of retanning and filling of the leather semi-finished product using MMD

by 2 and 1.5 times, respectively, and provides a complete replacement of the imported mineral filler tanicor AFP at a complex retanning and filling, a qualitative formation of the dermis structure and the obtaining of skins characterized by filling, softness, elasticity, high-quality surface characteristics and high hygienic and operational properties and meet the requirements of the standard DSTU2726-94 “Upper shoe leather”. It makes it possible to reduce the consumption of retanning and filling materials by 8.5 % of the shaven semi-finished product weight and increase the efficiency of using leather raw materials by 5.1 %.

3.6. Modification of chromium hydroxocomplex montmorillonite with lignosulfonates

A complex of adsorption studies on the interaction of CHCM with anionic surfactants [55], in particular, lignosulfonates (LSN) MM 5000–100000, the choice of which is due to their widespread use in the leather industry, TU2455-002-00281039-00, was conducted during the development of the technology of retanning and filling of leather semi-finished products:



Due to the presence of a large amount of hydrophobic condensed benzene rings, sulpho- and other polar hydrophilic groups in the composition of LSN macromolecules, their colloid and chemical properties depend heavily on the *pH*-medium. As shown by the adsorption studies, presented in **Fig. 3.19**, the adsorption of LSN on CHCM is characterized by

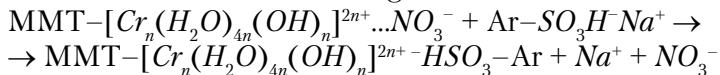


Fig. 3.19. Adsorption isotherms of SLS on CHCM with different pH of the medium: 2.0 (1), 5.5 (2) i 9.0 (3)

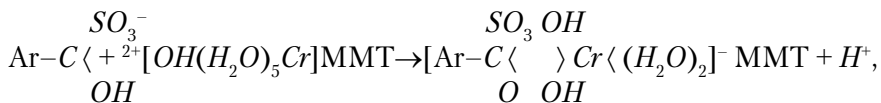
a higher level at a low pH -medium. Probably, this is due to the fact that at the $pH < 4,5$ the dissociation of sulfogroups of LSN molecules is almost absent, therefore the densest packing of non-ionized molecules occurs in the adsorption layer. As the pH rises, the adsorption of LSN decreases because of an increase in the negative charge of both LSN molecules, due to the ionization of sulfogroups, and the surface of the CHCM by recharging. At the pH 6, there is also a possible decomposition of hydroxochromium polycations and their transformation into $Cr(OH)_3$,

so the surface of montmorillonite acquires a constant negative charge. This further leads to a decrease in the adsorption of LSN.

Given the nature of functional groups and the state of lignosulfonates in the solution, such a mechanism of their interaction with a positively charged surface of the CHCM can be foreseen. As the molecules of LSN are well dissociated in the solution, the interaction between them and the surface of the modified MMT occurs predominantly by the mechanism of the anion exchange:



The result of this interaction is a partial neutralization of the positive charge of CHCM and, as a consequence, the destabilization of the disperse system. However, due to the action of additional specific Van der Waals forces during adsorption, it always occurs supraequivalently to the exchange capacity of a mineral. This causes recharging of the surface and stabilization of the dispersion with the opposite charge sign. The additional sorption of LSN is likely to have been caused the mechanism of ligand exchange:



where Ar is an aryl radical of LSN molecules.

The formation of chelate complexes of 1:1 type, in which, in the interaction with metal ions, only one sulfo group is involved [56, 57], may be the cause as well. As the LSN molecule, by joining the coordinate-unsaturated Cr^{3+} ion on the surface, displaces water molecules from the first coordination sphere of the chromium-ion, a reaction of exchange of ligands may occur. Such a mechanism of their interaction is confirmed by a decrease in the pH of the system after the contact of the LSN solution with CHCM. Thus, the adsorption of LSN on CHCM occurs simultaneously with the described reactions.

The results of the study of the electro-surface properties of LSN dispersions on the modified MMT (**Fig. 3.20**) show a similar flow of dependencies of specific conductivity and ζ -potential starting from the concentration of 2.5 g/dm³. In this case, the adsorption of LSN on the polar surface of the CHCM gradually increases. A sharp decrease in $-\zeta$ -potential of the dispersion indicates a surface recharge of the modified MMT particles, and the conductivity is linearly increasing.

Of course, the negative charge and strong hydration of functional LSN groups create a high barrier in the way of convergence and interaction with the polar surface of the adsorbent. A sharp increase in the adsorption of LSNs on the modified MMT corresponds to

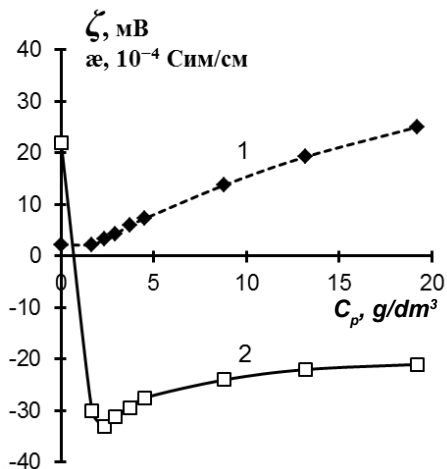


Fig. 3.20. Dependences of specific conductivity (1) and ζ -potential (2) of dispersions at the pH of 5.5 on the LSN concentration with the adsorption on BCS-MMT

a noticeable increase in the conductivity κ (denomination of electrical conductivity in **Fig. 3.20**) of the dispersion. This is explained by compression of the double electric layer on the surface of mineral particles and the decrease of the degree of hydration against the growth of the ionic strength of the solution. These two factors together contribute to the adsorption.

Considering the change in ζ -potential (**Fig. 3.20**), the initial ion exchange adsorption of LSN anions is accompanied by recharging of the surface of CHCM particles from positive to negative. By doing so, the level of ζ -potential of the mineral particle of dispersions after adsorption of LSN is $-20.0... - 25.0$ mV, which satisfies the conditions for effective diffusion and distribution of anionic reagents in the structure of the chrome semi-finished product. Increasing the concentration of LSN, adsorption of anions occurs on the same charged surface of mineral particles. The obtained maximum LSN adsorption values of 200–250 mg/g indicate participation of both outer and inner surfaces of CHCM in the adsorption. Taking into account [58] that the average area occupied by one mg of adsorbed humic and sulphonic acids of a similar structure is 1.5 m^2 , according to the maximum absorption of LSN, by adsorption of isotherms, a specific surface area is $190 \text{ m}^2/\text{g}$ (**Table 3.13**). Consequently, LSN penetrates into the interlayer space of MMT, which leads to structural changes in the mineral. This conclusion is confirmed by the radiographic analysis (**Fig. 3.21**).

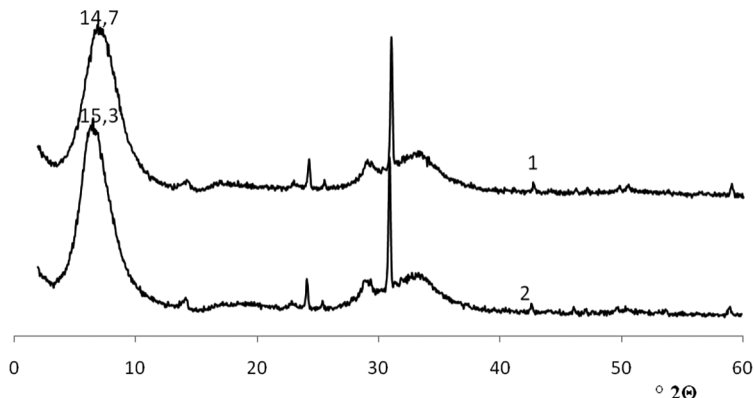


Fig. 3.21. Diffraction pattern of the initial CHCM (1) and the product of its interaction with 5% solution of LSN (2)

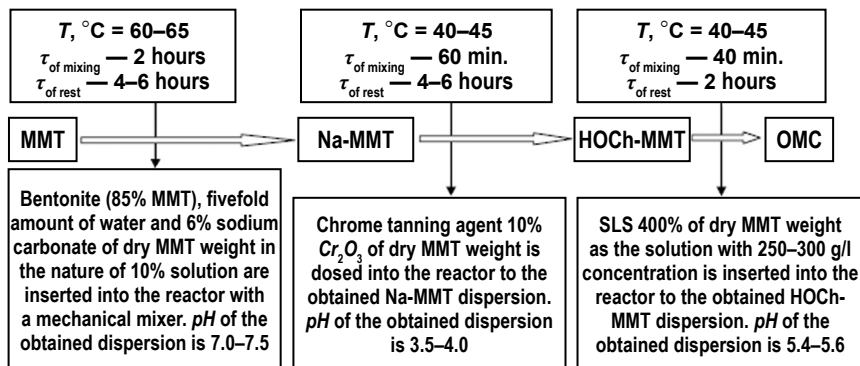


Fig. 3.22. Gradual montmorillonite medication and obtaining OMCs

The LSN adsorption is accompanied by the expansion of the MMT crystal lattice along the axis c , with the basal interlayer distance d_{001} varying within 14.7–15.3 Å. Therefore, the adsorption energy of LSN molecules is sufficient to overcome the forces of interaction between the structural layers of CHCM, and a result, the interlayer space of the mineral becomes approachable for lignosulfonate molecules.

On the basis of CHCM and sodium lignosulfonate, an organic-mineral composition (OMC) has been synthesized, its synthesis scheme is shown in **Figure 3.22**.

Thus, on the basis of studies of physical and chemical properties of chromium hydroxocomplex montmorillonite and its interaction with lignosulfonates, an organic-mineral composition, characterized by negatively charged dispersed particles, has been synthesized. It can be used as a technologically efficient reagent for forming the structure of leather semi-finished products during retanning and filling.

3.7. Organic-mineral retanning and filling

The development of new retanning and filling materials for leather manufacturing based on cationic forms of montmorillonite can expand the raw material base for retanning and filling with a wide spectrum of

technological properties [59]. The ability of montmorillonite mineral dispersions to modify the surface charge of particles and adsorb natural substances with the necessary tanning properties enables to obtain technologically effective compounds for the structure formation of a semi-finished product in the production of leather materials of a certain designation.

The effectiveness of synthesized OMCs for retanning and filling of leather semi-finished products was established as a result of the study of physical and chemical properties of a chrome semi-finished product [60, 61], with the thickness of 1.4–1.5 mm after the shaving. The research covered the processing of 5 groups of samples in the size of 50×120 mm, 8 pcs. in each group.

The treatment of chrome semi-finished product was carried out after the retanning with chrome tanning agent of 40 % basicity, neutralization with bicarbonate and sodium formate with the consumption of 4.0; 0.6, respectively; 1.0 % of the shaven semi-finished product weight and washing. Retanning and filling of the semi-finished product by Variant 1–4 (**Table 3.19**) was carried out by OMC containing lignosulfonates of 200, 300, 400, 500 % of dry mineral content mass, combined with acrylic filler tergotan PMB of *Clariant* company (Austria) with the consumption of, respectively, 2.5 % in terms of a dry mineral and 3 % of the shaven semi-finished product weight. Then, the fixing treatment of the semi-finished product with alumina potassium alums and sodium formate with the consumption of 1.5 and 0.5 % of the weight of the shaven semi-finished product was performed. The reference variant was 5r, which was carried out according to the scheme of the current methodology.

By organoleptic assessment, all leather samples were well-filled, soft, plastic, with a clearly defined crimp of the grain. The use of OMC for retanning and filling processes of leather semi-finished products with 400–500 % consumption of lignosulfonates of dry minerals weight allowed to effectively form the structure of the dermis and obtain leather materials with high operational properties, which, in comparison with the reference variant, manifests itself in the tendency to increase the tensile strength, in 4–5 % increase of the volume yield, the leather output in terms of area and thickness of 5.6–6.5 and 1.9–2.5 %, respectively, reducing the stiffness and obtaining more elastic, more filled leather semi-finished products without the use of high-priced vegetable tannins.

Table 3.19

Indicators of the leather structure formation

Indicator	Variant of treatment				
	1	2	3	4	5r
Leather yield, % of control: by thickness	96.5	100.5	102.5	101.9	100.0
by area	100.8	104.9	106.5	105.6	100.0
Volume yield, cm ³ /100 g of protein	241.0	250.0	260.0	256.0	246.0
Virtual specific mass, g/cm ³	0.638	0.621	0.611	0.615	0.645
Temperature of welding, °C	111	114	115	114	112
Stiffness on PZHU-12M, N	0.242	0.232	0.22	0.218	0.24
Ultimate tensile strength during stretching, 10 MPa	2.21	2.38	2.45	2.39	2.25
Elongation under stress 10 MPa, %	26.6	29.2	29.9	27.5	27.8
Content of, % for absolutely dry mass: mineral substances	7.2	7.5	7.7	7.8	6.6
chromium oxide	4.6	4.6	4.6	4.5	4.4
SEOS	6.4	6.3	6.3	6.5	6.5

Taking into account the established tanning and filling properties of the developed organic-mineral mixture on the basis of modified montmorillonite dispersions and sodium lignosulfonates, it is possible to predict the probability of removal of high-priced vegetable tanning materials of a foreign production from the existing technological scheme and to expand the range of materials used.

To investigate the influence of the components ratio, including OMC, and technological solution of liquid finishing on physical and chemical properties of the leather material, 5 groups of samples with 7 ones in each, with 120–170 mm in size and the thickness of 1.5–1.6 mm were assembled from the semi-finished product of a lightweight chrome cowhide after the shaving. The processing of semi-finished products was carried out according to the standard method of dyeing and fatliquoring processes. All liquid processes were performed identically for all the variants. The retanning process of the experimental variants included treatment with a synthetic tanning agent Tergotan RX, acrylic polymer

tergotan PMB and OMC based on lignosulfonates and modified montmorillonite (**Table 3.20**).

After the retanning and filling processes of the semi-finished product, the fixing treatment with alumina potassium alums and sodium formate was carried out, they were added into the spent liquor in the amount of 1.5 and 0.3 %, respectively, of the shaven semi-finished product weight. Retanning and filling of the semi-finished product of the reference variant 5c were carried out with the additional use of quebracho tannins and mineral filler Tanikor FTG of *Clariant* company. The

Table 3.20

Consumption of materials for retanning and filling of semi-finished products and leather properties

Material/indicator	Consumption of materials, % of the semi-finished product weight, according to variants				
	1	2	3	4	5c
CHCM	2.5	2.5	2.5	2.5	—
Sodium lignosulfonate	8.0	10.0	12.0	10.0	—
Acrylic filler Tergotan PMB	2.0	2.5	3.0	—	3.0
Syntan Tergotan RX	3.0	3.0	3.0	3.0	3.0
Quebracho tannins	—	—	—	—	4.0
Mineral filler Tanikor FTG	—	—	—	—	2.5
Indicators of finished leather					
Thickness, mm	1.48	1.58	1.64	1.62	1.56
Output of skin area, %	99.7	103.6	102.9	102.8	100.0
Virtual specific mass, g/cm ³	0.644	0.630	0.640	0.620	0.651
Stiffness on PZHU-12-M, N	0.285	0.274	0.29	0.258	0.325
Ultimate tensile strength during stretching, 10MPa	2.25	2.36	2.31	2.3	2.68
Tension at the appearance of cracks of the surface grain, 10 MPa	1.87	1.90	1.82	2.01	1.75
Elongation under stress of 10 MPa, %	29.6	29.8	28.7	30.4	30.2
Temperature of welding, °C	107	109	107	109	108

increased consumption of the mixture components for retanning and filling (Variant 3) is accompanied by an increase in the skin thickness and a decrease in the virtual specific mass, which is associated with the preservation of a loose structure of the semi-finished product dermis. At the same time, its stiffness index decreases. The use of acrylic polymer compounds in the mixture (Variants 1–3) positively affects the formation of the dermis structure. It therefore increases the output of the finished skin area, but the increase in the consumption of acrylic filler tergotan PMB to 3 % slightly reduces its yield (Variant 3). The second treatment variant can be considered the optimum one.

For production testing, two batches of chrome semi-finished products were assembled from a lightweight steerhide with the thickness of 1.5–1.6 mm after the shaving. Tanning and processing of semi-finished products before neutralization were performed on its halves. For retanning of the experimental batch, OMC with the consumption of sodium lignosulfonate of 420 % of the mineral weight was used [36]. The consumption of OMK in terms of a technical product was 14 %, which corresponds to the amount of montmorillonite – 2.5 % of the weight of the shaven semi-finished product and a high value of the formation of the dermis structure of the obtained skins with almost the same hydrothermal resistance. In this case, the number of tanning compounds in lignosulfonates is about 40 %, which corresponds to 4.2 % of organic tanning compounds, and is similar to the consumption of kvebraho tannins in the control batch. The flow diagram of the subsequent treatments of the experimental batch is presented in **Fig. 3.23**.

Further dyeing, fatliquoring, drying-tempering and finishing processes were carried out identically for the experimental and control lots by the technology of upper shoe elastic leather manufacturing from raw cattle hides, operating at the leather enterprise *Slava* LLC.

According to the organoleptic assessment, the obtained skins of the experimental and control batches were well-filled, soft, without looseness, with a high quality surface characteristics. Indicators of their quality and grade (**Table 3.21**) show a high filling effect of OMK and forming ability, which allows to increase the uniformity of skin thickness in hide sections compared with the control ones by 1.6 % and to achieve an increase in the output of their area.

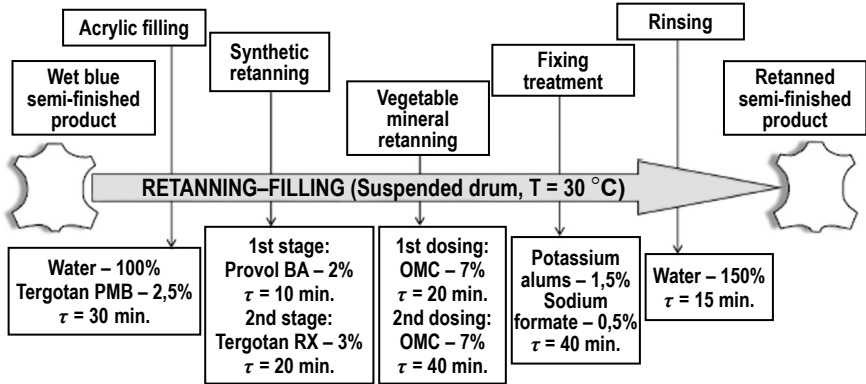


Fig. 3.23. Flow diagram of retanning and filling of leather semi-finished product with OMCs

The obtained data of a complex evaluation of operational properties (**Table 3.22**) indicate that by physical and mechanical properties and chemical composition the experimental leathers are similar to those obtained by the existing technology, which involves the use of expensive materials. At the same time, the adhesion of the coating film for leathers obtained by the developed technology is higher by 32–48 N/m.

The findings testify to the effectiveness of the use of OMCs in technological processes of liquid finishing of leather semi-finished

Table 3.21

Quality of leather materials

Indicator		Technology	
		developed	standard
Change in the hide thickness according to hide sections, % of a shaven semi-finished product	Shoulder	86	84
	Belly	94	93
	Shell	94	92
	Mean value	91.3	89.7
Raw material consumption per 100 m ² of hides, % of a normative standard		88.2	91.2
Quality grade of finished hides, % of high quality items		91.2	91.1

Table 3.22

Physical and chemical properties of leather materials

№	Indicator	Technology	
		developed	standard
1	Thickness, mm	1.55	1.52
2	Ultimate tensile strength during stretching, 10 MPa	2.11	1.99
3	Tension at the appearance of cracks of surface grain, 10 MPa	1.77	1.64
4	Elongation under stress of 10 MPa, %	36.0	34.5
5	Stiffness on PZHU-12M, N	0.257	0.272
6	Content of, % on an absolutely dry substance:		
	– mineral substances	7.84	6.59
	– chromium oxide	4.85	4.62
	– SEOS	8.4	8.7
7	Temperature of welding, °C	115	115
8	Vapour permeability, mg/cm ² per hour	1.63	1.54
9	Vapour capacity per 1 hour, %	0.53	0.49
10	Hygroscopic property, %	13.9	14.1
11	Water yielding capacity, %	11.7	10.8
12	Soaking, %:		
	– in 2 hours	69.7	76.2
	– in 24 hours	76.5	81.4
13	Resistance of a protective film to multiple bending, points	4	4
14	Resistance of a protective film to wet friction, rotations	736	728
15	Adhesion of a protective film, N/m, in the state:		
	– dry	415	367
	– wet	257	225
16	Thickness of a protective film, mg/dm ²	197	197

products. Removal of quebracho tanning agent and mineral filler tanikor FTG from the technology of liquid finishing and the treatment of the semi-finished product with the developed OMS increases the output

of the area and the leather quality grade, which positively affects the effectiveness of the use of leather raw materials.

