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BIODAMAGES AND PROTECTION OF LEATHER AND FUR

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Abstract. The paper presents the information about biodamages and protection of leather and fur. The contributors put a special emphasis on rawhide microflora, putrefied hide microflora, effect of prior operations on bioresistance of leather, interesting facts, fur skin structure and properties changes by microorganisms and the methods of leather preservation against microorganism impact.

Keywords: biodamage, protection, fur, leather, bioresistance.

1. Introduction

Solving of polymers degradation and stabilization problems is a very important task for pure and applied chemistry [1-32]. If we can double the life span of materials it will be the same as doubling the production of these materials. It is very important to exactly predict the materials exploitation and storing time. Being the natural protein material, leather assumes its commercial properties via a multistage treatment by various reagents and represents a culture medium where bacteria and mold fungi can develop [15, 16, 21, 27-32].

Animals' hide has a complex structure and various ways of microorganism permeation into it. Hide of an animal while alive carries a lot of microbes appeared from the environment (water, air, soil), because it has direct contacts with it (dipping, rolling on the ground, dust deposition). If the animal care is insufficient its hide may carry a vast number of microbes (up to 1–2 billion/cm²). Microbes found on the hide after flaying were present on the living animal and partly appeared after flaying due to further contamination. After killing and flaying the hide is secondarily contaminated by microbes sourced from dirty floor and baskets, animal dung and dirt. Specific microbial flora of killing chambers and raw leather warehouses

consisting of microbes greatly propagating on both molding production waste and stored raw materials and tools is of great importance. Air in these facilities is usually full of specific microflora, mold spores, salt microbiosis, *etc.* [32].

Rawhide contamination by microorganisms largely depends on the purity of keeping of appropriate compartments and the hide handling. If the rawhide is poorly handled the number of microbes on it significantly increases, that may cause subsequent significant damage to the raw material. The external side of just flayed hides contains a lot of microbes, whereas the external side is sterile. However, already after two hours the rawhide completely loses commercial properties due to microorganism effect. It is therefore immediately preserved by solutions with introduced biocides. However, since before treatment by preservative agents, the hide is attacked by microbes, which can occur on it from both the epidermis side and the living hypoderm. While inspected, their external layers demonstrate various kinds of microorganisms, the upper layer of epidermis being most favorable for their habitation and consisting of separated flat keratinized cells losing connection with one another. The animal papillary dermis represents a dense connective tissue consisting of the main substance, intercellular fibrous formations and cellular elements; it is loose, unstable and non-resistant to microorganisms' impact [1].

The reticular layer primarily consists of complexly and densely tangled collagen fiber yarns; therefore, if the hide is just flayed its reticular layer contains no microbes. However, the internal part of the layer adjacent to subcutaneous fat is loose and more permeable for microbes. Four structural levels of collagen, the dermis protein, are distinguished: primary – polypeptide chain; secondary – spiral (the α -form); tertiary – triple spiral (protofilament); and quaternary – supermolecular structure associated with the regulated packing of protofilaments (fibril). Collagen organization

level next to fibrils is represented by fibers. In the dermal layer of the skin, collagen fibers are submerged into glycosaminoglycan (GAG) structures, which act as an interfibril “cement” [27-32].

2. Results and Discussion

Hydrated GAG cause a very strong effect on the structure of collagen fibers: they protect protein fibers of fibrils against fusion and increase their mobility, thus providing fiber integrity.

It is known, for instance, that fairly preserved samples of medieval vellum consist of densely packed collagen fibrils submerged into the interfibril amorphous substance. However, some cases have been described when the vellum transformed to bonded protein due to the damages caused by microorganisms [1, 32]. After storing bovine dermis in water during 9 months, the intense differentiation of fibrils and their isolation into fibrils is observed. This testifies to predominant decay of interfiber and interfibril substance, *i.e.* basically GAG [17, 32]. At the initial stages, microbiological degradation is similar to hydrolysis forming particles, which consist of amino acid groups. These particles, along with separate amino acids, are rapidly subject to further transformation. Microbiological protein degradation products commonly contain ammonium, fatty acids, amino acids, aldehydes, and amines [30-32].