Thus, the developed technology of retanning and filling of the leather semi-finished product with the use of modified montmorillonite dispersions and lignosulfonates in comparison with the existing technology, which involves the use of only high-price chemical materials, provides the receipt of filled leather with an effective structure formation that meets the requirements of the standard DSTU2726-94 "Upper shoe leather. Technical requirements"; it is pleasant to touch and has high operational properties.

Thus, the given technology makes it possible to completely replace the use of high-priced quebrach tanning agent, expand the range of chemical materials for liquid finishing and increase the efficiency of using leather raw materials by 3 %.

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Questions for self-control

1. Chemical structuring and stabilization of capillary and porous structure of the dermis collagen while tanning raw hides and skins.

2. The most common technology of rawhide tanning using chromium compounds in the elastic leather manufacturing.

3. Influence of rawhide liming on the fixation of chromium compounds and hydrothermal stability.

4. Results of the use of anionic MCS form with varied basicity in the context of harmonious exploitation of raw hides and skins.

5. Possibility to reduce the consumption of chromium compounds due to their use in anionic initial form and concentrated state at the first stage of tanning.

6. Objective need to develop resource-saving and environmentally-oriented technology of hide and skin treatment.

7. Findings from the physical and chemical analysis of graphic dependencies received on the basis of mathematical models of the study of raw hide tanning process.

8. Effectiveness of low-waste tanning technology using the basic chromium sulphate.

9. Advantages of chromium compounds for recharging and obtaining polyfunctional materials for liquid finishing of leather semi-finished products.

10. Actuality of regular technological research into replacement of toxic chromium compounds in tanning for environmentally safe chemical reagents.

11. The main methods to prepare hydroxysulphate chromium montmorillonite dispersions.

12. Effects of the interaction of highly dispersed minerals with chromium (III) compounds.

13. The study of MCS consumption effect on modification of MMT dispersions through the evaluation of regularities of kinetic viscosity and the *pH* level.

14. The most important result of the simultaneous entering of equal in size monomer and polymer hydroxochromium cations into the interpacket space of montmorillonite.

15. Possibility to modify montmorillonite with anionic and non-ionic ligand-containing organic compounds, in particular with surfactants, dyes, etc.

16. Chrome montmorillonite tanning of the semi-finished product.

17. The promise of technology of leather elastic materials production using polyfunctional properties of the structuring and filling agents combined in montmorillonite, modified with chromium complexes, is explained by the reduction in the consumption of toxic materials.

18. Efficiency of a combined use of modified hydroxosulphatechromium complexes and the BCS.

19. Retanning and filling of the leather semi-finished product using montmorillonite dispersions.

20. The conditions for the most positive effect on the structural changes of the dermis.

21. The main characteristics of the semi-finished product formed with the use of montmorillonite dispersions modified with sodium polyphosphate.

22. The influence of different materials on the quality of finished hides that should be taken into account in the process of development of retanning and filling technology of the leather semi-finished product.

23. The role of synthetic tanning materials in the production of finished leather.

24. Effectiveness of mineral filling technology of the leather semi-finished product.

25. Modification of chromium hydroxocomplex montmorillonite with lognosulphonates.

26. Organic-mineral retanning and filling.

27. Assessment of the use of the BCS in technological processes of liquid finishing of the leather semi-finished product.

28. Tanning technology alternative to chrome tanning.

29. Method of organic tanning with the use of glutaraldehyde.

30. Physical and chemical peculiarities of combined chromium-free tanning.

31. Chrome-free technology of leather manufacturing for various purposes.

32. Directions of combined tanning with the use of vegetable tanning agents and aluminium compounds.

33. Determination of the degree of the dermis collagen structuring with tanning substances of various nature.

34. The main results of the use of various means of organic and mineral tanning.

35. Tanning with mimosa tannins after treatment of the pelt with glutaraldehyde.

36. Principles of an effective combined tanning, predominantly chrome-free.

37. ASTA-tanning technology.

38. Technology of aldehyde silicon aluminium tanning and its improvement for increasing heat-resistance of the semi-finished product adding tannins into the tanning system.

39. Physical and chemical properties of leather semi-finished products obtained by aldehyde silicon tannin aluminium tanning technology with minimized consumption of organic tanning agents.

40. PTA-tanning technology.

41. The results of physico-chemical and hydrothermal tests of the semi-finished product after phosphonium-tannin-aluminium tanning.

42. The consequences of the use of the phosphonium-tannin-aluminium tanning technology by the leather enterprise CJSC *Chinbar* (Ukraine).

43. Liquid finishing of the leather semi-finished product using a suspended-type drum of VALERO Company (Italy).

44. Preparation of the pelt for tanning with tannins by various technologies.

45. Effectiveness of the use of the pelt tanning with glataraldehyde or phosphonium compounds to prepare raw hides for vegetable tanning.

4. FEATURES OF PROCESSING TECHNOLOGIES OF RAW FURS

Modern technologies for the production of natural materials must meet high requirements regarding the efficiency of the use of raw materials and raw chemical reagents, reduction in energy consumption, intensification of technological processes and sustainability, especially in chemical production, which uses large volumes of technological solutions with a significant concentration of reagents, including toxic ones. First of all, it concerns the fur production technology. Nowadays, popular processing technologies of raw furs in certain processes require consumption of water by 3–20 times higher [1, 2] than leather manufacturing, depending on their structural features. In particular, at the stage of soaking of air-dried hides its consumption per one ton of raw materials is, m³: for rabbit skin — 9, for sheep and fox skins — 17 and 25, respectively, and at the stage of fox skin coloring with oxidization of semi-finished products — 175, involving numerous rinses.

4.1. Soaking of air-dried raw materials with the use of activated water

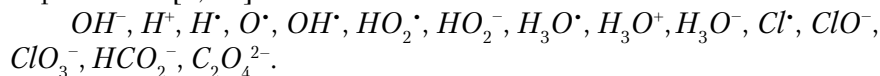
The technology of soaking of raw furs involves the structure restoration of the skin tissue primarily by the content of water and ensures the efficient carrying out of such technological treatments when converting it into fur. As the processing of raw materials requires the consumption of significant volumes of water, the use of activated water may be promising. It provides significant acceleration of biotechnological processes [3] due to an easy penetration into cells [4] and their combination. The following methods of water activation are known: under the action of a magnetic field, ultrasound, shaking, heat treatment (heating, cooling,

freezing with subsequent thawing) and electro-chemical activation (ECA), when which water acquires specific anomalous properties [5, 6]. The specific physical and chemical properties of ECA of water and solutions of chemical reagents are largely due to its declustered structural state, high oxidation reduction potential (ORP) and thermodynamic nonequilibrium [7–9], which is preserved for a long time.

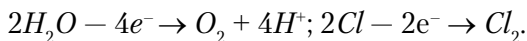
Studying the effect of water ECA on the structure and properties of biopolymers, it has been established that the use of the anolyte phase owing to bactericidal properties [10–12] makes it possible to remove atypical reagents from the technological process of soaking of raw furs. Using ECA of water with low *pH* as an active catalyst for the process of biological raw material soaking, it is also possible to remove acids from it.

The analysis of information sources shows a special relevance of the research concerning the use of ECA of water solutions in water and mass exchange processes in the production of fur materials. The use of activated water in protein material processing can become effective taking into account the stability of the characteristics of electro-activated aqueous solutions and chemical activity in the reactions of interaction with non-collagen components of skins and hides is high.

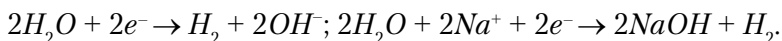
Increased chemical activity of the declusterized water system and technological solutions on their basis is caused by a number of electrochemical processes under the influence of electric current on water in the presence of an electrolyte. In this case, water is ionized with the formation of a large number of highly active ions and radicals, in particular [3, 13]:



The main reactions that occur in the electroactivator can be represented in the form of circuits —
on the anode:



on the cathode:



Thus, as the results of the study of physical and chemical properties of the obtained anolyte (**Fig. 4.1**) show, the *pH* slightly increases and its oxidation reduction potential decreases during its storage. At the same

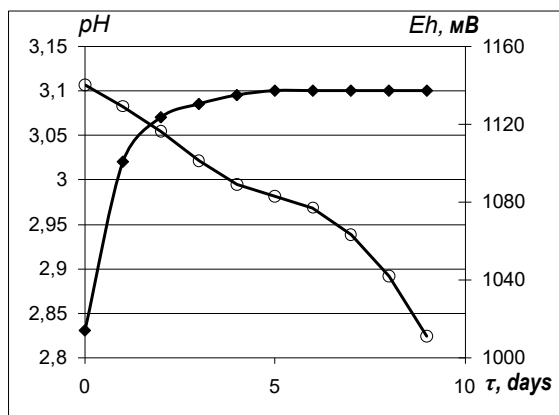


Fig. 4.1. Kinetics of anolyte pH change (1) and its oxidation-reduction potential (2)

time, the main changes in the pH of the activated water occur within the first two days of storage, while the ORP is reduced continuously. This may be caused by the neutralization of H^+ ions due to their interaction with oxide compounds formed by electrochemical reactions. The obtained results indicate quite a high anolyte stability

during storage, which can be used in the technological process of soaking of raw materials. To soak raw furs, the water was prepared in the electroactivator of the scientific and production company *Ekovod*, TU Y29.1-1285006876.001-2000 with a silicon anode, a steel cathode, and ion exchange membrane of a special interlacing cotton [14, 15] with the pH in the range of 2.8–3.9 for anolyte and 9.5–11.5 for catholyte.

Undressed air-dried nutria skins with 22.3 % content of fat substances, the area of 20–24 dm² (State Standard GOST 2916-84), and rabbit skins of 0.7–1.0 mm in thickness (State Standard GOST 2136-87), having a denser skin tissue, compared to nutria skins, underwent technological treatment. The watering of nutria and rabbit skins in fur semi-finished products was measured gravimetrically using scales of *AXIS* company, series AD200 (Poland).

Nutria skins were soaked using non-ionogenic surfactant for TU2484-014-22284995-99 CH-23 and SPK-50 dissolved in activated and distilled water (reference variant) at the temperature of 19–21 °C, with water consumption of 900 % of the mass of the skins. The concentration of surfactant for soaking and degreasing was 0.5 and 2.0 g/dm³, respectively. The tanning process of rabbit and nutria skins of the reference variant was performed on the spent solution of anolyte using alumina potassium alum $KAl(SO_4)_2 \cdot 12H_2O$ (State standard GOST 4329-

77) and basic chromium sulphate $Cr_2(SO_4)_n(OH)_{6-2n}$ (TU2141-033-541386-2003) with the basicity of 39 %, and with the water consumption of 900 %, tanning agent, g/dm³: alumina potassium alum 10, chrome tanning agent in terms of Cr_2O_3 – 1.6 for rabbit skins and 1.0 for nutria skins. The basicity of the tanning agent was increased by sodium carbonate solution to the *pH* of 3.7–3.9 with its addition twice in 15 minutes.

The obtained results were tested on the equipment of the experimental department of the leather enterprise CJSC *Chinbar* by the methods of raw furs processing [16–18], which involve the use of anolyte and catholyte. At the same time, the soaking of nutria skins was carried out with anolyte, and degreasing – with catholyte at the temperature of 28–32 °C without the use of additional reagents. After degreasing, they were washed twice, sammied and treated with anolyte to be prepared for the next tanning. Rabbit skins were chrome tanned at the temperature of 18–20 °C after soaking in the spent anolithic solution, removing subcutaneous tissue.

For a comparative analysis, fur skins were obtained by the standard technology [19], which involves the treatment of raw materials in the processes of their undressing at temperatures, °C: soaking of nutria and rabbit skins – 30 and 38, respectively, degreasing (for nutria skins) – 38, pickling and tanning – 30 and 40. The total consumption of chemical reagents for the treatment of rabbit and nutria skins, respectively, g/dm³ is the following: sodium chloride – 140 and 130, surfactant – 3.5 and 5.0, 40 % formalin – 1.0 and 0.5, sodium fluosilicate – 0.8 and 1.5, sodium thiosulfate – 17.0 and 8.0, tanning materials – 16.4 and 14.0. Drying and tempering processes and operations on the obtained semi-finished product were performed according to the known technology of rabbit and nutria skins processing. Its physicochemical parameters and properties were estimated according to the methods [20]. The load at break of the skin tissue of fur skins was determined on a tensile testing machine PT-250M at the speed of samples deformation of 80 mm/min.

In the process of watering the skin tissue of fur skins in an electrolyte solution of anolyte or catholyte, the corresponding functional groups of collagen are neutralized. If a solution of acids and alkali is a source of H^+ and OH^- ions in the standard technology, then using electro- active water of anolyte type, ion bonds between amino and carboxyl groups of

side radicals of collagen polypeptide chains are destroyed. As a result, amino groups of the biopolymer with the use of anolyte retain their positive (descending order), and ionised carboxyl groups change into (non-descending) state. Therefore, the degree of collagen hydration of the skin tissue is increased due to ion-dipole interaction and electrostatic repulsion, which in its turn contributes to increasing the degree of the skin tissue watering in raw furs. In the case of catholyte, unlike anolyte, the soaking process is accelerated by neutralizing the ionized amino groups of collagen.

The study of the influence of electrically activated aqueous solutions of catholyte containing only 25 % of surfactant, in comparison with the standard technology for treating nutria skins to accelerate the degree of skin tissue watering (**Fig. 4.2**), shows that the recovery of water lost in curing is very fast. By doing so, the bulk of the aqueous solution is absorbed within the first 1–2 hours, and then the process is slowed down and the next 20 hours the weight of the skins increases by 10 % only. This may indicate a redistribution of the diffused aqueous solution in the fibrous structure of the skin tissue, into which the technologi-

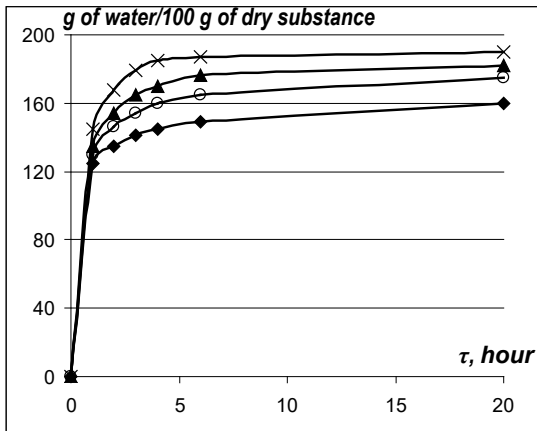


Fig. 4.2. Kinetics of the skin tissue watering of nutria skins using: catholyte (1, 2), distilled water (3, 4), surfactants CH-23 (2, 4) and SPK-50 (1, 3)

cal solution passes from the large pores to the interfibrillary and microfibrillary space of the fine collagen structure of the skin tissue. The use of catholyte compared to distilled water (reference variant) accelerates the direct diffusion of the working solution into the structure of the skin tissue.

The most effective reagent is the solution of SPH-50 surfactant in catholyte, because compared with the reference

variant of treatment, which involves the use of CH-23 surfactant at the concentration of 2 g/dm³ of distilled water (curve 4), it was by 18 % more efficient.

The parameters of the working solutions used for soaking and degreasing are given in **Table. 4.1**. It can be seen from the table that the *pH* of the spent anolyte increases, and of catholyte decreases by 1.3 and 1.5 times respectively, while the *pH* of the surfactant solution in distilled water changes insignificantly. This indicates an increased chemical activity of aqueous solutions of activated water and deep structural changes in the skin tissue and fur semi-finished product. A significant difference in the electrical conductivity of surfactant working solutions in catholyte and anolyte from distilled water indicates the increased chemical activity of the electro-activated solutions, especially of catholyte. This phenomenon is confirmed by the increased electrical conductivity of the initial working solutions of anolyte and catholyte against distilled water by 3.9 and 1.8 times. In this case, the electrical conductivity of the spent solution of catholyte increases by 2.1 times, and compared with distilled water after completing the treatment – by 2.4 times.

The results of the study of the skin tissue degreasing of nutria skins with the surfactant solution in catholyte are given in **Table. 4.2**. The analysis of their skin tissue after appropriate treatment has shown a higher degreasing effect of the skins using catholyte and SPC-50 surfactant compared with the use of distilled water. In this case, 60 %

Table 4.1

Physical and chemical properties of electro-activated working solutions before and after degreasing of fur with PAR SPK-50 surfactant

Indicator	Activated solution		
	anolyte	catholyte	distilled water
<i>pH</i> value	2.8/3.7	10.7/6.9	6.7/6.1
Specific electric conductivity, $\mu\text{S}/\text{cm}$	2800/2640	1270/2760	710/1160

Note. The numerator and denominator correspond to the initial and final values of the water solution.

Table 4.2

**Content of fatty substances in the skin tissue after
its soaking wetting and degreasing**

Variant of treatment	Water	surfactant	Content of fat substances, %, after		
			soaking 1	degreasing	soaking 2
1	catholyte	SN-23	9.71	3.32	3.07
2	catholyte	SPK-50	8.97	3.25	3.12
3	distilled	SN-23	13.20	4.09	3.71
4	distilled	SPK-50	10.11	3.66	3.25

of fat substances are removed during the first soaking and exceeds the reference variant by 13.7 %. A higher degree of the skin tissue watering using a solution of surfactant in catholyte contributes to its more effective degreasing.

An increase in the chemical activity of electro-activated technological solutions is observed in the processes of structuring collagen of nutria skin tissue when it is tanned with chromium compounds [19]. According to the results obtained (**Table 4.3**), after the sequential treatment of nutria skins, the effect of their structuring increases with the use of a surfactant solution in catholyte. In this case, the T_w of the skin tissue grows due to the removal of non-collagen formations, including fat substances, under the action of active products of the electrochemical reaction available in catholyte. This contributes to the

Table 4.3

**Hydrothermal stability resistance, °C of nutria skin tissue of
sodium after a series of technological treatments**

Variant of treatment	Physical and chemical process		
	degreasing, soaking 2	acid and salt treatment	tanning
1	58	56	76
2	58	56	79
3	57	54	72
4	57	54	73

increased diffusion of chromium tanning compounds into the structure of the skin tissue and their subsequent effective interaction with ionised carboxyl groups of polypeptide chains of collagen macromolecules with its volume structure. The effect is more noticeable when a degreasing working solution of non-ionogenic surfactant SPK-50 is used. The T_w after acid and salt treatment decreases as a result of the electrostatic effect amplification by repulsion between the amino groups of macromolecules of the skin tissue collagen.

Thus, the use of technological solutions based on electro-activated water with a significant reduction in the consumption of chemical reagents compared to the modern technology of processing raw furs provides an effective formation of the skin tissue structure with hydrothermal stability, which meets the standard requirements [21]. Such treatment of raw furs, even without the use of antiseptic agents, makes it possible to retain a high strength of bonds between the hair and with the skin tissue after degreasing.

The results of the research on the influence of electro-activated aqueous solutions of anolyte and catholyte on the processing of nutria skins were used in the implementation of the technology of fur production in the research workshop of the industrial enterprise CJSC *Chinbar*. Taking into account the high chemical activity and specific physical and chemical properties of anolyte and catholyte, they were used in the processing of fur raw materials without the surfactant at different stages of the technological cycle. After drying and tempering processes, the finishing of the fur skin tissue was carried out.

The physicochemical properties of nutria skins (**Table 4.4**) indicate that their samples, obtained with the use of anolyte and catholyte *pH* with a lower content of natural fat after degreasing, are formed with optimum indicators of the skin tissue compared to the samples of the current technology in the investigated interval. Increasing the *pH* of anolyte (Variant 2) helps to reduce the deformation of samples, which positively affects the following technological processes – fatliquoring and tanning. Compared with the samples of the reference variant, in addition to Variant 3, nutria skins, treated with the use of an activated aqueous solution without a surfactant, is characterized by higher deformation indicators of hydrothermal stability, strength of the skin tissue

Table 4.4

Physicochemical characteristics of nutria skins

Indicator	Variant of technology			
	1	2	3	current
<i>pH</i> of anolyte	2.9	3.4	3.9	10.7
<i>pH</i> of catholyte	9.7	11.2		—
T_w after tanning, °C	65.0	69.0	59.0	63.0
Mass fraction of, %, in the skin tissue unbound fat substances after degreasing				
– after fatliquoring	3.62	3.80	3.30	4.10
– Cr_2O_3	17.4	18.3	17.9	16.2
Stress at break of the unharmed skin, S	0.89	0.83	0.90	0.93
Deformation complete, %	65.0	64.0	58.0	62.0
– residual, %	15.0	13.2	10.4	12.7
	8.3	9.7	6.0	6.2

Note. The content of fatty substances and chromium oxide in the skin tissue is given in terms of based on a completely dry substance

at break and somewhat higher indicators of the content of unbound fat substances after the fatliquoring process.

Reduction of hydrothermal stability and strength while increasing the *pH* of anolyte over 3.5 is due to the uneven distribution of chromium compounds (III) in the depth of skin tissue after their dominant surface interaction with carboxyl groups of polypeptide collagen chains.

In order to detect the effect of the skin tissue density of the fur raw material on the treatment process and its properties, the samples of a fur rabbit with an average thickness were obtained without degreasing due to a significantly lower content of natural fat substances in the skin tissue compared to the nutria skin. The results of the test of skins obtained from the fur rabbit are given in **Table 4.5**.

The obtained fur skins have slightly increased elasticity, two-fold reduced shrinkage of the skin tissue, a larger volume yield by 10 % compared to the current technology, with the exception of the third treatment variant. During the treatment of skins with a higher density of the skin tissue, there is also a high chemical activity of anolyte in the manufacture of furs with plastic skin tissue. The achieved 185–190 % degree of watering while soaking can be considered sufficient for the formation of

Table 4.5

Physicochemical characteristics of the fur rabbit

Indicator	Variant of technology			
	1	2	3	current
<i>pH</i> of anolyte	2.9	3.4	3.9	—
Degree of watering, g water/100 g of a dry substance	190	185	170	180
T_w after tanning, °C	66.0	65.0	57.0	64.0
Mass fraction, %, of unbound fat substances	14.2	14.9	15.7	14.3
Cr_2O_3 in the skin tissue	1.27	1.21	1.14	1.33
Stress at break of the unharmed skin, <i>S</i>	74.0	79.0	68.0	71.0
Elasticity, %	21.0	19.0	16.0	17.0
Reduction of the skin tissue, %	1.2	1.4	2.2	2.8
Volume yield, cm ³ /100 g	240	244	200	220

the skin tissue in subsequent technological treatments, since the degree of watering for sheepskin with a loose structure at the level of 170–180 g of water/100 g of a dry substance, even with the use of an enzyme preparation [22] provides formation of a high-quality fur material.

Therefore, the use of activated water in the preparatory processes for the production of fur semi-finished products makes it possible to remove antiseptics, surfactants and other intensifiers of soaking from the technology, combine the processes of soaking, degreasing, pickling, tanning and fatliquoring, reduce the duration of liquid treatments twice. Application of technological solutions with *pH* 3.3–3.5 for acid-salt treatment increases the efficiency of electroactivated water influence on the destruction of bonds between collagen macromolecules and its other components as a result of the destructive action of the products of electrochemical treatment in the water — oxygen-containing free radicals.

Thus, the influence of physical and chemical properties of the obtained electroactivated technological solutions on the processes of soaking, degreasing, pickling, tanning, plasticization during the formation of the skin tissue structure of fur skins with different contents of natural fat substances has been studied. The specific influence of technological solutions on the basis of electroactivated water fractions and their

sequential use for the efficient treatment of fur raw materials without antiseptics and surfactants has been determined. It has been shown that the activating effect of electrochemically activated water on these treatment processes is due to its physical and chemical properties and the destruction of the cluster structure with the corresponding enhanced influence both on the chemical collagen structure and on the activity of technological reagents. The use of electrochemical activated water at the stage of restoration of the collagen structure of the skin tissue and its degree of hydration in removing globular proteins, hydrocarbons and lipids from it lead to a two-fold intensification of the process. At the same time, the stage of long-term acid-salt treatment is excluded from the technological process due to the use of electroactivated water fraction with high oxidation capacity.

The developed low-cost technology using solutions based on electrochemically activated water for the processing of raw furs with different amounts of fat substances involves significant reduction of water and chemical reagents, two- or three-fold intensification of soaking and tanning processes and the formation of fur materials with a necessary complex of physical and chemical properties. At the same time, removal of toxic reagents such as antiseptics (formalin and fluosilicone sodium) from the processing of raw furs gives grounds to consider the developed technology as environmentally safe in comparison with modern technology of fur production.

4.2. Tanning and fatliquoring of raw furs

The main disadvantage of a number of technologies that are used to undress the most common types of skins, such as sheep and rabbit skins, is a high consumption of chromium compounds. The same applies to the retanning process for increasing the hydrothermal resistance of the skin tissue of fur skins in their preparation for dyeing with acid dyes, which complicates the technological process and pollutes the environment.

Modern technology for the processing of fur skins includes combination of the tanning process with fatliquoring. In this case, the

availability and cost of chemical reagents were considered as decisive factors for their use in the technology of fur and wool sheepskin production [22, 23]. Industrial oil I-12A in the form of fat emulsion with the addition of a significant amount of surfactants was commonly used, due to its chemical inertness. In order to increase the effectiveness of the plasticization effect on the skin tissue of fat compositions, synthetic and natural fats with active functional groups were additionally added to their composition. However, despite the high diffusion capacity of the emulsion of industrial oil I-12A, its particles are not fixed in the skin tissue, and eventually it is released on the surface, greasing the hair.

4.2.1. Tanning and fatliquoring of wool sheepskins

A previously developed fatliquoring composition [24] with a reduced by 5–10 times content of the industrial oil I-12A for sheepskin plasticization in the process of pickling-tanning-fatliquoring of fur skins, in addition to the main ingredient – ester, contains some additional ingredients, including non-ionogenic surfactants. According to the previous studies [25], the non-ionogenic surfactant by 4.5–2.5 times exceeds the effect on the total elongation of the sheepskin tissue at the stress of 4.9 MPa and its tensile strength relative to the industrial oil I-12A and alkaline non-sulfated esters. Taking into account the results of studies on sheepskins, a fatliquoring composition based on the ester was developed [26] to remove I-12A oil from the combined process of pickling, tanning, and fatliquoring.

For a detailed study on the influence of components of the composition based on the ester, the mathematical planning of the experiment with the realization of the synthesized D-optimal plan by the pseudo-component method was used [27]. To determine the ratio of components in the fatliquoring composition, the following outcome variables are chosen: y_1 – absorption of fatliquoring emulsion by fur skins, %; y_2 – elongation at the stress of 4.9 MPa, %; y_3 – specific mass of the skin tissue, kg/m³. In this case, there are restrictions on the content of ingredients in the fatliquoring composition, mass %: industrial

oil I-12A $x_1 = 0-50$, diethylene glycol ester $x_2 = 40-94$, non-ionogenic surfactant $x_3 = 6-10$.

To develop a fatliquoring composition, a simplex-lattice design for incomplete Scheffe Cubic model was used. As a model, the polynomial of incomplete 3 descending order was chosen:

$$\hat{y} = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3, \quad (4.1)$$

where $\beta_i, \beta_{ij}, \beta_{ijk}$ – required polynomial coefficients, and $i \neq j \neq k \neq 1, 2, 3$.

Do to the violation of the condition $0 \leq x_i \leq 1$, the experimental area is transformed into a new coordinate system (z_1, z_2, \dots, z_q) . In this case, the simplex apexes are taken as independent ingredients of the mixture, so called pseudocomponents. For the experimental area, we have:

$$0 \leq z_i \leq 1, \quad (i = 1, 2, \dots, q), \quad z_1^{(u)} + z_2^{(u)} + \dots + z_q^{(u)} = 1, \quad (4.2)$$

where u – any points of the experimental area.

The dependence between the coordinate systems (x_1, x_2, \dots, x_q) and (z_1, z_2, \dots, z_q) , which provides the conditions (4.2), is given by the matrix equation $X = AZ$:

$$\begin{vmatrix} x_1^{(u)} \\ x_2^{(u)} \\ \vdots \\ x_q^{(u)} \end{vmatrix} = \begin{vmatrix} x_1^{(1)} & x_1^{(2)} & \dots & x_1^{(q)} \\ x_2^{(1)} & x_2^{(2)} & \dots & x_2^{(q)} \\ \vdots & \vdots & \dots & \vdots \\ x_q^{(1)} & x_q^{(2)} & \dots & x_q^{(q)} \end{vmatrix} \times \begin{vmatrix} z_1^{(u)} \\ z_2^{(u)} \\ \vdots \\ z_q^{(u)} \end{vmatrix}. \quad (4.3)$$

In this equation, the elements of the matrix A are the coordinates of the apexes of the simplex, and $x_i^{(u)}$ i $z_i^{(u)}$ ($i = 1, 2, \dots, q$) are the output and new coordinates of u transformed point.

To obtain a model of incomplete 3 descending order $\{3, 3\}$, experiments are conducted according to the working plan (Table 4.6). The results of the corresponding experiments are shown in Table 4.7. The optimum composition of reagents is determined by the method of scanning.

After statistical analysis of the experimental data obtained using the program of <http://mnk-online.narod.ru> site, adequate mathematical models in pseudo-coordinates were received:

$$\hat{y}_1 = 98.69997z_1 + 89.09999z_2 + 72.99999z_3 - 7.199989z_1z_2 - 19.39999z_1z_3 - 16.19998z_2z_3 + 51.44444z_1z_2z_3; \quad (4.4)$$

$$\hat{y}_2 = 46.99999z_1 + 41z_2 + 25.99999z_3 - 2.275856 \cdot 10^{-6}z_1z_2 - 10.00001z_1z_3 - 17.99999z_2z_3 + 58.03191z_1z_2z_3; \quad (4.5)$$

$$\hat{y}_3 = 0.5509998z_1 + 0.5749999z_2 + 0.66z_3 + 4.000405 \cdot 10^{-3}z_1z_2 + 0.1460001z_1z_3 + 5.800007 \cdot 10^{-2}z_2z_3 - 0.7258554z_1z_2z_3. \quad (4.6)$$

The adequacy of the models is checked by additional experiments at experimental points 8 and 9 (Table 4.8).

The obtained models are used to find the optimal composition of the fatliquoring composition by means of a generalized desirability function, which is compiled from these models with restrictions on output variables that correspond to their best and worst values: $y_1 - 99.5$ and 40.0 , $y_2 - 50$ and 30 , $y_3 - 0.55$ and 0.7 . By the method of scanning

Table 4.6

Simplex-lattice design

Experiment	Design in pseudo-components			Working plan			Output variable
	z_1	z_2	z_3	x_1	x_2	x_3	
1	1	0	0	0	0.94	0.06	\bar{y}_1
2	0	1	0	0	0.9	0.1	\bar{y}_2
3	0	0	1	0.5	0.42	0.08	\bar{y}_3
4	0.5	0.5	0	0	0.92	0.08	\bar{y}_{12}
5	0.5	0	0.5	0.95	0.68	0.07	\bar{y}_{13}
6	0	0.5	0.5	0.25	0.66	0.09	\bar{y}_{23}
7	0.33	0.33	0.33	0.167	0.753	0.08	\bar{y}_{123}

Table 4.7

Results of the study on a composition for fatliquoring

Output variable	Experimental point						
	1	2	3	4	5	6	7
y_1	98.7	89.1	73.0	92.1	81.0	77.0	84.0
y_2	47.0	41.0	26.0	44.0	34.0	29.0	37.0
y_3	0.551	0.575	0.660	0.564	0.642	0.632	0.591

Table 4.8

Values of the output variables at experimental points

Experimental point	Working plan			Output variable					
	x_1	x_2	x_3	y_1		y_2		y_3	
8	0.08	0.84	0.08	89.6	89.1	41.5	42.0	0.573	0.577
9	0.08	0.82	0.1	84.2	84.5	35.0	36.0	0.604	0.599

with step 0.01, the optimal composition of the fatliquoring composition in pseudo-components has been obtained: $z_1 = 1$, $z_2 = 0$, $z_3 = 0$. After their reduction to the relative composition of the initial components according to the matrix equation (4.3), the following composition has been obtained, fraction mass: $x_1 = 0$, $x_2 = 0.94$, $x_3 = 0.06$. In this case, the output variables have the following meanings: $y_1 = 98.7\%$, $y_2 = 47.0\%$, $y_3 = 0.551 \text{ kg/m}^3$, and the value of the desirability function $D = 0,7782$.

Therefore, the composition of diethylene glycol ester without adding industrial oil I-12A is more efficiently absorbed in the course of fatliquoring fur skins and evenly distributed in the structure of the skin tissue, while its formation in the process of tanning intensifies and plasticity increases. The application of the developed composition with the optimal content of a surfactant makes it possible to increase the elongation of the skin tissue under stress of 4.9 MPa and reduce its specific mass.

In order to expand the assortment of new fatliquoring materials and study the peculiarities of their use in the process of pickling-tanning-fatliquoring together with the technological properties of the diethanolamine ester emulsion, the properties of DPGE and DPGES emulsions were also investigated. They are active fatliquoring materials, but the fat content in the hair when using their emulsions decreases by 2.5–3.3 times compared to the industrial oil I-12A emulsion. In addition, in the course of dyeing fur skins by the method of immersion and chemical cleaning of fur products in organic solvents, a large number of fat substances are removed from the depth of the skin tissue, which causes the loss of its plasticity, softness, and filling, the appearance of dryness and shrinkage of the products.

For the purpose of the study, the samples of wool semi-fine fleece sheepskin of the air-salted method of curing, undressed according to the standard method, were degreased with dichloroethane with 1.6 % content of fat substances in the skin tissue in the apparatus “Bove” (Germany). Then their sheepskins were fatliquored with emulsions of esters at the $LQ = 8$, the temperature of 35–37 °C and the pH of 6.2–7.4 in the presence of sodium chloride at the concentration of 30 g/dm³ to prevent overwatering of the skin tissue. For the purpose of the sheepskin tissue testing [28], after appropriate fatliquoring, the samples were taken from the identical symmetrical areas located at equal distances from the vertebral line. The control samples were degreased and sheepskins were re-fatliquored with the emulsion of industrial oil I-12A at the concentration of 10 g/dm³. Efficiency of the used compositions for fatliquoring of the wool sheepskin tissue was determined by physical and mechanical research (Table 4.9).

Table 4.9

Physical and mechanical properties of the wool sheepskin tissue at spherical deformation

Indicator	Sheepskins refatliquored with emulsion			
	DEGE	DPGE	DPGES	I-12A
Ultimate tensile strength while stretching, 10 S, skin grain	31,0/ /29,0	31,0/ /30,0	32,0/ /31,0	30,0/ /24,0
	23,0/ /21,0	23,0/ /20,0	24,0/ /22,0	19,0/ /14,0
Meridian elongation, %, in the event of a crack in the grain at break of the skin tissue	34,0/ /32,0	34,0/ /32,0	37,0/ /35,0	31,0/ /21,0
	61,0/ /60,0	63,0/ /60,0	66,0/ /63,0	59,0/ /42,0
Resistance of the skin tissue under fixed stretching, 10 S	8,3/ /8,5	10,7/ /10,9	9,8/ /8,9	9,2/ /11,7

Note. Values of the numerator and denominator were obtained according to the consumption of fat substances with the concentration of 10 and 4 g/d³

As it can be seen from **Table 4.9** that using ester emulsion for fatliquoring with the consumption of 10 and 4 g/dm³ almost the same values of the skin tissue resistance to the given deformation were received. It increases its strength and strength of the grain with the consumption of 4 g/dm³ compared to the emulsion of industrial oil I-12A. In this case, the obtained absolute values of the strength of the grain and the stress at break exceed the values of the corresponding control samples by 18.0 %. The most elastic is the skin tissue of sheepskins, fatliquored with an emulsion of sulfated dipropylene glycol ester. Reduction in the consumption of industrial oil I-12A to 4 g/dm³ greatly increases the resistance of the skin tissue to stretching. Mechanical values are reduced due to the spherical stretching of sheepskin tissue, which is especially true for the strength of the grain.

The results of physical and mechanical tests of wool sheepskins tissue after degreasing with organic solvents and subsequent fatliquoring are evidenced by a high fatliquoring effectiveness of ester emulsions (**Table 4.10**). The degreasing of wool sheepskins is accompanied by a decrease in the tensile strength while stretching and in deformation properties of the skin tissue. During further fatliquoring with the emulsion of the ester type, the physical and mechanical indicators of the skin tissue do not only recover, but also increase significantly.

Table 4.10

Physical and mechanical properties of wool sheepskin tissue with a monaxial deformation

Indicator	Sheepskins refatliquored with emulsion			
	DEGE	DPGE	DPGES	I-12A
Ultimate tensile strength, MPa	84,0/116,0	86,0/114,0	78,0/156,0	84,0/105,0
Elongation, %, at 4.9 MPa	74,0/113,0	79,0/116,0	88,0/134,0	74,0/104,0
at break	92,0/108,0	91,0/108,0	82,0/123,0	92,0/105,0

Note. Indicators of the numerator and denominator are given in % of the initial value, respectively, after testing degreased and refatliquored sheepskins

However, this is less relevant to the deformation characteristics. The most significant strengthening of sheepskin tissue and the improvement of its elastic properties is observed when using the sulfated ester emulsion after degreasing.

Consequently, the use of the investigated diethylene and dipropylene glycol esters for fatliquoring wool sheepskin tissue after degreasing makes it possible not only to restore its physical and mechanical parameters, but also to strengthen the structure reducing the consumption of fat substances by 2.5 times. This effect is enhanced by the use of a sulfated dipropylene glycol ester, which contributes to 40–50 % increase of tensile strength and elasticity of the skin tissue. At the same time, it prevents dryness and shrinkage of the skin tissue of fur skins, especially those that are capable of having grain cracks, so the emulsions of the investigated esters are recommended for further research in the combined processes of pickling, tanning, and fatliquoring of raw furs.

An electrolyte-resistant sulfated dipropylene glycol ester was proposed to be used instead of multi-component fatliquoring compositions for the development of a more efficient energy-saving technology of tanning and fatliquoring of wool sheepskins [29]. The main parameters of the investigated process are the concentration of sodium chloride, a mixture of organic and mineral acids, chromium tanning agent with an initial basicity of 35–40 %, a fat substance in an emulsion with the constant LQ and pH of the medium. Since acid-salt treatment is a preparatory stage of the wool sheepskin structure for tanning that dehydrates it and subsequently affects the basicity of BCS, these parameters are fixed at the level of technological requirements. Developing such technology, mathematical modeling of the investigated process and multi-criteria optimization have been used [30].

The factors that significantly affect the tanning and fatliquoring process are assumed to be the concentrations of chromium tanning agent of the specified initial basicity – X_1 , $g/dm^3 Cr_2O_3$ and DPGAS – X_2 , $g/dm^3 FS$, as well as the pH of the medium at the second stage of tanning – X_3 , since its value strongly influences the physical and mechanical properties of wool sheepskins. In this case, preliminary studies of emulsion fatliquoring with glycol esters in the process of pickling and tanning [31–33] make it possible to vary X_1 , X_2 , X_3 factors at two

levels with the appropriate interval of 0.5, 1.0, 0.25, and place the design center in the factor space with the coordinates 1.0, 4.0, 3.5. The need to reduce the initial concentration of BCS and DPGES in the developing technology is explained by incomplete absorption of reagents using the standard technology, when more than 50 % of Cr_2O_3 and about 60 % of fats remain in the spent technological solution.

In the developed method of tanning and fatliquoring, chromium (III) compounds are used in the anionic initial form. Since the competitiveness of technology and its ecological efficiency depend not only on the consumption of chemical materials with the corresponding production quality of furs, but also on the effectiveness of their use, the output variables are taken as follows: the welding temperature of the semi-finished product – y_1 , °C; concentration in the spent technological solution BCS and DPGES, respectively – y_2 , g/dm³ Cr_2O_3 and y_3 , g/dm³ FS; tensile strength while stretching – y_4 , MPa and complete elongation under stress of 4.9 MPa – y_5 , %.