For the microorganism development, subcutaneous fat is a particularly favorable medium, where they propagate and from which penetrate into dermis. When appearing in the reticular layer, in the interfibril space, microbes may induce the putrefactive process deep in the hide. Meanwhile, blood remained in vessels due to poor bleeding and intercellular substance of the dermis and the reticular layer are proper nutrition for microorganisms. Regarding environmental conditions and sponginess of the reticular layer microbes can form numerous colonies on its surface or penetrate into upper layers, propagating and destroying them. They can move easily and rapidly by interfiber and interfibril spaces destroying the dermis substance and various intercellular components. For example, moving by the fiber, rod-shaped microbes penetrate into collagen filaments and then spread in the surrounding tissues, whereas cocci penetrate into hair bags. Mold mycelium spreads either along collagen fibers or, occurring in the interfibril space, in all directions forming dense entanglement [30-32].

By chemical composition, leather tissue represents a medium favorable for fast microorganism propagation. The rawhide contains both inorganic and organic substances. Inorganic substances in the leather tissue are water (50–70 %) and mineral substances (0.35–0.5 %).

Organic substances in it are lipids (fats and fat-like compounds), carbohydrates, non-protein nitrogen-containing components and proteins forming the histological structure base of the leather tissue. The most important components of this structure are fibrous proteins, such as collagen, keratin, elastin and reticulin. In addition, cutaneous covering contains globular (albumins, globulins) and conjugate proteins. Albumins and globulins, whose sufficient amounts are contained in the rawhide, degrade most easily. Fats are affected by specific lipoclastic microbes [32].

High amounts of proteins present in the leather tissue are one of the factors which cause its extreme sensitivity to destructive impact of putrefactive microbes. This is also promoted by the medium response (rawhides have pH 5.9–6.2). The skin coating contains vitamins, enzymes catalyzing chemical reactions and affecting development of biochemical processes in tissues, and substances which increase (activators) and suppress (inactivators) enzyme activity in the hide. If one of activators or inactivators is absent, biochemical processes in the hide change. For example, rawhide aging increases protease activity, which induces protein breakdown and promotes development and propagation of microorganisms.

Increasing fat content in the leather tissue entails relative decrease of water content, which increases leather resistance to the action of various microorganisms. Depending on chemical composition of the leather tissue, *i.e.* whether amounts of proteins, fats, *etc.* in it are high or low, its resistance to microbial activity is different. It has been found that the kind of microorganisms inhabiting the rawhide depends on animal feeding. In the absence of vitamin *B*₂ and biotin, for example, dermatitis and loss of hair by the skin coating are observed, that promotes permeating of microbes into the hide [1, 32].

2.1. Rawhide Microflora

The so-called putrefactive microorganisms, including cocci and rods, sporous and asporous, aerobes and anaerobes, are abundant in the rawhide. The general feature of these microorganisms is their ability to degrade proteins. Without getting into specifics of every species of microbes, several groups of them most commonly observed in the raw material should be highlighted. The majority of them are rod-like, both sporous and asporous. The group which includes *Proteus* represents asporous mobile rods; this group has clearly proteolytic ability and degrades proteins to final products. A group composed by *E. Coli* bacteria, generally occurring from dung and being short rod shaped, represents the intestinal flora, both mobile and immovable. This group's representatives induce peptone decay to amino acids with the indole

formation. The sporogenous group, including *Bac. subtilis*, *Bac. mesentericus*, *Bac. mycoides*, and *Bac. megatherium*, mostly represent mobile rods generating high stability spores. These microbes also feature pronounced proteolytic ability and breakdown proteins to final products.

To a lesser extent, the group of cocci, including micrococci and pilchard generally producing pigments (yellow, ochreous, brown, red, and white), is observed. Many of them produce enzymes affecting partly degraded protein. A group of actinomycetes has optimum development at pH 7.0–7.5. They are also able to degrade protein. Bacteria of this species is frequently observed in soils, wherefrom they, apparently, appear in the hide. Sometimes bacteria of the fluorescent group occur on the hide. These are asporous gram-negative rods. Many species dissolve gelatin and decompose fats. They are mostly psychrophilic bacteria. These kinds of microbes most often occur in water, among which *Bact. Fluorescens*, etc. All the above groups of microbes are aerobes. Yeasts observed on the raw material are so-called wild, wide-spread in the nature, namely, white, black and red yeasts [21].