The study of the absorption (A) kinetics of fat substances at the pH of 6.8–7.4 and the temperature of about 40 °C by the tanned skin tissue of semi-fine fleece sheepskin from DPGES and DPGE emulsions compared to the emulsion of industrial oil I-12A (**Table 4.11**) using *F*-ration [30] allowed to obtain mathematical models of the fatliquoring process:

$$A_1 = 79.1 \tau_1 + 50.59 \tau_1^2 - 36.69 \tau_1^3; \quad (4.7)$$

$$A_2 = 50.3 \tau_2 + 20.56 \tau_2^2 - 17.2 \tau_2^3 + 2.58 \tau_2^4; \quad (4.8)$$

$$A_3 = 50.88 \tau_3 - 10.44 \tau_3^2 + 0.69 \tau_3^3. \quad (4.9)$$

The obtained analytical dependences by the maximum value of *F*-ratio at the minimum value of residual dispersions indicate a high degree of their adequacy to the actual process of absorption of fat substances. The indicated values of absorption of FS by sheepskins show the need for different duration of their contact τ with the corresponding emulsions and more active absorption of FS by the sheepskin tissue of dipropylene glycol esters compared with the industrial oil I-12A.

As it can be seen from the above equations (4.7)–(4.9), sheepskin tissue most effectively absorbs fat substances from DPGES emulsion,

Table 4.11

The absorption kinetics of fat substances by tanned sheepskin tissue in the process of emulsion fatliquoring

Indicator		Duration of absorption of fat substances, hours		
		τ_1	τ_2	τ_3
Absorption, %:	25.1	0.85	0.45	0.55
	49.9	0.5	0.85	1.3
	75.2	0.72	1.45	2.7
	81.0	0.76	1.65	4.0
	87.5	0.83	2.0	—
	92.5	0.92	3.0	—
	96.4	1.2	—	—
<i>F</i> -ratio		1031	6473	469847
Residual dispersion		0.75	0.308	0.035

Note. Indicators 1–3 respectively indicate emulsions DPGES, DPGE, I-12A

slower from DPGE, and the least — from the emulsion of the industrial oil I-12A. The amount of analyzed absorbed FS within a specified time is calculated by means of the fatliquoring process models. So, if τ is one hour, sulfated and non-sulfated dipropylene glycol esters will be absorbed by a microporous tanned sheepskin tissue by 2.30 and 1.65 times more in relation to the industrial oil I-12A, and in course of time this difference will increase.

Absorption dependence on its duration confirms the nature of the materials used, the stability of fat emulsions and the nature of their interaction with the tanned skin tissue. First of all, a higher degree of dispersion and electrolyte-resistant esters contributes to their diffusion in inter-structural spaces and uniform distribution, and the presence of polar groups — to their fixation with the formation of hydrogen and ionic bonds, in contrast to only dispersion links of industrial oil I-12A.

It should be noted that the dipropylene glycol esters work out much deeper and are absorbed by the tanned sheepskin tissue at the *pH* of 6.8–7.4 and the temperature of about 40 °C by 2.0–3.3 times faster compared with the emulsion of the industrial oil I-12A, which even in the case of a pre-formed microporous structure of the skin tissue is

absorbed by 80 % only. Therefore, due to the three-fold accelerated and more efficient absorption with more than 96.0% working out, it is expedient to use diglycol esters of mixed aliphatic and naphthenic acids in tanning and fatliquoring of wool sheepskins, while their initial concentration can be reduced twice as compared to the emulsion of industrial oil I-12A.

To obtain a mathematical description of the tanning and fatliquoring process of wool sheepskins, the Box-Hunter CCRD was used (Table 2.2).

Experimental data presented in Table. 4.12, were processed on the computer by the program of <http://mnk-online.narod.ru> site. Adequate nonlinear mathematical models were obtained:

$$\hat{y}_1 = 75.15868 + 7.554527x_1 + 3.286234x_3 - 2.516605x_1^2 - 1.453674x_3^2; \quad (4.10)$$

Таблица 4.12

Результаты исследования процесса дубления-жирования меховой овчины

Output variable	Experimental point									
	1	2	3	4	5	6	7	8	9	10
y_1	82,0	67,0	80,0	66,0	73,0	62,0	74,0	63,0	84,0	53,0
y_2	0,23	0,07	0,18	0,05	0,32	0,10	0,39	0,07	0,38	0,01
y_3	0,31	0,39	0,07	0,11	0,22	0,34	0,06	0,09	0,13	0,38
y_4	13,3	15,0	13,9	14,1	14,4	14,6	13,0	12,4	12,1	11,0
y_5	32,0	28,0	25,0	23,0	42,0	29,0	34,0	26,0	24,0	18,0

Table 4.12 cont.

Output variable	Experimental point									
	11	12	13	14	15	16	17	18	19	20
y_1	76,0	74,0	78,0	65,0	75,0	76,0	76,0	75,0	76,0	74,0
y_2	0,07	0,09	0,04	0,26	0,08	0,06	0,07	0,08	0,06	0,05
y_3	0,47	0,02	0,10	0,02	0,06	0,04	0,05	0,05	0,04	0,06
y_4	15,0	13,1	14,0	11,7	14,5	14,7	14,8	14,6	13,9	14,3
y_5	49,0	27,0	40,0	47,0	45,0	44,0	43,0	43,0	45,0	42,0

$$\hat{y}_2 = 6.899538 \times 10^{-2} + 0.1063848x_1 - 5.273804 \times 10^{-2}x_3 - 0.03125x_1x_3 + 5.065681 \times 10^{-2}x_1^2 + 9.911359 \times 10^{-3}x_2^2 + 3.471295 \times 10^{-2}x_3^2; \quad (4.11)$$

$$\hat{y}_3 = 4.489408 \times 10^{-2} - 5.056871 \times 10^{-2}x_1 + 0.1235635x_2 + 2.230887 \times 10^{-2}x_3 + 7.507578 \times 10^{-2}x_1^2 + 7.153273 \times 10^{-2}x_2^2 + 5.985676 \times 10^{-3}x_3^2; \quad (4.12)$$

$$\hat{y}_4 = 14.503 + 0.5197583x_2 + 0.4224321x_3 - 0.8041492x_1^2 - 0.3435463x_3^2; \quad (4.13)$$

$$\hat{y}_5 = 44.289 + 2.717519x_1 + 4.394348x_2 - 2.547491x_3 - 8.983685x_1^2 - 2.960438x_2^2 - 1.011742x_3^2. \quad (4.14)$$

The degree of influence of the factors on the output variables that characterize the tanning and fatliquoring process of wool sheepskins is determined similarly to the analysis of the original equations (2.2)–(2.4). On the basis of the equations (4.10)–(4.14) graphic dependences were obtained. In particular, the degree of their influence on the concentration of Cr_2O_3 in the spent technological solution in the zones of minimum and maximum is shown in **Fig. 4.3**. As it can be seen from the analysis of the figure and other similar dependences, the output variables, except for y_3 , are most affected in both zones by the concentration of BCS with the initial basicity of 35–40 %, and, this effect on the content of FS in

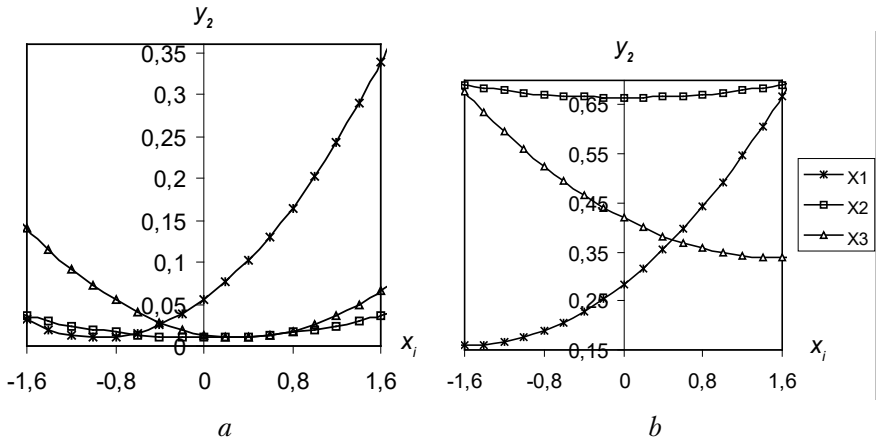


Fig. 4.3. Ranking of factors by the degree of influence on the output variable y_2 in the zones of minimum (a) and maximum (b)

the spent solution is 1.5–1.6 times weaker than the initial concentration of dipropylene glycol sulfated ester. The concentration of Cr_2O_3 in the spent solution depends on its initial concentration and the pH value of the medium at the second stage of tanning. In addition, the effect of the concentration of Cr_2O_3 in the zone of maximum relative to the pH value of the medium decreases by 1.6 times compared with the effect in the minimum zone, and the initial concentration of DPGES hardly affects. Similarly, but in the opposite direction, the factors influence the temperature of welding.

The physicommechanical properties of the skin tissue are strongly influenced by all factors that are analyzed, and the effect of the concentration of Cr_2O_3 on the tensile strength while stretching the skin tissue only by 1.25 times exaggerates the effect in both zones and to the same extent both the concentration of DPGES and the pH of the medium at the second stage of tanning. The total elongation of the skin tissue at the stress of 4.9 MPa is very dependent on the initial concentration of Cr_2O_3 , which exceeds the effect of the initial concentration of fat by 1.6 times and by 3.0 times the pH at the second stage of tanning affecting the skin tissue elongation.

Significant excess of the influence of the initial concentration of Cr_2O_3 on elongation compared with the pH factor of the second stage indicates its value approximate to the optimum, which is consistent with the mechanism of collagen stabilizing. Increasing the initial concentration of Cr_2O_3 and the pH of the medium at the second stage of tanning will promote excessive formation of the third type bonds, that is, the deposition of chromium tanning agent on the surface of ultrastructural elements of the skin tissue and their transformation into stiffer structure fibers that can reduce production and application properties of furs.

After tabulating the quasi-one-factor dependences of the general type (2.5) for each of the factors fixing other variables at ± 1.68 levels and in the center of the design from equations (4.10)–(4.14), graphic interpretations of the results of the study which, in particular for the concentration of Cr_2O_3 in the spent technological solution, are shown in **Fig. 4.4**.

As it can be seen from the figure that reducing the initial concentration of chromium tanning agent with the initial basicity value of

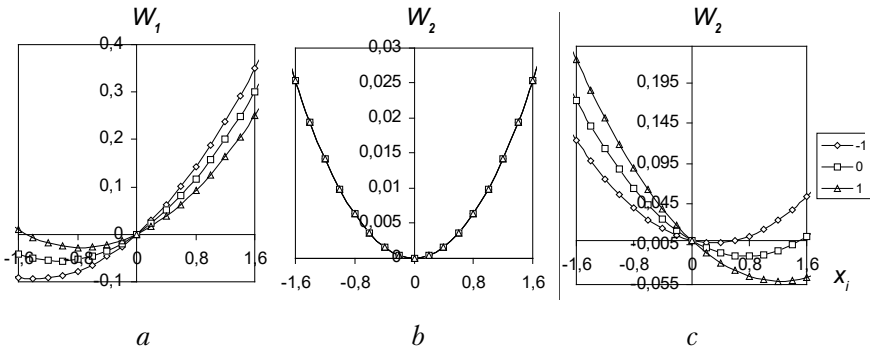


Fig. 4.4. Degree of influence of x_1 (a), x_2 (b), x_3 (c) factors on the output variable y_2

35–40 % with $x_2 = x_3 = -1.68$ in the concentration of Cr_2O_3 in the spent solution decreases. The x_1 factor requires an experiment in the negative zone. In this case, the maximum absorption of chromium tanning agent is achieved under its influence. The bend of this curve indicates the ambiguity of influence of the analyzed factors on y_2 . x_3 factor is opposite to x_1 — the pH value at the second stage of tanning, which, by fixing other factors at 1.68, has the weakest effect on the residual concentration of Cr_2O_3 , and its reduction is accompanied by an increase in its content in the spent technological solution. It is desirable for x_3 factor that the sheepskin tanning process be completed in the positive zone of the experiment and have the greatest impact on the output variable by fixing other factors at +1.68. Thus, the process must take place under the conditions in which the optimal effect of each of the factors x_1 and x_3 on y_2 will be taken into account.

The initial concentration of ДПГЕС shows one-valued effect on the concentration of Cr_2O_3 in the spent solution, regardless of the influence of x_1 and x_3 factors, whose optimal effect is reached in the center of the design. This is evidenced by an optimization search (**Fig. 4.5**).

Increasing the initial concentration of Cr_2O_3 and the pH at the second stage of tanning leads to an increase in the welding temperature of the skin tissue, and the process must take place in the positive zone of the experiment. To reduce the concentration of fat in the spent solution, the experiment, by contrast, must be carried out in the negative zone for

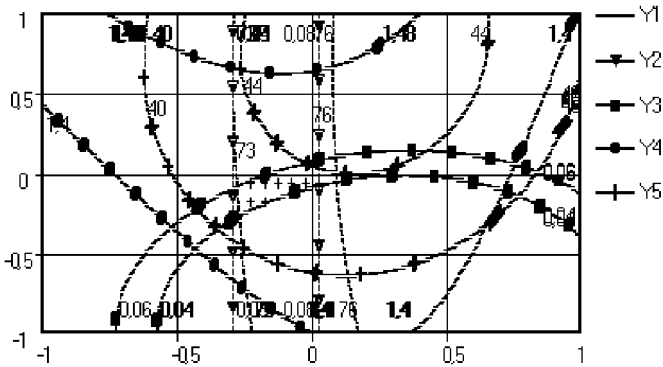


Fig. 4.5. Compromise area of sheepskin tanning and fatliquoring in coded coordinates

x_2 and x_3 factors with a slight shift from the center of the design towards the positive zone of x_1 factor. Physical and mechanical properties of the skin tissue are improved with the growth of x_2 , and this factor linearly affects the strengthening of the skin tissue. To improve the indicator of the skin tissue elongation at 4.9 MPa, it is desirable to conduct the experiment in the positive zone at x_2 , and in the negative one at x_3 .

Consequently, ambiguous and often opposite effects of factors on output variables strongly influence both technological and application properties, as well as ecological safety of the environment, they require a compromise search for the zone of the tanning and fatliquoring processes of wool sheepskins for its optimization.

The search for optimal values of the tanning and fatliquoring mode is carried out by means of a generalized desirability function [34] prepared according to the given models. According to this approach of obtaining the optimal process control vector, the limits to the output variables that correspond to their best and worst values are the following: y_1 – 73.0 and 76.0 °C, y_2 – 0.08 and 0.05 g/dm³, y_3 – 0.06 and 0.04 g/dm³, y_4 – 1.39 and 1.48 MPa, y_5 – 42.0 and 45.0 %. The optimal parameters of the investigated process have been obtained by finding the maximum of a generalized desirability function by the method of scanning with the search accuracy of 0.01 in the range $-1...+1$ for all factors by the

program given in Annex B. In this case, the control vector of the technological process is located at the point with the coordinates: $X_1 = 1.01$ g/dm³, $X_2 = 3.91$ g/dm³ and $X_3 = 3.55$, and the output variables have the following values: $y_1 = 75.8$ °C, $y_2 = 0.064$ g/dm³, $y_3 = 0.041$ g/dm³, $y_4 = 14.5$ MPa, $y_5 = 43.0$ %. A compromise area for $x_3 = 0$, obtained in a coded form, is presented in Fig. 4.5. For comparison, the output variables have been determined after the process by the modern technology and the following experimental data have been obtained: $y_1 = 76.0$ °C, $y_2 = 0.48$ g/dm³, $y_3 = 6.2$ g/dm³, $y_4 = 13.0$ MPa, $y_5 = 35.0$ %.

Thus, a low-waste ecologically-oriented technology of tanning and fatliquoring of wool sheepskins with the use of sulfated dipropylene glycol ester has been developed. The technology, due to the application of anionic initial form of chromium (III) complexes and higher than the industrial oil I-12A dispersion of particles of the emulsion, makes it possible, in comparison with the modern technology, to reduce the consumption of chromium tanning agent by 33 %, and fat substances by 2.5 times without the use of surface-active substance and turpentine. In this case, finished sheepskins comply with the State standard of Ukraine and achieve virtually complete absorption of chromium tanning agent and fat substances from the technological solution.

4.2.2. Tanning and fatliquoring of the fur rabbit

The results of the development of low-waste tanning and fatliquoring technology of wool sheepskins using dipropylene glycol sulfated ester in the process of tanning [32, 35] contributed to the invention of the technology of anion-cationic tanning of rabbit skins. The technology of processing raw furs with a dense structure of the skin tissue involves changing the concentration of chemical reagents in a wide range, depending on its thickness. The use of emulsions of fat materials with active groups in the technology for processing rabbit skins and changing the mode of transforming anion BCS into a soluble state makes it possible to significantly reduce the consumption of reagents and the processing time by low-waste technology. At the same time, rabbit skins with the skin tissue thickness of up to 0.7 mm are treated

with a combined variant of pickling-tanning-fatliquoring without the use of aluminum potassium alum.

The electrolyte fatliquoring emulsion ДИПЕС is added to the acid-salt solution one hour after the beginning of pickling. Sodium thiosulfate is added in accordance with the requirements of the standard technology depending on the thickness of the skin tissue, mm: up to 0.5 – in 4 hours, 0.5–0.7–8 hours after the beginning of pickling, and in one hour, on a one-off basis, it is added to the technological solution of BCS. Two hours after the addition of chromium tanning agent with the full coloring of the skin in the rump area, the *pH* of the technological liquid is adjusted by small portions of sodium bicarbonate solution to the value of 3.6–3.3. Tanning continues for two more hours to the welding temperature of the skin tissue that is equal to the technological requirements (58–60 °C). The mode of mixing of the technological solution meets the requirements of the standard technology.

For skins with the thickness of more than 0.7 mm, the pickling is carried out according to the standard technology during the second soaking, followed by laying for 80–90 hours, shaking, staking, and shaving. Tanning is carried out in the presence of 7 g/dm³ of electrolyte-resistant fat emulsion, the ingredients of which, apart from dipropylene glycol sulfated ester, may be an emulsion of mixtures of sulfated and unsulphated esters in the ratio of 3/2. At the beginning of the process, sodium thiosulfate and fatliquoring emulsion are added together with sodium chloride, and BCS, two hours after the loading of skins. Five hours after the beginning of the process, after the complete dyeing process, the basicity of chromium compounds increases in small portions of 5 % aqueous sodium carbonate solution (0.3–0.4 g/dm³) to the *pH* of 3.7–3.9. The welding temperature, which must meet the technological requirements, is checked 2–3 hours later, after adjusting the *pH* of the fatliquoring and tanning solution.

The results of the study of spent solutions, the chemical composition of the skin tissue and the standardized properties of undressed rabbit skins, obtained according to different variants of the technology (**Table 4.13**), indicate significant differences in the corresponding indicators from the samples of a fur rabbit skins obtained by the previously known technology.

Table 4.13

Properties of rabbit skins of anion-cation tanning

Indicator	Initial concentration of Cr_2O_3 , g/dm ³			
	0,75	0,90	1,00	1,60
The skin tissue thickness, mm	0,47	0,64	$\frac{1,24}{0,47}$	1,24
Concentration of Cr_2O_3 after tanning, g/dm ³	0,23	0,31	$\frac{0,23}{0,52}$	$\frac{0,86}{0,98}$
Content in the skin tissue of, %, Cr_2O_3	1,48	1,45	$\frac{1,36}{1,27}$	$\frac{1,65}{1,47}$
unbound fat substances	18,6	19,1	$\frac{17,9}{19,3}$	$\frac{17,3}{19,6}$
Welding temperature of the skin tissue, °C,				
after tanning	61,0	59,0	$\frac{61,0}{63,0}$	$\frac{72,0}{62,0}$
after 12 hours	73,0	72,0	$\frac{75,0}{67,0}$	$\frac{79,0}{66,0}$
Ultimate tensile strength while stretching the straps, MPa	13,9	14,6	$\frac{12,4}{11,8}$	$\frac{13,2}{12,0}$

Note. Experimental data of the denominator were obtained according to the standard undressing technology of fur rabbit skins

Significant differences are observed with the use of Cr_2O_3 concentration of 1 g/dm³, which corresponds to a standard version of the treatment of a fur rabbit skins with the skin tissue thickness of up to 0.5 mm. While tanning and fatliquoring rabbit skins with the thickness of the skin tissue of 1.24 mm according to the research technology developed for wool sheepskins, even with a two-fold reduction in the technological time of tanning and fatliquoring, in comparison with the standard technology, the skin tissue with the welding temperature (after laying the rabbit skins for 12 hours) by 8 °C higher compared to the reference variant of the technology.

The use of chromium tanning agent in the anion initial form adding the emulsion of dipropylene glycol sulfated ester or its mixture with a dipropylene glycol ester in the ratio of 3/2 contributes to the more effective use of chromium compounds (III) compared to the standard technology due to higher diffusion ability, followed by an active interaction with carboxyl groups of collagen. When tanning the samples of rabbits with the same skin tissue thickness (1.24 mm) according to the experimental and standard technologies, the concentration of Cr_2O_3 in spent solutions is, in the first case, three times less than the lower initial consumption of the tanning agent, and the temperature of welding after laying is by 9 °C higher even with less content Cr_2O_3 in the skin tissue. Indicators of the tensile strength while stretching straps of the skin tissue in both cases practically do not differ and meet the requirements of the standard.

Therefore, the use of an emulsion of dipropylene glycol sulfated ester of its mixture with diethylene glycol ester in the ratio of 3/2 and the anion initial form of chrome tanning agent allows a twofold reduction of the tanning process duration. At the same time, it reduces by 25–37 % the initial concentration of chromium compounds in technological solutions without the use of aluminum compounds and surface-active non-ionogenic substances, or relating to the variant of the standard technology, which involves the use of chromium tanning agent of two basicities (5.0 and 35–40 %), allows two- or threefold reduction in the environmental load due to a significant decrease in the content of chromium oxide (III) in the effluent water. Due to a number of advantages of the developed low-waste energy-saving technology of tanning and fatliquoring of wool sheepskins and rabbit skins, they can be promising for the processing of other types of raw furs.

4.3. Manufacture of high-quality fur semi-finished products with increased hydrothermal stability

The use of acid dyes and a higher temperature of the process in the technology for dyeing the hair of furs are explained by the need to

increase the hydrothermal skin tissue resistance of the semi-finished product. The use of acid dyes for a relatively simple and environmentally friendly coloring method, in comparison with oxidizing semi-finished products, in practice makes it possible to get brighter, light-resistant products with a rich coloration of a wide range of colors and shades. However, in this case the process takes place at higher temperatures (55–65 °C). For this purpose, the standard technology of dyeing of fur skins implies an additional process – retanning of the semi-finished product. Thus, wool sheepskins are retanned after sammying, and rabbit skins – after receiving the undressed semi-finished product, respectively, for the LQ of 8 and 15 with the consumption of, g/dm³: BCS – 3.5 and 3.0 Cr₂O₃, sodium chloride – 40.0 and 20.0, sodium carbonate – up to 0.5, and the non-ionogenic surfactant – 0.5.

After dyeing the semi-finished product, a two- or three-fold washing is performed, and the first one – using the non-ionogenic surfactant in the amount of 1.0–2.0 g/dm³ (depending on the color). It is finished with salting and fatliquoring with the consumption of, g/dm³: emulsion of industrial oil I-12A – 11.0, sodium chloride – 20.0 and turpentine – 0.5. To reduce the consumption of chemical materials, achieve their higher absorption and reduce the length of the technological process, the technology of obtaining the skin tissue of fur skins with increased hydrothermal resistance has been developed immediately in the process of tanning.

Under this technology [60] in the process of combined pickling and fatliquoring, semi-fine wool sheepskins are treated with ДИТЕС or ДИПЕ emulsion with the respective consumption of 5.0 or 5.5 g/dm³, which has dispersing properties in relation to natural fat substances that are left in the skin tissue, instead of the emulsion of industrial oil I-12A with the concentration of 11 g/dm³ by the standard technology in the presence of turpentine. During the subsequent tanning, АКЕА is added to the technological solution in the amount of 0.5–1.0 g/dm³ for NK or 1.0–2.0 g/dm³ for AC, and after 30 minutes – the calculated amount of BCS with 30–40 % basicity (**Table 4.14**). After one hour of treatment, sodium thiosulfate is added to the working solution, as by the standard technology in the amount of 2 g/dm³, and in 1.5–2.0 hours, after end-to-end dyeing of a dense part of the skin tissue, the

Table 4.14

Properties of fur skins after anionic-cationic tanning

Indicator	Initial concentration of chromium oxide (III), g/dm ³									
	2,10	2,30	2,30	2,50	2,90	1,6+3,0*	2,50	1,5+3,5*		
Kind of raw materials	rabbit skin									
Thickness of the skin tissue, mm	1,18	1,18	0,64	1,18	1,18	0,96	1,80	1,80	wool sheepskin	
Basicity of a chrome tanning agent, %	27	30	37	35	42	35	35	35	35	
Concentration of Cr_2O_3 , g/dm ³ , after tanning	1,24	1,17	1,13	1,29	1,58	2,60	1,21	2,63		
Alkyl carboxy ethanalamine, g/dm ³	0,5	0,70	0,85	0,85	1,20	—	1,00	—		
Content in the skin tissue, mass %, Cr_2O_3 unbound fat substances	2,59 19,2	2,89 18,2	2,87 18,4	2,98 19,6	3,28 17,0	2,82 12,1	3,12 17,3	3,75 10,7		
Temperature of welding, °C, after tanning	82,0	88,0	90,0	91,0	92,0	87,0	91,0	93,0		
after 12 hours of laying	84,0	90,0	93,0	93,0	94,0	90,0	94,0	95,0		
Ultimate tensile strength while stretching, MPa	12,5	12,9	12,4	13,6	11,3	10,9	13,2	11,0		
Total elongation at 4.9 MPa, %	29,0	39,0	39,0	37,0	33,0	31,0	48,0	36,0		
Surface yield, % of raw skins	79,9	86,7	86,3	87,1	81,1	80,1	85,2	79,0		

Notes:

1. The symbols * correspond to the concentrations of Cr_2O_3 in the two-stage tanning of skins according to the standard technology
2. Mass % is calculated in terms of a completely dry substance

rump, in small portions 5 % aqueous solution of sodium carbonate up to the pH of 3.8. In one hour of tanning after adding sodium carbonate, the hydrothermal resistance of the skin tissue reaches the technological requirements (90 °C).

Rabbit skins are treated in a similar way, but due to significant fluctuations in the thickness of their skin tissue, the duration of the tanning process varies according to the groups of skins recommended by the standard technology. Because of this, the development of tanning technology of rabbit skins with an increased hydrothermal resistance of the skin tissue was carried out without its shaving after acid–salt treatment. Unlike the tanning technology of wool sheepskins, the treatment of rabbit skins significantly depends on the duration of pickling for varied thickness of their skin tissue, which is carried out in accordance with the standard technology.

After the specified duration of technological laying and beating of rabbit skins, they were treated with the consumption of 40 g/dm³ of sodium chloride. The consumption of sodium thiosulfate was increased to 4 and 6 g/dm³, respectively, for thicknesses up to 0.7 mm or more, and the pH was adjusted to 3.9 by sodium carbonate solution, as provided by the standard technology. DPGES or DPGE emulsions are spent in the amount of 7 g/dm³ instead of the industrial oil I-12A emulsion or one of the greasing emulsions obtained from the imported materials Grassan A, Chromopol UFW of *Trumpler* company (Germany), taken in the amount of 16.5 or 10 g/dm³, respectively.

The results of testing of the rabbit and wool sheepskin tissue treated with technology [36] are shown in **Table 3.32**. It is evident from the experimental data obtained with different initial concentrations of BCS that the hydrothermal resistance of the rabbit skin tissue of 1.15–1.20 mm thickness in the raw material grows with the increase in BCS concentration, but disproportionate to its content in the technological solution. Thus, initial concentrations of BCS in the amount of 2.5 and 2.9 g/dm³ of Cr_2O_3 allow to receive the same hydrothermal resistance of the skin tissue in 12 hours after tanning – 93 °C, which is connected with different initial basicity of chromium complexes (III) that corresponds to 35 and 42 %. This increases the content of Cr_2O_3 in the spent solution. This is caused by some steric complications with

the diffusion of chromium complexes (III) into the dense structure of the rabbit skin tissue. Obviously, the size of stabilized AKEA chromium complexes (III) with the basicity of 42 % complicates their placement between collagen macromolecules in the depth of the skin tissue.

Decreasing the initial BCS concentration of 27 % basicity in a tanning solution up to 2.1 g/dm^3 of Cr_2O_3 prevents the achievement of the required hydrothermal resistance. Increasing the same concentration of BCS up to 2.3 g/dm^3 of Cr_2O_3 and the basicity up to 30 % makes it possible to obtain the rabbit skin tissue with the required hydrothermal stability only after 12 hours of laying after tanning. The BCS concentration of 2.5 g/dm^3 of Cr_2O_3 and higher with 35 % basicity makes it possible to achieve the desired result. However, the efficiency of the use of chrome tanning material is reduced, which is indicated by an increase in its concentration in the spent solution and the content of Cr_2O_3 in the skin tissue (more than 3 %), which is not stipulated by the State Standard of Ukraine.

The semi-fine wool sheepskin with a lower density of the skin tissue structure of a greater thickness (1.75–1.85 mm) is capable of absorbing chromium complexes more actively. It is expressed in the achievement of its sufficient hydrothermal stability at the initial concentration of BCS in the technological solution of 2.5 g/dm^3 of Cr_2O_3 .

Thus, by the developed technology, with a significant reduction in the consumption of chemical materials and duration of the tanning process, fur rabbit skins, which have hydrothermal stability of the skin tissue, sufficient for their dyeing with acid dyes, were obtained.

Descending order with hydrothermal stability the chemical nature of fat substances has an important influence on physical and mechanical properties of the skin tissue [29]. The use of DPGSE in the pickling and fatliquoring process, which has a high sorption capacity, contributes to the increase in the content of fat substances in the skin tissue to the upper limit (20 g/dm^3) provided by the standard. In the case of chemically inert industrial oil I-12A, as provided by the standard technology, that is weakly kept in the skin tissue and in the retanning process, as evidenced by the data, it is easily desorbed and released into the technological solution, and therefore, there is 38.0 % decrease in the content of unbound fat substances in the skin tissue.

The nature of the interaction of used greasing substances with the skin tissue [29] affects the growth of its tensile strength while stretching and full elongation at 4.9 MPa by 19.0–25.0 and 19.0–33.0 %, respectively. At the same time, the full elongation of wool sheepskins at 4.9 MPa exceeds this figure by more than 20 % for rabbit skins. In this case, stronger and more elastic fur skins are obtained in one-stage tanning in comparison with a two-stage process using the emulsion of industrial oil I-12A. In addition, the growth of the area yield of fur skins increases, which is explained by the uniform distribution of fat substances in the structure and the decrease of its agglomeration in the process of removing moisture from the depth of the skin tissue. AKEA, introduced in the process of tanning, partially shields the active centers of collagen and stabilizes dinuclear complexes of chromium (III) [37], contributing to the optimal structure of the skin tissue in the process of anion-cation tanning.

Thus, the developed one-stage resource- and energy-saving technology for tanning and fatliquoring of fur skins using chromium tanning agent of anionic initial type and alkyl carboxy ethanolamines as stabilizers of the basic chromium sulfate and the tanning process and plasticizers of the skin tissue, as well as of dipropylene glycol esters as plasticization and fatliquoring reagents, is characterized by a significant decrease in the consumption of chemical materials. In particular, removal of aluminum potassium alum from the technological process and reduction in the consumption of the basic chromium sulfate and fat substances, respectively, is 1.8 and more than twice when reducing the duration of the process by almost three times compared with the standard technology of two-stage tanning and fatliquoring. Fur skins obtained according to the developed technology with the consumption of BCS g/dm³ of Cr₂O₃ have a 7.8–8.7 % greater area yield than the standard technology, they meet the technological requirements for hydrothermal stability for dyeing with acid dyes and the requirements of the relevant standards in terms of strength and ductility indicators.

4.4. Waterproofing of wool sheepskin

When waterproofing velour and sheepskin tissue [38–40], the alkenemaleic composition is used, which is applied by the spraying method. Due to the hydrophilic nature of the fibrous structure surface, the skin tissue of fur products absorbs moisture relatively quickly. At the same time, sanitary-hygienic, heat-shielding and other application properties, as well as form-stability, deteriorate. After drying, they give shrinkage, rigidity of the skin tissue increases, physical and mechanical parameters decrease.

According to the data obtained (**Table 4.15**), the porosity of the skin tissue of wool sheepskins varies extremely depending on the consumption of the alkenemaleic composition, reaching 74 %, which is by 30 % higher than the corresponding index of wool sheepskin tissue, obtained by the standard technology.

Thus, the experimental wool sheepskin retains the general (open and closed) highly developed porosity with significant diffusion and sorption properties. The increase in porosity observed after waterproofing is caused by a partial decrease in the interaction between hydrophilic areas modified by hydrophobic molecules during moisture removal and the consequent increase in interstructure distances. Excessive consumption of alkenemaleic composition results in its deposition in pores, which is why this indicator decreases. The air permeability, which determines the open porosity, changes in the same way as porosity, that is, the alkenemaleic composition makes it possible to obtain a wool sheepskin with a maximum volume of open pores.

The high degree of waterproofing of the skin tissue surface, obtained by the developed method, can be evidenced by high values of the edge angle of its tempering. The nature of the change in the duration of absorption of a water drop with an increase in the consumption of alkenemaleic composition can be explained by the characteristics of waterproofing of the semi-finished product surface. Collagen fibers are covered with water-proofing agent and their ability to absorb water decreases due to increased surface tension. Reducing waterproofing properties of the fleece surface may lead to a reorientation of water-proofing agent molecules. As a result of an increase in the waterproofing

Table 4.15

Physical and chemical indicators of wool sheepskins

Indicator	Consumption of, g/dm ²						
	alkenemaleic composition						oil emulsion I-12A
	0.15	0.3	0.6	1.0	1.5	2.0	2.0
Porosity, %	59	71	74	70	66	60	57
Air permeability, relative, ml/cm ² ·hour	78.0	110	124	98.0	70.0	48.0	53.0
absolute, min.	7.7	5.4	4.9	6.7	8.6	12.6	13.8
Absorption of a water drop, min.	54	90	94	90	54	53	0.5
Edge angle of tempering, de- gree, after min.:							
1	140	142	140	139	139	137	—
30	119	123	130	120	120	—	—
Vapour permeability absolute, mg/cm ² ·hour	2.84	2.42	2.76	2.51	2.23	2.31	1.90
relative, %	49.0	41.0	47.0	42.5	37.0	40.0	36.0
Water permeability in dy- namic conditions, min.	5.9	18	28	22	20	22	1.0
Soaking, %, after hours:							
2	195	135	130	135	140	140	248
24	240	180	160	160	180	180	270
Porosity, %	67	71	74	70	66	60	57

degree, the effect of water absorption by the sheepskin tissue is reduced to the consumption of alkenemaleic composition of 0.3–0.6 g/dm², and then it remains almost unchanged. During the action of mechanical deformations on the wool sheepskin sample, the duration of watering increases to a certain limit, which indicates an increase in the resistance of water diffusion in the structure of the sample.

The nature of the change in vapor permeability correlates with porosity, which corresponds to the mechanism of moisture passing

through the depth of the wool sheepskin tissue sample by sorption-desorption of water molecules under the action of the pressure gradient. Consequently, vapor permeability, on the one hand, characterizes waterproofing and features of the porous structure of the skin tissue, and on the other hand, the maximum combination of these indicators can be considered as one of the most important in-service and sanitary-hygienic indicators. Waterproofing reveals the plasticization effect of the alkenemaleic composition on the physical and mechanical properties of the skin tissue (**Table 4.16**). At the increased concentration of the waterproofing composition, the amplifying and orientational effects of the sorbed molecules of the modifier on the structure are observed. This is manifested in increasing the ultimate tensile strength and elongation, but when the composition is over 0.6 g/dm², the significant weakening of interfibrillary interactions prevails over the orientational effect that is accompanied by a decrease in these parameters. At the same time, relative residual elongation shows the similar dependence.

The comparative analysis of physico-chemical and physico-mechanical properties of the experimental wool sheepskin, obtained by the standard technology indicates a significant advantage of the developed

Table 4.16

Physical and mechanical indicators of wool sheepskins

Indicator	Consumption of, g/dm ²							By the standard
	alkenemaleic composition						oil emulsion I-12A	
	0.15	0.3	0.6	1.0	1.5	2.0	2.0	
Ultimate tensile strength at break, MPa	9.5	11.2	12.6	11.5	9.2	8.6	8.2	not < 7.8
Elongation under stress 4.9 MPa, %	36.0	38.0	52.0	50.0	56.0	45.0	37.0	not > 30
Elongation relative, %, at break residual	62.0	74.0	86.0	82.0	79.0	70.0	58.0	—
	15.0	18.0	19.0	19.0	21.0	23.0	16.0	—

technology by using a synthesized composition based on α -alkenes polymerized with maleic anhydride. Unlike the standard technology, which involves the use of an inert fatliquoring material with a surface-active non-ionogenic agent Prevocel W-OFP-100 from BASF company (Germany), the developed composition actively interacts with the dermis fibers. This provides plasticization effect on the structure and optimal combination of hydrophilicity of the skin tissue collagen, its porosity with providing a water-repellent effect.

Therefore, significantly increased application properties of wool sheepskins give grounds to remove the formation of film coating on the surface of the skin tissue for the manufacture of sheepskin products. The use of the developed composition for hydrophobic treatment of suede leather, fur velour, wool sheepskin and products made of them, containing α -alkene polymerase with maleic anhydride, makes it possible to obtain fur materials having 30 % higher porosity, in 1.5–1.8 times increased vapor permeability, and by over 20 times less water-absorption in dynamic conditions compared to the material obtained by the standard processing method of wool sheepskins. The invented technology of its processing makes it possible to effectively use the technology of hydrophobization instead of labor- and material-consuming nappalan coating and use products under severe atmospheric conditions without oiling the surface.

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Questions For Self–Control

1. Features of processing technology of raw furs.
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4. Physical and chemical properties of nutria skins after their treatment with activated water.
5. Physical and chemical properties of rabbit skins after their treatment with activated water.
6. Tanning and fatliquoring of the fur semi-finished product.
7. Tanning and fatliquoring of wool sheepskins.
8. Use of the composition of diethylene glycol ester without the addition of industrial oil I-12A in the process of greasing fur skins.
9. Physical and chemical properties of the wool sheepskin tissue with its spherical deformation.
10. Physical and chemical parameters of the wool sheepskin tissue with its uniaxial deformation.
11. The use of diethylene glycol esters of mixed aliphatic and naphthenic acids in the process of tanning and greasing of wool sheepskins.
12. One–stage resource–saving tanning and fatliquoring technology of wool sheepskins using chrome tanning agent of anion initial type and alkyl-carboxy ethanolamines as modifiers of BCS.
13. Tanning and fatliquoring of fur rabbit skins.
14. Properties of fur rabbit skins of anion-cationic tanning.
15. Production of fur semi-finished products with increased hydrothermal stability.
16. Properties of fur skins of anion-cationic tanning.
17. Waterproofing of wool sheepskin.
18. Formation of special purpose fur materials.
19. Influence of washing on the wool sheepskin properties.
20. Flow diagram of aldehyde-silicon-chrome-aluminium tanning of wool sheepskins.
21. Comparative characteristics of the production technology of medical wool sheepskins.

5. ECONOMIC AND ECOLOGICAL EFFICIENCY OF LEATHER AND FUR PRODUCTION TECHNOLOGY

The current state of industrial production in Ukraine, economic efficiency and sustainability of the light industry enterprises are of particular relevance. This is especially true for the productions that involve the use of a wide range and large volumes of environmentally hazardous materials. One of the main directions of solving the problems that occur in the ecological and economic sphere is the formation of a balanced system of nature management and technology ecologization in the industry [1].

The ecological and economic estimation of modern production technology is very important in the context of Ukraine's economy transition to a sustainable development, as it is the basis not only for the substantiation and selection of innovative projects taking into account the level of strategic importance of economic, environmental and social issues, but also the basis for ecologically oriented development of the industries based on the resource saving and reducing the negative environmental impact. To do this, modern methods of solving production and management tasks based on the effective use of resource production potential are required through the introduction of innovative nature, energy, resource-saving, non-waste (or low-waste) technologies, sustainable organization of manufacturing processes and technical re-equipment of the production.

5.1. Methodological provisions of ecologically oriented development of leather and fur production

Under the conditions of a noticeable deficit of all kinds of resources, including the ecological direction investments, one of the main oppor-

tunities for a radical solution to the ecological problem is the transformation of eco-friendly products and services into the product effective for the national economy. At the same time, the three groups of goals are combined: increasing the export potential of Ukraine's industrial complex at the expense of a promising group of environmentally friendly goods and services; solving environmental problems in the country through the use of ecologically oriented production technologies of a new generation; solving the problems of material and energy supply, mainly due to a significant reduction in the need for appropriate resources.