Molds representatives often occur on the rawhide. Many of them have pronounced proteolytic ability. Fungi of *Mucor*, *Rhizopus*, *Aspergillus*, *Penicillium*, and *Oidium* genus are observed on the hide. As mentioned above, microbes commonly occur on the surface of the raw, freshly flayed hide, both at the side reticular layer and epidermis. Microtomy on the rawhide shows the absence of microbes in the tissue, both in near-surface and deep-in layers. Single cocci may only be infrequently observed in hair bags.

2.2. Putrefied Hide Microflora

Unpreserved hide is easily putrefied. High temperature and humidity, stocking of uncooled hides and their contamination lead to fast propagation of putrefactive microbes in the hide [32].

Aerobic putrefaction starts from the surface and gradually penetrates deep into the layers. Three putrefaction stages are distinguished. The first stage is characterized by fast microbial propagation on the hide surface causing no visible reflex. The second stage has visible hide changes: sliming, color change, odor, and doze. This period coincides with commencing permeation of microflora into the dermis thickness. The third stage is characterized by intensification of visible displays in line with hair and epidermis weakening and deep microbial permeation and spreading by the hide layers (Fig. 1).

Hide putrefaction demonstrates gradual change of the species composition of the microflora. Coccus species of bacteria, whose significant amount is observed in the

rawhide, are gradually substituted by highly propagating rod forms, namely, *Proteus vulgaris*, *Bac. subtilis*, *Bac. mesentericus*, clubbing, etc. Microtomy of unpreserved putrefactive rawhides demonstrates particularly rod forms penetrated deep in the hide layers [19].

2.3. Effect of Prior Operations on Bioresistance of Leather

Rawhide preservation. Immediately after flaying, the raw skin is affected by microorganisms, which results in damages and reduces quality of rawhides and the yield of leather. Primary signs of the hide decomposition are surface sliming and flesh side color change. Then characteristic putrefactive odor occurs, hair root bonding with their bags is weakened, hairslip occurs followed by exfoliation. Finally, pigmentation occurs and mechanical strength reduces down to massive fracture [17].

All the above necessitates rawhide preservation within two hours after flaying. Otherwise leather will lose its commercial properties. The preservation goal is to create unfavorable conditions for bacterium and enzyme action. This may be reached by moisture elimination and impacting protein substances of the hide by reagents. At the preservation stage, aerobic bacteria of *Bacillus*, *Pseudomonas*, *Proteus*, and *Achromobacter* genus possessing proteolytic enzymes manifest the highest activity. These bacteria are capable of damaging the hair side, its globular proteins, lipids, and carbohydrates. Some of them are capable of causing collagen decomposition [16].

To prevent putrefactive processes, rawhides are preserved by three methods: flint-dried, dry salting and wet-salting. Flint-dried and dry salting cure is based on suppressing vital activity of bacteria and activity of proteolytic enzymes by reducing raw material humidity to 18–20 % due to treatment by dry sodium chloride and sodium silicofluoride. Meanwhile, optimal condition of the flint-dried cure is a definite temperature mode 293–308 K, because the process at lower temperature may cause bacterial damages and hide decay due to slow water removal. Special requirements are also set to relative air humidity in the compartment which is to be 45–60 %, and good circulation of air is required [15].

Wet-salting cure is performed by sodium chloride salting from the internal side of the hide (fleshing side) or treatment by saturated sodium chloride aqueous solution – brining, with further hides add salting in stock piles. Wet salting generally removes free water from the hides. Meanwhile, greater part of asporous bacteria dies and development and propagation of other microorganisms and action of enzymes is terminated or suppressed. At dry salting the preservative effect of sodium chloride is based on hide dehydration and at wet salting – on breaking

intracellular processes due to sodium chloride diffusion into cells. However, sodium chloride does not provide full protection against microorganisms and may even be a substrate for halophilic (salt-loving) bacteria and salt-tolerant bacteria (*Bacillus subtilis*), which possess the proteolytic capability. To protect against them at brining, sodium metabisulfide is added as bactericide [14].