For the first time set in the 1970s, the problem of global environmental emissions identified by the members of the Club of Rome, was further developed in the works of scientists from all over the world, and was reflected in the environmental policy of the governments of many countries, including Ukraine. The choice of the ecological direction of the Ukrainian economy development is caused by a number of reasons [2]:

- environmental problems in the modern world are some of the factors that most of all worry the countries with different levels of development, and the need for eco-friendly goods and services will only increase in the nearest future;
- the greater number of environmental problems in Ukraine has a transboundary character, which enables the country to take leading positions in the international environmental programs;
- ecologically-oriented improvement of the production systems, especially through the reduction of energy intensity and material content of the unit, can become a significant reserve of the investment funds that can be used for the development of promising directions of the economy and a further increase in its efficiency;
- the production of sustainable goods and services is a sphere of production based on a strong scientific potential of Ukraine;
- ecologization of the economy, production of eco-friendly products is an internationally recognized noble goal, which can be implemented through the money of appropriate international funds and rich, economically developed, countries;
- the readiness of the international community to perceive eco-friendly goods.

In 2007, the adoption of the Concept of the National Environmental Policy Strategy for the period up to 2020 (hereinafter – the Strategy) became the result of the work of the Cabinet of Ministers of Ukraine [3]. The purpose of the Strategy is to stabilize and improve the ecological status of the territory of Ukraine by adopting the national environmental policy as an integrated factor in the social and economic development of the country in order to ensure the transition to a sustainable (ecologically balanced) development and implementation of an ecologically balanced system of the nature management. The Concept proclaims the main principles on which the national environmental policy is based: the principle of equality of the three components of the state development (economic, ecological, social); the principle of the ecological responsibility; the principle of environmental risks prevention; the principle of integrating the environmental component into the sectoral policies; “The polluter and the user pay the full price” principle; the principle of a cross-sectoral partnership and the involvement of a wide range of stakeholders into the policy implementation.

An integral part of this Concept is the provision on the State Ecological and Economic Program for the Implementation of Clean Production that offers the solution to top priority tasks, including: training of specialists in the field of environmental management, quality management systems and in the field of environmental protection in the production and the service sector; demonstration projects in the field of international cooperation as well. Financial support for the state policy in this area is expected to be carried out at the expense of budget assignments, deductions from enterprises and organizations, environmental protection funds, investment resources, international aid projects, etc.

The methodological provisions and the development of the methodology for the effectiveness estimation of the economic and ecological activities of the leather industry enterprise on the example of soaking and liming processes of leather production of CJSC *Chinbar* (Ukraine, Kyiv) are presented in this Chapter.

As the research has shown, in order to implement production ecologization in the industry, it is necessary to improve:

- a system of indicators that will meet the information needs for high-quality and truthful information on the state of the

- environmental components of the economic development at all levels of users;
- the methods of ecological and economic estimation of the applied technology, their compliance with the requirements of “clean production” and the readiness to implement its ecologization program;
 - the system of environmental monitoring and regulation of a sustainable activity of economic entities in all spheres (ecological, economic, social and spiritual);
 - the system of specialists’ training in the field of audit, monitoring, inspection and management of sustainable activities of business entities;
 - the mechanism of environmental regulation that is at the stage of its formation, and the main instruments of which are regulators that restrict the destructive activity of commodity producers, rather than inducing them to introduce innovative sustainable methods of farming, the introduction of innovative ecologically oriented technology.

Thus, nowadays, every leather and fur enterprise faces the challenge of transforming the entire complex of technological processes in such a way as to avoid or minimize its negative impact on the environment, using modern advances in science, engineering, technology, and making effective management decisions. This requires not only considerable efforts and material costs, but also the will, desire and some environmental knowledge of managers, engineers, technicians and workers at enterprises of all forms of ownership, raising the population’s ecological consciousness.

At the present stage, in order to prevent the environmental implications of human activity, new approaches to the strategy of industrial enterprises development are needed, and the methodology of their formation should be based on one of the main principles of sustainable development – the principle of ecological and economic equilibrium. At the same time, improvement of the use and reproduction of natural potential is realized through the process of social production ecologization, which acts as a complex system of measures of organizational, legal, economic, and technological nature, aimed at ensuring the eco-friendly properties of economic processes.

The analysis of theoretical approaches to solving the issues of ecological and economic estimation of production technologies [4] has shown that studies in this area are devoted to the issues of economic efficiency of innovative environmental projects, the formation of a system of indicators for the diagnosis of economic and environmental safety of economic systems, indicators of an integrated impact of both individual enterprises and their aggregates on the ecological status of a particular territory, ecological and economic level of technologies (operations, processes), improvement of methods of project analysis in terms of their environmental impact, etc. They point out that due to the existence of technology that has a negative impact on the environment and is characterized by a high level of resource intensity, in context of the transition to sustainable development, there should be developed an innovative methodical approach to the estimation of applied and advanced production technology, formed a system of indicators, and improved methods of assessing the national and regional ecological status associated with the processes of restructuring both the industry and other sectors of the Ukrainian economy.

The need for an environmental impact estimation appears when designing, constructing, renovating, placing, commissioning, putting enterprises, buildings and facilities into operation, analyzing existing and substantiating new production technology, etc. This raises the question of the formation of a system of indicators by which an estimation of economic activity impact on the environment will be carried out. Along with the standard indicators of investment analysis and those that estimate the environmental risks, benefits and costs associated with the implementation of projects, the task of finding parameters that will more fully take into account the specifics of production technology in various industries and of environmental investment projects.

In the world practice, for the estimation of the system of environmental protection measures the following indicators are used:

- absolute indicators (amount of emissions, discharges, waste);
- relative (changes in the amount of emissions, discharges, waste compared to the previous years or with the use of alternative technologies);
- economic (costs to protect the environment);
- integral indicators of cleanness and isolation.

The indicators of economic and environmental safety [5], which characterize the degree of protection against a negative environmental impact to achieve the goals of the social and economic system, include the following ones: “green” GDP; emissions of harmful substances; the share of potentially hazardous industries (of chemical, petrochemical, metallurgical, energy industries) in the industry structure; the share of manufacturing industry in the total volume of industrial production; material and energy intensity of products; the level of losses from the emergencies of anthropogenic nature; costs of preservation and destruction of secondary raw materials; the area occupied by waste; capital investments and current expenditures (major repairs of the main means of environmental protection, radiation safety, biodiversity and habitat conservation, research activities) of enterprises, organizations, institutions for the protection and management of natural resources according to the sources of financing (according to the types of economic activity and the regions), as well as environmental payments for the environmental pollution (presented and actually paid), etc.

In assessing environmental innovation projects, the indicators that should be given priority are: the level of progressive environmental innovation according to the environmental pollution level, the weight and degree of suppressed harmful emissions, the indicator of ecological and resource intensity, energy intensity, the degree of the technological cycle completion, the degree of resources and waste recycling.

The research conducted at the enterprises of leather and fur sectors of the light industry made it possible to identify the following groups of indicators that determine the ecological level of soaking and liming technology:

I. Indicators that characterize the sustainability of the production process (the content of chemicals in working solutions, the harmfulness of chemicals used for their preparation by hazard classes, water consumption in order to fulfill the process of production and energy; the harmfulness of working conditions).

II. Indicators that characterize the environmental impact of technology on the environment (volumes of spent solutions, the content of chemicals used for their preparation, the disposal of waste solutions, the harmfulness of chemicals (by classes of hazard), the possibility of reuse of waste solutions).

III. Indicators of ecological cleanness of products (harmfulness of products for the user and the environment at the stage of its utilization).

Ecological impact estimation is a definition of the nature and the extent of all potential effects from the projected economic activity and the expected environmental and economic consequences of possible implementation of projects. Its main objective is to promote environmental safety, restoration and reproduction of resources on the basis of: comprehensive study of the environmental impacts of the programmed activities in the region, careful study of possible alternatives to achieving one or another goal; analysis of the effectiveness of the proposed measures concerning environmental safety, prevention of emergencies; strengthening of environmental priorities in the process of making economic decisions.

The impact on the environment can be determined through the estimation of:

1. A new project to make a decision on its implementation.
2. Modern enterprises in order to reduce the negative impact on the environment through their reconstruction, the introduction of new environmentally oriented production technologies.
- 3 The level of environmental protection measures in order to increase their efficiency (modernization and implementation of new treatment facilities and other modern facilities for the environmental protection).

Very important in this case is resource conservation, which is a factor in the nature use rationalization, which enables not only to obtain the maximum final economic result with a minimum use of resources in the production process, but also prevents pollution of the environment. Resource conservation has a dual orientation: on the one hand, the formation of a modern economic system requires the full and careful use of all kinds of resources, but on the other hand, it is a prerequisite for the environment rationalization. The central part of resource conservation is the elimination of losses and inappropriate consumption of raw materials.

The theoretical search and practical research (comparison of the four previously described methods of soaking and liming, in particular a typical technology of one-stage liming technology (hereinafter

OSL-T) commonly used at most enterprises of the leather industry and new ones – one-stage and two-stage liming (OSL, TSL-1, TSL-4)) resulted in a method of ecological and economic estimation of soaking and liming technology in leather production [4], which covers the following stages.

Stage I. Analysis of the relative level of resource intensity of the investigated technology. At this stage, on the basis of information on the costs of material and energy resources per one ton of raw materials when various technologies are applied, individual and group indicators of the relative level of their resource intensity are calculated.

The individual indicators of the relative level of the resource intensity of technology are determined by means of standardization relative to the reference value by the formula:

$$q_{ij} = \frac{p_i^{em}}{p_{ij}}, \quad (5.1)$$

where p_i^{em} – costs of i type of resource per one ton of raw materials when applying the reference technology (natural units); p_{ij} – costs of i type of resource per one ton of raw materials when applying j technology (natural units).

The group indicators of the relative level of the resource intensity of technologies are determined by the method of the additive convolution of the individual:

$$R_j = \sum q_{ij} \cdot \alpha_i, \quad (5.2)$$

where α_i – validity of i type of a resource.

The validity of individual indicators α_i that characterize the relative level of technology resource intensity by different constituents is defined as the share of costs of i type of resource in the total cost of all consumed resources:

$$\alpha_i = \mathcal{Z}_i / \sum_{i=1}^n \mathcal{Z}_i, \quad (5.3)$$

where \mathcal{Z}_i – costs of i type of resource per 1 ton of raw materials, UAH (calculated as the product of the price per unit of resource P_i and norms of consumption of this resource per one ton of raw materials H_o).

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The results of calculations of individual and group indicators that characterize the relative level of resource intensity of the investigated technologies are shown in **Table. 5.1**.

Table 5.1

Calculation of unidual and group indicators of resource intensity in soaking and liming technologies of leather production

Resources	Technology			
	OSL3	TSL-1	TSL-4	TSL-T
Sodium sulfide	20.00	20.00	21.00	29.50
α_i	0.47			
q_{ij}	1.48	1.48	1.40	1.00
Calcium hydroxide	24.00	30.00	33.00	80.80
α_i	0.48			
q_{ij}	3.37	2.69	2.45	1.00
Water	5.00	4.20	4.80	11.50
α_i	0.04			
q_{ij}	2.30	2.74	2.40	1.00
Energy	22.70	18.60	20.60	38.30
α_i	0.01			
q_{ij}	1.69	2.06	1.86	1.00
R_j	2.42	2.12	1.95	1.00

As it can be seen from the data in **Table 5.1**, the OSL technology is in priority by the level of resource intensity, the group indicator of the relative level of the resource intensity of which has a value of 2.42. In comparison with this, these indicators for TSL-1, TSL-4 and OSL-T technologies are lower (2.12, 1.95 and 1.00, respectively). This shows that the technology of OSL is the most resource-saving and therefore economically the most attractive among the studied ones.

Stag II. Estimation of the impact of technologies on the environment.
At this stage, based on information about the content of spent liquid

of harmful substances in one dm³, an analysis of the relative level of technology impact on the natural environment is carried out.

In accordance with the proposed methodology, it is assumed that the relative individual and group indicators of the level of influence of the investigated technologies on the environment are to be calculated (Table 5.2).

Table 5.2

Calculation of individual and group indicators of soaking and liming technology impact on the environment

Pollutant	Technology			
	OCL	TSL-1	TSL-4	OCL-T*
Sodium sulfide	4.30	4.80	4.60	8.00
α_i	0.4			
q_{ij}	1.86	1.67	1.74	1.00
Keratin	19.00	0.80	0.50	19.00
α_i	0.4			
q_{ij}	1.00	23.75	38.00	1.00
Calcium hydroxide	3.60	4.00	4.20	16.00
α_i	0.2			
q_{ij}	4.44	4.00	3.81	1.00
R_j	2.72	7.02	9.82	1.00

When doing this, the formulas offered at the first stage can be used. But in this case, the symbols in the formulas (5.1) and (5.2) acquire a different meaning: q_{ij} – relative individual values of the influence of the technological process on the environment when applying j technology; p_i^{em} – content of i pollutant type in one dm³ of spent liquid when applying the reference technology; p_{ij} – content of i pollutant type in one dm³ of spent liquid with the application of j technology; R_j – relative group indicators of the impact of the technological process on the environment when applying j technology; α_i – validity of i pollutant type.

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Given the peculiarities of this stage of calculation, the validity of the indicators of content of spent liquid of harmful impurities in one dm³ should be determined, based on the hazard class and substance hazard, according to the ranked estimation method (**Table 5.3**). It is known that all harmful chemicals are divided into IV classes of hazard. In this estimation, as at the first stage, they should be considered as a destimulators (a lower grade is assigned to safer substances).

Table 5.3

Determination of the importance of the indicators of the impact of technology on the environment according to the classes of hazardous pollutants

Pollutant	Class of hazard	Rank	α_i
Sodium sulfide	II	2	0.40
Keratin	II	2	0.40
Calcium hydroxide	III	1	0.20
Amount	–	5	1.00

Stage III Analysis of alternative technologies and their ranking in order of their priority decreasing in making decisions on their production applications, taking into account the achievement of strategic goals – minimizing the impact on the environment and reducing the resource intensity.

The conducted studies make it possible to regulate technologies that are analyzed, according to their priority in achieving the set goals – environmental, economic, ecologico-economic (**Table 5.4**). It is evident from **Table 5.4** that in justifying the choice of production technology it is necessary to take into account the priorities of enterprise development. Thus, TSL-4 technology is the most promising from the point of view of achieving environmental goals.

So, this technique makes it possible to choose the technology that meets the goals of ecologically-oriented development of enterprises of leather production. The solution to this problem is possible by replacing the standard technology (quite harmful to the environment and inefficient in modern conditions) with the newest ecologically oriented

Table 5.4

Ranking of technologies in order of their priority decreasing

Goals that are achieved	Ranks			
	1	2	3	4
economic	OCL	TSL-1	TSL-4	OCL-T
environmental	TSL-4	TSL-1	OSL	OCL-T

one, which together with the development and implementation of an environmentally-oriented strategy will give the company a number of competitive advantages. Such advantages are achieved through the efficient use of resources; positive relationships with stakeholders; improvement of information support; guarantees of compliance with the requirements of the current legislation; improvement of product quality; reduction of insurance payments; reduction of negative consequences of environmental risks; improvement of relations with the local population; reducing financial payments and sanctions, etc.

5.2. Economic and environmental estimation of innovative technologies

The global nature of environmental problems that affect the modern economic development of industrial enterprises, necessitates systematic research in the field of assessing the economic and environmental aspects of the effectiveness of technology and the activities of the enterprises of leather production in general. Eurointegration processes and the state strategy of sustainable development of Ukraine are encouraging domestic enterprises to operate in accordance with modern economic, environmental and social requirements. Efficiency of the industrial enterprise management, along with innovative technologies, largely determines their economic and environmental performance. In this case, a significant role belongs to the mechanism of ecologization of production processes [6] in the direction of ecologically-oriented development of production; environmental product life cycle – the one

that has the least impact on the environment during the manufacture, consumption and disposal, as well as the reduction of environmental pollution; utilization of secondary production resources [7].

In today's conditions, the quality of the transformation of the economic system depends on the factors that provide intensive economic growth, which, first of all, should include, scientific, technical, environmental and social factors. Therefore, the complex solution to modern economic and environmental problems will be facilitated by the ecologization of enterprises in the industrial sphere through the introduction of innovations, in particular, ecologically oriented technologies. The economic aspects of the development of light industry enterprises, including fur and leather ones, are usually considered separately from the environmental aspects. Consequently, certain ecological and economic aspects of their development, in particular, the fur and leather industry, are an urgent topic. The issue of economical and environmental estimation of the efficiency of innovative technologies of fur and leather production requires a further development. In connection with this, a complex of tasks related to the formation of a methodical approach to the environmental and economic estimation of innovative technologies for the production of fur and leather materials is considered.

The analysis of the development of production of fur and leather materials shows that the following factors are responsible for the ecologization of enterprises of the fur and leather industry: the use of a wide range of chemical reagents, including environmentally harmful ones; high resource and material production processes; their significant technogenicity. At the same time, the development of innovative technological processes of fur and leather production is aimed at ensuring not only high technical and economic indicators, but also at reducing the negative impact on the environment. Therefore, there is a need for the formation of appropriate methodological approaches to environmental and economic estimation and the choice of innovative production technologies.

For the implementation of environmental and economic estimation of innovative technologies, it is important to determine their scientific and technical level. To solve this problem it is recommended to determine the scientific and technical level of technology by the most important

technical indicators important for future users, in particular, such as productivity, reliability in operation of technological equipment, energy and material resources of the technology, its ecological compatibility. These parameters are measured for compliance with certain standards or generally accepted levels and used as restrictions in this estimation [8].

According to technical and economic indicators – labour, material and energy intensity, cost value, quality and ecological cleanness – scientists and practitioners recommend to determine the level of perfection of products and technology of their production. It should be noted that the labour, material and energy intensity significantly affects the level of cost value and depends on the organizational and technical level of the enterprise. An important technical and economic indicator is the level of product quality, which determines the possibility of making a profit by the enterprise. Quality does not only depend on the level of technology, but also on market conditions.

When providing ecological and economic estimation of the effectiveness of technologies, it is important to identify such technical and economic indicators as prime cost, quality of products, ecological cleanness of technology and products. At the same time, the introduction of innovative technological solutions at the enterprise is aimed at increasing its efficiency, and therefore, the basic condition is the estimation of economic efficiency necessary for the correct choice of one or another variant of innovation.

The conducted research has shown that the considered methods of environment and economic estimation of innovative technologies are made taking into account the industry features, while the methods of estimation of economic efficiency of scientific developments should have a universal character. In addition, the set of indicators, by which the estimation was conducted, depends to a large extent on the object and purpose of the estimation. Environmental indicators that reflect the specific character of production in the fur and leather industry include the following: the content and harmfulness of chemicals (by classes of hazard) in working solutions; volume and harmfulness of spent solutions (content of harmful chemical reagents in one dm³ of the spent solution); the possibility of reuse and disposal of spent solutions and solid waste from production; ecological cleanness of products (safety of products

for human health in the process of their use); harmfulness of working conditions. The most important technical parameters proposed to be used as a limitation in the estimation are the following: the length of technological processes, their labour intensity, the possibilities of mechanization and automation of production processes.

The algorithm of ecological and economic estimation and selection of innovative technological projects is shown in **Fig. 5.1**. As it can be seen from it, this algorithm involves a certain sequence of research conducting to select the most promising innovative technological project

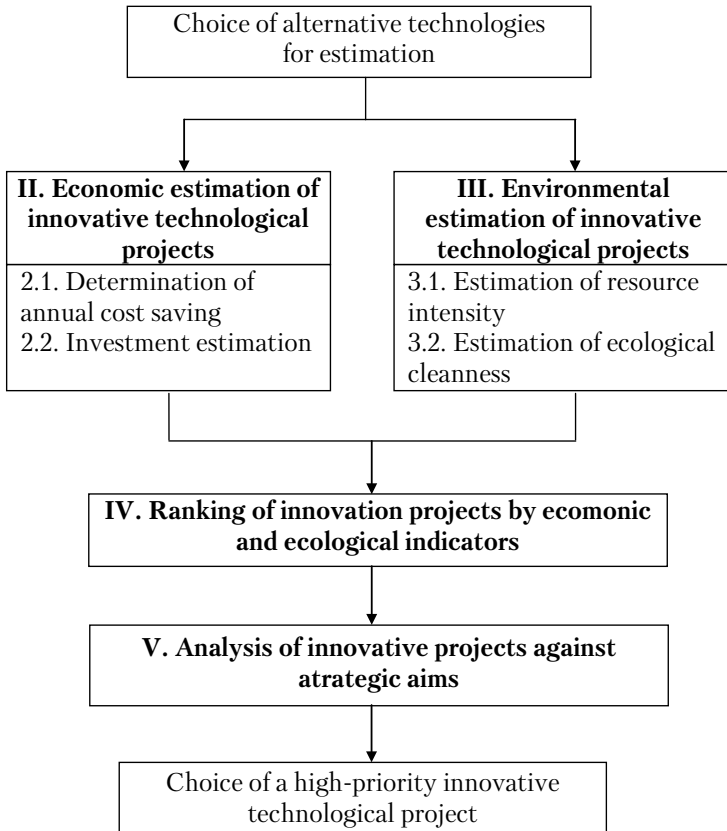


Fig. 5.1. The algorithm of economic and ecological estimation and selection of innovative technological projects

from the economic and ecological point of view. At the same time, for such an analysis, the following processes were chosen in the production of elastic leather made of splitted semi-finished products in relation to the chrome tanning method: chromobentanite and anion-cationic ones in comparison with the existing method.

The estimation of resource intensity is based on information on the consumption of material and energy resources needed to obtain 50.000 dm² of chrome leather materials by comparing innovative technologies with the available one (**Table 5.5**). The indicator of resource intensity of technologies was determined by the formula:

$$R = \frac{\sum B_i}{B_{ich}}, \quad (5.4)$$

where $\sum B_i$ – total consumption of resources by i technology, UAH; B_{cyu} – total consumption of resources by the available technology, UAH.

From the calculations given in **Table. 5.5**, it is clear that the technology of anion-cationic tanning, which has the lowest indicator of resource intensity, is considerably more resource-efficient compared with the existing technology and chromobentanite one. In the case of replacing the existing technology of chrome tanning with the technology of anion-cationic tanning, the cost value reduction of products will amount to 13.8 thousand UAH.

Along with the determination of the degree of resource intensity of chrome tanning technology, the ecological cleanness of the developed technologies was estimated on the basis of the information on the residue of chemical reagents in the spent solution (**Table 5.6**).

The individual indicators of the ecological cleanness were determined by the formula:

$$q_i = \frac{Q_i}{Q_{cyu}}, \quad (5.5)$$

where Q_{ich} – the residue of the chemical reagent in the spent solution with the use of the existing technology, kg; Q_i – the residue of chemical reagents in the spent solution with the use of the innovative i technology, kg.

The group ecological cleanness indicators are determined by the additive convolution of the individual ones as follows:

Table 5.5

Determination of resource intensity of tanning processes in the production elastic leather from splitted semi-finished products

Names of resources	Consumption of resources by the tanning technologies		
	chromo-bentanite	anion-cationic	standard
1. Sodium chloride, kg	180	75	180
Price, UAH/kg	1.03		
<i>Cost</i>	<i>185.4</i>	<i>77.25</i>	<i>185.4</i>
2. Formic acid (85 %), kg	6	–	9
Price, UAH/kg	17.5		
<i>Cost</i>	<i>105</i>	–	<i>157.5</i>
3. Sulphuric acid (100 %), kg	–	–	24
Price, UAH/kg	2.5		
<i>Cost</i>	–	–	<i>60</i>
4. Chrome tanning agent, kg	120	132	240
Price, UAH/kg	8.75		
<i>Cost</i>	<i>1050</i>	<i>1155</i>	<i>2100</i>
5. Sodium carbonate, kg	9	4.95	9
Price, UAH/kg	3.75		
<i>Cost</i>	<i>33.75</i>	<i>18.56</i>	<i>33.75</i>
6. Electrolyte resistant emulsion, kg	–	20.4	–
Price, UAH/kg	10		
<i>Cost</i>	–	<i>204</i>	–
7. Water, t	1.8	0.6	2.1
Price, UAH/t	8333		
<i>Cost</i>	<i>14999.4</i>	<i>4999.8</i>	<i>17499.3</i>
8. Energy, kW	110	44	210
Price, UAH/kW	1.2146		
<i>Cost</i>	<i>133.606</i>	<i>53.4424</i>	<i>255.066</i>
Total expenses, UAH	16507.16	6508.05	20291.02
Complex indicator of technology resource intensity	0.81	0.32	1.0

$$R_i = \sum q_i \cdot \alpha_i, \quad (5.6)$$

where α – the validity of the chemical reagent

The validity of the chemical reagent was determined based on its class of hazard by the ranking method, when the highest rank was assigned to the reagent with the highest class. The validity of a chemical reagent is calculated by the ratio of its rank to the sum of the ranks of chemical reagents by i technology. The received calculations (**Table 5.6**) showed that the technology of anion-cationic tanning is the most environmentally clean. At the same time, unlike the existing technology of chrome tanning, environmentally harmful sulfuric acid, which belongs to the 1st class of hazard, is not used in its innovative technologies.

Therefore, as a result of the research, an economical and ecological estimation of the innovative technologies for the production of leather materials was made taking into account the consumption of chemical

Table 5.6

**Determination of ecological cleanness of tanning processes
in the production of elastic leather**

Names of chemical substances	Class of hazard (rank)	The residue of chemical reagents in the spent solution with the technology of tanning		
		chromo-bentanite	an-ion-cat-ionic	exist-ing
1. Sodium chloride, kg	IV (1)	162	67.5	162
<i>Individual indicators of the environmental cleanness</i>		<i>1</i>	<i>0.42</i>	<i>1</i>
<i>Validity</i>		<i>0.25</i>		
2. Chrome tanning agent, kg	II (3)	2.56	0.60	14.5
<i>Individual indicators of the environmental cleanness</i>		<i>0.18</i>	<i>0.04</i>	<i>1</i>
<i>Validity</i>		<i>0.75</i>		
Complex indicator the ecological cleanness of the technology		0.39	0.14	1

5. Economic and ecological efficiency of leather and fur production technology

reagents, water and energy consumption, and the determination of the ecological cleanness by the content of environmentally harmful reagents in spent solutions. The methodology for determining the effectiveness of the developed technologies was based on the consideration of the specific importance of individual indicators of resource intensity and environmental friendliness of technologies. Innovative technologies in production of leather materials in comparison with the existing ones have considerably 1.25–3 times lower complex indicators of resource intensity. Regarding ecological cleanness, these indicators are also lower by 2.6–7.4 times. The developed algorithm of economic and ecological estimation and selection of technologies of leather production can be used for the purpose of estimation of efficiency of innovative technological decisions in other branches of industry as well.

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Questions for self-control

1. Formation of a balanced system of the nature management as one of the main directions of solving problems in the ecological and economic sphere.
2. The significance of ecological and economic estimation of modern technologies of leather and fur production.
3. Methodological principles of ecologically oriented development of leather production.
4. Justification of the ecological direction in the development of the Ukrainian economy.
5. Basic principles (strategy) of the state environmental policy of Ukraine for the period up to 2020.
6. State ecological and economic program for the introduction of clean production.
7. The method of efficiency estimation of economic and ecological activity of the leather industry enterprise (on the example of soaking and liming processes of leather production of CJSC Chinbar (Ukraine).
8. Means of prevention of ecological consequences of human activity.
9. World practice in evaluating the environmental protection system.
10. Indicators of economic and ecological safety.
11. The grouping of indicators that determine the ecological level of soaking and liming technologies for the processing of animal skins.
12. Types of impact estimation on the environment.
13. Method of ecological and economic estimation of soaking and liming technologies of leather production.
14. Calculation of individual and group indicators of the resource intensity of soaking and liming technologies of leather production.
15. Individual and group indicators of soaking and liming technology influence on the environment.
16. Determination of the importance of parameters of the influence of leather production technology on the environment by the hazard classes of pollutants.
17. Ranking of technologies of leather production by their priority in achieving the set goals — ecological, economic, and ecologico-economic.
18. Ecological and economic estimation of innovative technologies of leather production.
19. Reasons for the necessary production ecologization of the enterprises of the fur and leather industry.

20. Economic indicators that reflect the specific character of production in the fur and leather industry.

21. The algorithm of environmental and economic estimation and selection of innovative technological projects of leather production.

22. Determination of resource intensity in the production of elastic leather from splitted semi-finished products.

23. Achievement of the ecological cleanness of tanning processes in the production of natural elastic materials.

6. TECHNOLOGY OF GRADING FOR RAW FURS AND SEMI-FINISHED PRODUCTS, FUR PRODUCTS AND CLOTHING

From the ancient times people used fur hides and skins, and later natural furskins as the main material for making clothes. These were mostly hides of large animals – bears, wolves, leopards and others. At first, people fixed hides on the body, and then they began making fur coats of furskins. In addition to hides for lining and hats, they used skins of small animals, in particular, martens, otters, beavers, ermines, sables, squirrels, etc. Skins of domestic animals, especially sheep and goats, were also used. For a long time, hides were raw. Processing of hides and skins by the tanning method appeared at the beginning of the 18th century.

Nowadays, hides of big (deer, cattle, seals, and louts), medium size (foxes, sheep, rabbits, etc.) and small animals (moles and the like) are used for making clothes.

6.1. Assortment of raw furs and definition of its quality

The range of raw furs is extremely diverse in terms of species and many characteristics within a single species, in particular the size of skins and the hair state. In the standards [1], raw furs are divided according to ridges, sizes, colors, grades and categories of defects. Since the commodity properties of raw materials of the same species vary depending on the geographical region of the existence of the fur animal – the ridge¹, skins are divided by a package of their characteristic commodity properties, which differ from the skins of the adjacent areas. These

¹ In some standards the term “ridge” is replaced by a number.

properties include their size, woolliness, height and thickness of the hair, its coloration, silkiness, thickness of the skin tissue and weight of the skin. Furs are divided into three groups according to the height of the hair: long-haired (fox, arctic fox, etc.), medium-haired (rabbit, marten, squirrel, etc.), short-haired and curly (Karakul-Persian lamb group).

The specifications required for grading of the main types of raw furs of winter species are given in **Table 6.1** [1, 2]. The commodity parameters, determining the type of fur skins are woolliness, thickness, length and softness of the hair that contains guard hair and underwool. These characteristics have their own peculiarities for the fur of each kind. Most types of fur pelts are divided into three grades, and more valuable ones – into two grades. These parameters depend on the heat-protective properties of skins and, accordingly, their designation. The density of the hair also affects the wear-resistance of fur pelts.

The first grade includes fur skins with high guard hair and thick underwool, the second – with underdeveloped guard hair and underwool, the third – semi-haired skins, with not very developed guard hair and underwool. The fourth grade is distinguished for some animals, such as white fox. The second grade generally includes early-spring skins, and the third or unsorted one – skins of squirrel. They have signs of the beginning of spring shedding (thin dull hair).

Skins are divided according to the categories of defects depending on the presence of defects in the skin tissue and hair. Most types of raw furs are divided into four categories: full-size, small, medium and large or massive defects, respectively.

Due to the fact that commodity-related characteristics of hair are evaluated organoleptically, the grading of fur skins according to the ridge requires extensive experience and long-standing practice. Skins are classified by size when they are influenced by sex and strongly vary in size and change with age [2]. In particular, these are skins of mink, Siberian weasel, ermine males, which are larger than females. The degree of the hair development of the skin depends on the period of the year (season) of harvesting and is characterized by a set of certain commodity properties – a grade. In assessing the quality of raw materials, the hair appearance is also taken into account, its natural coloration, lustre, and creasing. Attachment of the hair to the skin tissue is also an important characteristics.

Table 6.1

Conditions for the grading of raw furs of winter species by ridges

Product family and species	Ridge	Size	Grade	Categories of defects
Lutrinae: otter	Northern Southern	large, medium, small	I, II	three (first, second, third)
mink	Caucasian Northern Siberian	not provided	I, II, III	full-size skins, with small, medium, large defects
Canidae: red fox	Altaian, Amur, Western Siberian and others (18 in total)	the same	I, II, III	four (first, second, third, fourth)
silver fox and cross fox	Camchatka, Southern, Northern Siberian		the same	the same
Tartar fox	Astrakhan, Kazakh		– “ –	– “ –
white fox	Yenisei, Obdorsk, Pechora, Yakut	– “ –	I, II, III, IV	full-size skins, with small, medium, large defects
wolf	Kazakh, Southern, Arctic, Siberian, Central	– “ –	I, II, III	full-size skins, with small, medium, large defects (apart from wolf cubs)
Mustelidae: sable	Altaian, Amur, Barguzin and others (18 in total)	– “ –	I, II Less valuable species have three grades	full-size skins, with small, medium, large defects; four (first, second, third, fourth)
pine marten	Kuban, Northern Caucasian (including raw materials from Ukraine),			
stone-marten	Middle Asian		I, II, III	the same

Table 6.1, cont.

Ferret family: steppe polecat	Orenburg, Saratov, Middle Asian, South-eastern	sizes by ridges	I, II, III	full-size skins, with small, medium, large defects
Siberian weasel	Amur, Bashkir, Trans-baikal, Yenisei Tobolsk Yakut	large, medium, small, but each ridge has its own indicators	I, II, III	four categories (first, second, third, fourth)
ermine	Barabinsk, Berezovsk, Trans-baikal and others (8 in total)	the same	the same	full-size skins, with small, medium, large defects
Felidae: Pantherinae (tiger, snow leopard, leopard, cheetah, lynx) Felinae (manul)	Southern, Northern the same	large, medium, small the same	 I, II, III	the same three (first, second, third)
Leporidae: white hare brown hare	Northern, Siberian, Ural, Central Transcaucasian, Menzelinsk, South-eastern, Ural, Central	not provided the same	the same – “ –	three (full-size, first, second) the same
Sciuridae: squirrel	Altaian, Amur, Trans-baikal and others (11 in total)	– “ –	– “ –	full-size skins, with small, medium, large defects

Skins of winter species of animals that are not subdivided by ridges, in particular farmed mink and white fox [3, 4] are sorted by species, coloration, size, grade and categories of defects, and skins of rabbits and muskrats [5, 6] – by size of skins, their grade and categories of defects (**Table 6.2**). Skins of the species that have a pronounced variability in the hair color are divided by colour. There are strong changes in the hair color of caged animal skins: mink, nutria, and the like.

Table 6.2

**Conditions for grading of raw furs of winter species
that are not divided by ridges**

Product family and species	Size of skins	Colour	Grade	Categories of defects
Castorinae: Eurasian beaver	large, medium, small	not provided	I, II	four (first, second, third, fourth)
nutria		white, black, golden, brown, pastel, pearly	I, II, III	the same
Mustelinae: farmed mink	extra large A, extra large B, large, medium, small	black, dark brown, blue, white	I, II, III	full-size, with small, medium, large defects
Procyonidae: common raccoon			The same	four (first, second, third, fourth)
Arvicolinae: muskrat	large, small	not provided	I, II, III, non-standard	four (first, second, third, fourth) and non-standard
Russian desman	not provided	the same	I, II	full-size, with small, medium, large defects

Table 6.2, cont.

Mustelidae: kidus (a marten and a sable crossbreed) yellow-throated marten	the same	– “ –	I, II, III	four (first, second, third, fourth)
Canine: raccoon dog caged white fox (blue)	selected category, first	extra, first, second	the same I, II	the same – “ –
Mustelidae: forest polecat	not provided	black	– “ –	full-size, with small, medium, large defects the same
marbled polecat	large, medium, small	not provided	I, II	
mountain weasel	the same	the same	the same	four (first, second, third, fourth)
least weasel	– “ –	– “ –	– “ –	the same
Felidae: felinae (caracal, wild cats: Amur, barkhan, woodland, reed and steppe)	– “ –	– “ –	I, II, III	three (first, second, third)
Leporidae: hares (all species) rabbits	not provided; extra large, medium, small, except for the third grade	– “ – – “ –	the same – “ –	three (full-size, first, second) the same
Sciuridae: spermophilus	large, medium, small	– “ –	I, II	full-size, with small, medium, large defects
chipmunk	not provided	– “ –	not divided	full-size, first, second

Spring fur pelts have a specific grading, which takes into account not seasonal, but the age-related variability and defects of raw materials, that is, a set of relevant commodity properties characteristic of hides of domestic animals, which are harvested at a certain age and have approximately the same hair development. Spring fur skins are conditionally skins of gopher, tarbagan marmot, and badger (**Table 6.3**) due to the impossibility of winter harvesting because this is a period of hibernation, and hunting is allowed only in autumn after the end of their shedding.

Table 6.3

**Conditions for grading of raw furs of spring species
and sea mammals**

Product family and species	Size of skins	Grade	Categories of defects
Sciuridae: ferret	large, medium, small	I, II	full-size, with small, medi- um, large defects
chipmunk	not provided	not divided	full-size, first, second
gopher	large, medium, small	I, II, III	full-size skins, with small, medi- um, large defects
tarbagan marmot	the same	the same	– “ –
Mustelidae: badger	– “ –	– “ –	three (first, se- cond, third)
Sea mammals: skins of a harp seal	by age: harp seal pup, hooded seal pup, bearded seal, harp seal, eared seal;	by habitat, I and II grades for a harp seal pup.	four (first, second, third, fourth)
fur seal	extra large A, axtra large B, large, medium, small	I, II, III	the same

Note. Gopher and tarbagan marmot skins are sorted according to three and two ridges respectively.

In Ukraine, there are more than 50 types of fur mammals and animals [7]. In order to preserve and expand the number of fur mammals and increase the stock of their raw materials in our country, valuable species of fur animals (muskrat, nutria, American mink, common raccoon) are acclimatized, a system of conservation areas, fur and Karakul farms have been created. The work on cage breeding of red Kamchatka fox, wild French mink, raccoon dogs, ferrets and the like continues.

One of the main types of fur and wool raw materials is sheepskin [8] (**Table 6.4**). Its share accounts for over 60 % of the total volume of fur semi-finished products.

Table 6.4

Conditions for grading of sheepskin product family

Product family and species	Length of fleece, cm, sheepskin			Grade
	wool	semi-wool	low-wool	
Sheepskin: – fine-wool – semi-fine wool	over 3.0	1.0–3.0	does not exist	I, II, III, IV
– semi-coarse wool sheepskin – coarse wool sheepskin (Russian, Steppe)	over 6.0	2.5–6.0	1.5–2.5	the same
– Romanov mature sheep – teg wool	over 5.0	1.5–5.0	does not exist	– “ –

Pure-bred Karakul-Persian lamb and kid pelts are graded according to the corresponding DSTU [9–12] (**Table 6.5**). At the same time, they are sorted according to the method of curing. The Karakul is divided depending on the size of its curls: by width – narrow, medium, wide; by height – short, medium, high.

Fur calfskins, foalskins and reindeer calf skins are sorted by color, grade and categories of defects (**Table 6.6**).

Commodity properties of the fur semi-finished product, which depend on the combination of natural characteristics of the hair and skin tissue of raw materials, should not deteriorate during long-term storage [13], which makes it possible to process plastic natural materials with sufficiently high

Table 6.5

**Conditions for grading of Karakul-Persian lamb, lambskin,
and kid pelts**

Product family and species	Size of skins	Hair coloration	Groups of curls	Grade	Category of defects
Lamb skin: pure-bred Karakul black "Arabi"	large, medium, small, extra small	black and black-multicolour	jacket, Caucasian, ribbed-flat	I I, II I, II	first, second
– grey	the same	grey (blue), dark grey, black-grey, light grey	half-round, flat, fringe, Caucasian	I, II, III	the same
– coloured	– “ –	Sur, brown, pink, white, variegated, variegated and other colouration	the same	the same	– “ –
– cross-breed	– “ –	black, grey, Sur, variegated, unicoloured, coloured	I, II, III, non-standard	– “ –	– “ –
pure-bred astrakhan pure-bred – half-breed Karakul-astrakhan-golyak	large, medium, small	black, grey, Sur, variegated, coloured, multicolour, pink		– “ –	– “ – not divided
jahobab skin – Persian lamb		black, coloured, multicolour		– “ – I, II	four
krimmer lamb	two (depending on the type of curing)	black, grey, unicoloured black, multicolour		I, II, III	first, second
moire skin and klyam merlushka lamb – Russian tryasok, sak-sak lyamka	over 3 dm ² over 4 dm ² 4–18 dm ²			I, II	the same
kid	4–24 dm ²			I, II, III, golyak	small, medium and large, except for golyak

Table 6.6

**Conditions for grading of calfskins, fur foalskins
and reindeer calf skins**

Kind of raw materials	Size of hides	Hair coloration	Grade	Categories of defects
Fur calfskin		black, red, variegated	I, II, III	two categories (first, second)
Foalskin: slunk suckling calf yeanling	large, small	black, multi-coloured, dark-steel, red, variegated	not divided three grades two grades	the same
Reindeer calves: still-born calf-skin murrelet nebluj adult deer pelt – deer	0.8–1.0 dm ²	sole-coloured, variegated	two grades three grades two grades	three categories

physical and mechanical indices for the manufacture of a wide range of fur and woolskin clothes [14] and hats. Thus, a wide range of raw furs from both wild and domestic animals makes it possible to produce various fur semi-finished products, the quality of which directly depends on both the storage of raw materials and the level of technological treatments.

6.2. Features of processing technology of raw furs

Commodity value of fur and woolskin materials is determined primarily by the type and quality of raw materials, the level of production technology and market conditions. It should be noted that when using valuable types of raw furs such as sable, marten and others, their cost is about 90 and 70–80 % of the cost of manufactured fur semi-finished products and natural products, respectively. The quality of furs and raw materials is determined by a variety of consumer properties, which

include physical and mechanical ones, in particular wear-resistance, heat-shielding, hygienic, aesthetic, and environmental properties. At the same time, the skin tissue generally provides physical, mechanical and hygienic properties, and the hair – thermal and aesthetic properties. One of the main conditions for the development of modern production and the extension of economic ties in the domestic and foreign markets, and increasing the competitiveness of fur materials and products in the world market is to increase their quality and expand the range.

Because of the biological sensitivity of raw furs to the environmental impact, curing is a prerequisite for their preservation. This is due to the seasonal nature of receiving skins of wild animals and the slaughter of domestic animals as they contain up to 75 % of water and 25–40 % of protein in a green condition, which requires timely and qualitative dehydration. The presence in nature of more than 150 species of animals, whose skins are characterized by not only a wide range of sizes, skin density, thickness and height of the hair, the area of raw material harvesting, but also the content of natural fat substances requires specific treatment for the production of fur materials and fur products. At the same time, it is necessary to note a significant difference in the strength of the skin tissue of some small animals, in particular, the least strong are mole and ermine skins, and the strongest are seal and otter skins, which requires special technological approaches. In addition, for their proper quality before processing into fur materials, special methods of curing are used, namely air-dry or dry-salted method is generally used for small raw materials, while wet salting is used for larger sizes, and the Karakul-astrakhan group of raw materials is processed by souring using bread kvass.

The processing of cured raw furs into materials and related products involves consistently monitored carrying out of a number of processes and operations, and the quality and cost of production depend on their performance. In accordance with the increased conditions for the quality of fur products, the technological processes of fur raw material processing are continuously improved. This is evidenced by modern technology of processing the most common types of raw furs of domestic and wild animals, which are noted by controllability at all stages of production and high quality of semi-finished products [15], while reducing the consumption of chemical reagents and duration of treatment. For the processing of raw furs into materials, lots of skins are packed, and their size depends

on the type and volume of the corresponding technological equipment. The ridge, the type of raw material, the method of its curing, the area of harvesting, the area and thickness of skins, etc. are taken into account.

Uncuring of sorted raw materials occurs during their soaking in an aqueous medium in the presence of antiseptics and process accelerators. Occasionally, an acidic medium is used for this purpose. The “water: raw materials” ratio and the duration of processes depend on the type of raw materials and their state. Particularly, this ratio is equal to 9:1 for air-dried rabbit skins and 25:1 for white fox and fox at the ambient temperature of 35–38 °C, and depending on the thickness of the skin tissue for 14–26 and 4 hours, respectively. For green raw materials, the duration of the process is reduced by 4–5 times in the first case, while in the second one it is reduced by only 25%. In order to intensify the process of soaking the raw material of fresh and dry curing, it is recommended to use electroactivated technological aqueous solutions [16–18] characterized by antiseptic and increased surface-active properties, ensuring an efficient process without additional use of chemical reagents. For the acceleration of soaking, a terpenic-based preparation is also suggested [19].

Skins high in natural fat in the skin tissue, in particular, nutria, sheepskins, etc., are to be degreased in an alkaline medium using surfactants and antiseptic preparations at the temperature of 38–40 °C. This treatment can be performed in electroactivated water – catholyte [18] without the use of surfactants and antiseptics at the temperature 8 °C lower. It should be noted that sheepskins are degreased twice – before and after the removal of muscle-fat layer – the fleshing. This rather labor-intensive operation is performed either on the appropriate fleshing machine or manually.

At the second stage of the production of fur materials for the formation of increased plastic properties of the skin tissue, acid-salt treatment of the skin – is performed – pickling for at least 24 hours for rabbit skins, followed by their laying flat, stacked vertically for a long time, in particular for nutria skins for 24 hours, and rabbit skins – 80–90 hours. The duration of this process depends on the thickness and density of the skin tissue. Pickling of sheepskins is recommended to be carried out in electro-activated water – anolyte [20] for 5.0–5.5 hours.

In order to stabilize the formed skin tissue in the acid-salt treatment, its chemical structuring, tanning, is carried out and it can be combined

with acid-salt treatment and subsequent plastification of their structure – greasing. In particular, this concerns sheepskins. In order to accelerate the tanning process, it was suggested using the anion-cation form of a chromium tanning agent [21, 22], which contributed to two- or three-fold intensification of this process. For chrome-free tanning, the use of zirconium compounds [23–25] was suggested, which significantly reduces pollution of the environment, and the use of aldehyde-tannin-aluminum tanning agents [26], which made it possible to produce sheepskins, resistant to sweat, washing and oxidation.

The third stage of the fur semi-finished product processing involves plasticization of the skin tissue structure, which provides the use of fat substances of natural and synthetic origin in the form of an emulsion. This process is often combined with pickling and tanning. In this case, the fat emulsion is added to the acid-salt solution and it must be resistant to electrolytes or applied to the surface of the skin tissue of the semi-finished product after removal of capillary moisture by centrifugation. Due to insufficient electrolyte resistance of the fat emulsion, fat particles can be deposited on the surface of the hair and the skin tissue and grease them. To eliminate this, instead of using an insufficiently stable emulsion, obtained from inert industrial oils I-12A in the process of combined fatliquoring of sheepskins, it was suggested to use ethylene-, propylene glycol esters of natural naphthenic and synthetic fat acids [27]. This made it possible to increase the quality of raw sheepskins and reduce the consumption of fat substances twice.

If necessary, the change in the hair coloration of the fur semi-finished product, the technology involves the process of dyeing, which uses semiproducts and dyes harmful to the environment. In [28, 29], it is proposed to replace semiproducts of oxidative nature with polyphenols in the form of vegetable and synthetic compounds.

The fourth stage of the formation of the fur semi-finished product structure is the removal of the basic weight of capillary moisture by centrifugation. Further 20–25% removal of moisture from the fur semi-finished product occurs in the drier. Then, it is moisturized in a moving drum during final drumming and is cleared from residues on the hair and from fat particles in the skin tissue under the effect of moistened dust. Subsequently, the skins are subjected to mechanical treatment by stretching, re-cleaning

from contamination in the drum and removing residues of dust from the hair. The resulting fur semi-finished product is sorted and graded.

At the same time, the number of processes and operations can significantly increase due to the properties of fur pelts and the functional purpose of the material. In particular, when processing fur sheepskins, additional processes and operations related to straightening and lustering the hair, etc. are implemented.

Therefore, even a brief description of the technology of the formation of fur materials shows that the specific properties of different types of raw materials determine the multi-stage and multifactor processing of raw materials into natural materials. At the same time, as the received patents show, the decisive role in the technology of processing of raw furs is played by chemical reagents. Despite the intensive development of the industrial production of textile and artificial furs on its basis and their wide range in the domestic and foreign markets, the attractiveness of natural fur materials is primarily caused by their high consumer qualities [30]. The increased demand for natural materials determines the urgency of innovative developments in the direction of improvement of the existing fur production technology and development of a new one, which would ensure the reduction in the cost of their production and the competitiveness of fur materials and products of multifunctional use.

6.3. Assortment of fur semi-finished products

In modern conditions, the starting point for the formation of assortment, its level of quality and planning of the quantity of goods being produced is to meet the needs of consumers. Thus, commodity science goes from the analysis of individual consumer properties of goods to the establishment and evaluation of quality of goods in terms of the degree of satisfaction of relevant needs. Commodity research is actively involved in solving problems of quality management at all stages of the product life cycle – design, production, marketing and consumption. Particular attention is paid to the development of rational conditions of transportation, storage, use of goods and rules for their care. The

approach of commodity research to the study of a range of goods is changing. In addition, the problem of developing the optimal destination of fur products and forecasting their range is being put forward.

The semi-finished product [31] is made of the corresponding types of raw furs both in a natural form with the natural coloration of the hair, and dyed fur skins and sea mammals (**Table 7**). Trade classification of fur semi-finished products is based on the indicators of the most important consumer properties, which primarily include hair of the fur. Depending on the season of harvesting, there are two commodity subgroups – winter and spring species, each of which contains 10 and 6 types, respectively, which are subdivided into product families.

As important product characteristics are the height and density of the hair, the average weight of the skin, its color, size, type of the

Table 6.7

Product family and type of fur semi-finished products and their characteristics

Product family of fur semi-finished products	Product family	Market type	Height of the hair	Thickness of the hair in the spinal area, thousands of hairs/cm ²	Average weight of a skin, g	Sizes of skins, dm ²
Winter species	Lutrinae	otter sea otter mink	long-haired the same medium-haired		280–350 the same 60–90	25.0–50.0 the same 3.5–12.0
	Castoridae	beaver nutria	long-haired the same		– 170–220	30.0–50.0 15.0–25.0
	Talpinae	muskrat Russian desman	medium-haired the same	– “ –	40–60 – “ –	5.0–10.0 – “ –
	Ursidae	polar bear – brown – black	extra full-haired	0.8	– “ –	65.0– 150.0
	Mustelidae	wolverine	the same		– “ –	19.0–30.0
	Melinae	badger	– “ –		– “ –	20.0–25.0

6.3. Assortment of fur semi-finished products

Table 6.7, cont.

	Canidae	raccoon dog	– “ –	8,5		– “ –	
	Canine	all species of foxes	– “ –	– “ –	– “ –	10.0–25.0	
		wolf	– “ –	3–6	800–	20.6–30.0	
		jackal	– “ –	3–6	1000	– “ –	
		corsac	– “ –		150–200	– “ –	
		white and blue fox	– “ –		150–200	12.0–24.0	
	Mustelidae	sable	medium-haired	10–20	– “ –	3.0–7.0	
		marten	the same	10–20	– “ –	– “ –	
	Mustelinae	European polecat	– “ –	8–16	– “ –	2.5–6.0	
		Siberian weasel	– “ –	– “ –	– “ –	2.5–6.0	
		Mountain weasel	short-haired extra short-haired	– “ –	5–10	1.2–3.0	
		ermine		4–6	6–8	1.5–3.0	
		least weasel	the same	2–5		0.6–1.2	
	Felidae	all species of wild cats	medium-haired	3–9	110–200	15.0–30.0	
	Leporidae	all species of hares	the same	18–22	85–110	4.0–13.0	
	Sciuridae	squirrel	short-haired	8–10	– “ –	3.0–5.0	
Vernal species	Geomuidae	marmot	the same	3–5	110–150	3.5–17.0	
		tarbagan	– “ –	4–6	130–180	3.0–17.0	
	Sigmodontinae	gopher chipmunk	extra short-haired				
		water rat	short-haired	2–3	10–30	1.0–4.5	
		spalax, edible	the same	1.5–2	3–6	0.6–1.0	
		dormouse	– “ –	2–3	6–7	0.9–2.0	
		dipodid	– “ –	2–3	5–7	1.3–5.0	
	Talpidae	hamster	– “ –	2–4	6–10	1.3–5.0	
		mole	– “ –	2–3	8–22	1.3–5.0	
			– “ –	12–17	5–8	0.4–1.5	

section (not shown in the table); these indicators are provided when determining the quality of the fur semi-finished product. This range can be used both for clothes and their parts (lining, padding), hats, collars and clothing related items (rugs, sleeping bags, etc.).

6.4. Features of fur and sewn products

Speaking about fur products, it is worth paying attention to the obvious thing – they are exclusively peculiar to fur production. In addition to the preparation of semi-finished products, which we have already considered, they cover closely related preparatory technological operations for their acceptance, production sorting and designation, batching, selection and packing of skins, their preparation for cutting and cutting itself, which, in fact, finish by sewing finished products [32].

The purpose of production sorting is the selection of homogeneous lots according to their product and technological characteristics: height, density, lustre, silkiness, shade, shape (tube, layer) and sexual characters, in particular for mink skins in order to make certain types of products.

The production lots are made up of homogeneous hides and skins according to the specifications, determined in standards and technical conditions for fur and furskins, and by features foreseen for the production sorting as well. In particular, for a women's coat they should consist of about 1500–1700 Karakul skins, 1000–1200 rabbit skins of colored dyeing or 700–1000 skins dyed in black. A production lot of valuable furskins such as mink, Siberian weasel, nutria, muskrat and other natural skins for outerwear should consist of 800–1000 fox and white fox skins, for women's hats and collars – 100 sable skins and more.

It is clear that, like every skin, their production lot is distinguished by height, density, lustre, tint, and the shape of a curl inside each group of skins. Therefore, to obtain a production lot of more homogeneous skins, they are usually combined with groups with less differences by such features. This is achieved by their re-sorting, collecting and packing, which involves distributing the collected skins according to patterns of the manufactured product, depending on their quality,

height of the hair, luster, tint and other features, and designation of each skin in this product. Their laying on the body (back) begins with its first row from the middle part. In this case, the back bone of the skin is laid on the middle of the product. First, they are laid on the back, then sequentially on the right and left foreparts. When they are placed on the sleeves, the best skins are placed on the top of the part, skins of the lower quality – on the subfacial parts. The best skins are put on the right side on women's collars and on the left side on men's ones. Darker skins are placed in the lower rows of the body with a gradual transition to lighter shades in the upper rows. Skins with higher (well-grown) hair are allocated in lower rows, and skins with low hair – in the upper ones. Skins, assembled in this manner, are forwarded for cutting. At the same time, collection and packing operations are often combined.

While preparing for the cutting, technological operations of tempering, laying and straightening are performed. Tempering is used to provide the skin tissue with plasticity, to bring it to the condition where it enables the area to be enlarged and takes the form required for making the cut of this or that product.

Cutting of skins is one of the main technological processes in fur production. By doing so, simple and complex methods are used. The simple methods involve cutting the skins selected for the product according to patterns of even sizes and shapes and providing them with the forms of plates of different contours. For this purpose, patterns of rectangular, oval, hexagonal, wedge-shaped and parallelogram forms are used. The simple methods of cutting also include a transverse connection of skins (direct, oval and saw-toothed). In direct connection, the neck and shell pieces are cut off along a straight line, after which they are sewn together. To make the seam less noticeable, the connection is provided with a form in which the length of the transverse seam is the smallest. For this purpose, an oval or saw-toothed connection is used. Several varieties of crosslinking of skins are known: wavy, semicircular, small and large conical, small and large rectangular. They are simple and only distinguished by form, height, step and angle of inclination. Schemes of cross-sectional connections for different methods of cutting of one or another skins are different.

When sewing fur products, sewing machines of different classes are used: 63 – one-keel lockstitch for forepart tacking of their top and side

lining; 65 — also a one-keel sewing machine, whose purpose is tacking armholes in the manufacture of all types of coats, short coats, jackets, blazers, etc.; 53 — a semi-automatic machine for sewing wire hooks and loops to them. In the process of sewing fur products, also a ironing press with a hydraulic drive 4P-2, 5, whose purpose is internal process and their final wet-heat treatment, is used. In this case, sewn (finished) fur products should be thoroughly cleaned of dust, cotton-wool residues, ends of threads, cut hair, and their hair covering should be well-combed, and in places of joints of parts it should be even and smoothed.

Making products of natural furskins, as well as any clothing made of textile materials, also includes processes of modeling and design [33]. In doing so, the following conditions should be taken into account:

- promising fashion trend and modern technological level of fur production, in particular, fur-sewing industry;
- conformity of products to their intended purpose, service conditions, sex and age of the consumer;
- conformity of used materials and fur semi-finished products to a certain purpose of products and their form.

During modelling, they try to create samples of comfortable and practical fur clothes. To do this, the properties of the semi-finished product are taken into account. In particular, the outerwear is virtually not made of heavy types of semi-finished products (otters, beavers) and long-haired ones — of raccoon, badger, wolverine and the like. At the same time, the composition of products is designed in such a way as to emphasize the natural beauty of fur pelts. Since fur products have a long period of exploitation, they are designed in a straight silhouette, sometimes semi-fitted and loose. To observe the proportions of a fashionable silhouette, garments made of natural furskins are manufactured a bit longer.

In accordance with the existing division of fur apparel for the intended purpose — male, female and for children, fur semi-finished products are also conditionally divided. The assortment of semi-finished products for men's fur products is relatively small: beaver, muskrat, seal, Karakul, wool sheepskin, otter, kril, murrelet, and calfskin. It is not common to produce men's clothing from the semi-finished products of white fox, ermine, marten, astrakhan lamb, sable, mink, and fox skins. For children's products, light, inexpensive types of fur semi-finished products (rabbit,

sheepskins, etc.) are used. Women's clothing is made of virtually all types of semi-finished products, with the exception of wolf, bear, and beaver.

The compositions of fur coats depend both on the properties of the hair and the skin tissue. They include height, color, woolliness, luster, pattern of the hair and thickness, stiffness, density, strength of the skin tissue. Products without decorative elements are designed from furskins with high and thick hair — of straight and semi-fitted silhouettes. Semi-finished fur products with short hair is suitable for creating various compositions of clothing, decorative elements — pockets, half belts, and the like. Skins with thick skin tissue are used for simple shapes, and with thin skin tissue, which is easily draped, products of any silhouettes can be made.

When creating an ensemble of clothes, fur semi-finished products of different types are selected in such a way that their individual elements are harmonized in color and appearance. The aesthetic properties of the ensemble can be improved using contrasting colors, for example, for a dark coat — a light collar and a hat, of a different kind of semi-finished fur product — for a Karakul coat, a mink collar and a hat. In addition, when designing new models of fur clothes, fur is often combined with other materials: leather, suede, fabrics or knitwear. Interesting formulas can arise when combining materials by color and texture.

The design of fur products and the creation of patterns are basically similar to the design of sewing products, but they have some features that relate to the most important properties of fur — height of the hair, thickness and ductility of the skin tissue; size, weight, section features and heat-protective properties of fur pelts. Designing products made of fur semi-finished products, in contrast to clothes made of fabrics, more allowances are given for loose fitting of items on the shoulders, chest, armholes, waist and hips. In particular, the allowance for loose fitting depends on the height of the hair.

The volumetric form of fur products is created in a design way, since it is impossible to form the fur by a moisture-thermal treatment. On the basis of the design, working patterns are developed on the cutting of fur and applied materials. The modern pace of life and the high cost of fur products require an unconventional approach to the design process: more novelty, the complexity of solutions of a constructive and technological nature, the originality of decor elements and accessories and bold creative experiments.

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Questions for self-control

1. Classification of raw furs according to the standards.
2. Standards for the classification of raw furs.
3. Classification of raw furs by grades and categories of defects.
4. Types of fur skins that are sorted by their size.
5. Standards for the classification of raw furs that are not sorted by ridges.
6. Sorting of spring raw furs and furs of marine mammals.
7. Measures to preserve and expand the number of fur animals and increase the stock of raw furs in Ukraine.
8. Grading of skins from the sheepskin commodity group.
9. Requirements for the sorting of Karakul-Persian skins, lambskins and kid skins.
10. Sorting of fur calfskins, foalskins and reindeer calf skins.
11. Determination of the commodity value of fur and sheep/woolskin materials and finished goods.
12. Determination of the quality of raw furs and fur materials.
13. The importance of curing of fur skins.
14. Grading of raw furs by the strength of the fur fabric.
15. Stages of fur materials production.
16. Features of the initial (first) stage of fur production.
17. Characteristics of the second stage of fur production.
18. The third stage of fur production.
19. Technological operations, common for the fourth stage of fur production.
20. The basic principle for the formation of the range of fur products, its level of quality and quantity planning.
21. Product family and type of fur semi-finished products and their characteristics.
22. Characteristics of fur and sewn products.
23. Sorting and batching of fur semi-finished products.
24. Cutting of skins as the main technological process of fur production.
25. Sewing machines and other basic equipment used in the production of fur items.
26. Modelling and design processes in the production of natural fur items.

EDUCATIONAL EDITION

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MATERIALS PRODUCTION**

Monograph

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