In addition to the above listed preservation methods, rawhide freezing can be used as a temporary measure. At low temperature activity of bacteria and enzymes is terminated; however, procurement organizations must defrost the frozen material and cure it by wet salting. Irradiation is considered to be an effective method of rawhide protection against microorganism action. After rawhide irradiation in 1 kJ/kg dose, it can be stored during 7 days without noticeable signs of bacterial damage. Irradiation by 3 kJ/kg dose extends the storage period to 12 days. In this case, rawhides need no additional chemical curing. A combination of wet salting and irradiation of the rawhides, in turn, almost completely eliminates microflora, whose activity in the rawhides is terminated for 6 months [32].

2.3.1. Basic operations of rawhide processing to leather

The rawhide processing to leather is a multistage process. At various stages of this process quite favorable conditions for microorganism growth and development on the leather may be created [13]. The danger of leather bacterial damage occurs already at the initial stage (soaking) aimed at preservatives removal from the rawhide and making it as close to just flayed state as possible. Soaking is water treatment at 303 K, mostly with electrolyte adding. Salt concentration in the leather thereby abruptly reduces, that promotes occurrence and development of bacteria, which become active in water, especially at higher temperature. In this case, bacterial damage starts from the grain side, and biologically unstable components at this stage are globular proteins. Among 10 species of bacteria detected during soaking more than a half of bacteria have proteolytic enzymes [12].

At this stage, sodium silicofluoride is used, which is active in neutral and weak acid media. At the next stage of *liming*, to remove interfiber protein substances and to loosen fibrous structure of the dermis, hides are treated by caustic lime solution. The aim of liming is to weaken hair and epidermis bonding to dermis, which promotes their further free mechanical removal. Moreover, dermis free from interfibrous proteins becomes more permeable, its volume is formed, and tannin diffusion into the dermis is accelerated. As regards bioresistance, the liming process is characterized by the fact that asporous bacteria die in the

lime bath and the sporous ones stop growing and propagating [11].

Then hides without hairs (pelt) are subject to preliminary tanning operations, which are *deliming and drenching*. The first operation is performed at 298–303 K, most often using ammonium sulfate or lactic acid. Drenching in turn represents a short-term pelt processing by enzyme compounds in water at increased temperature 310–311 K. As a result, leather becomes soft and elastic, with interfiber proteins and collagen decomposition products eliminated, and breathable. However, at this stage favorable conditions for bacterium propagation are formed. With respect to drenching fluid composition, bacteria of *Sarcina*, *Staphilococcus*, *Pseudomonas*, *Bacillus*, etc. genus have been extracted. Therefore, to avoid biodamages duration of operations should be controlled and preset treatment time should not be exceeded. Thus at all stages of rawhide processing to leather conditions may be formed that promote microorganism growth and development on the leather [7].

Interesting facts. When using fire, the ancient man has discovered preservative properties of smoke. For tanning hides Indians applied a mixture of chopped liver, brain and fat. After currying the leather was smoked. Clothes from such leather were not hardened under the effect of water and microbes and its odor repelled mosquitoes. Another tanning method also existed. Leather was wrapped around the leg, then wrapped by foot wraps and carried until it gained best properties; or leather was soaked in urine or dug in sheep manure.

Tannage process. Tannage consists in injection of tanning substances into the dermis structure and their interaction with functional groups of protein molecular chains, which results in formation of additional stable cross bonds. Tannage is one of the most important processes for leather manufacture. This stage in the leather industry radically changes dermis properties, transforming it to tanned leather. Finally, the dermis property change defines leather behavior during dressing, manufacture and operation of articles from it. As compared with the pelt structure, the tanned leather structure features increased fiber separation assumed during preparation and fixed by tanning. The fiber separation defines a number of basic physical and mechanical properties of leather: tensile strength, compression strength, toughness, hardness, elasticity, etc. [5].

Tanning starts with the penetration of a tanning agent into the collagen structure *via* channels formed by fibrils, diffusion of these compounds from these and linking to structural elements of collagen. Initially, adsorptive interaction occurs between tanning agents and collagen, followed by stronger chemical bonding. Tanning

causes strengthening of the collagen spatial structure due to the formation of crosslinks by tanning substances between the molecular chains of the protein structure. The type and strength of stable crosslinks formed during tanning depend on the tanning agent which is used [4].

Tannage is accompanied by increasing dermis resistance to hydrothermal impact, *i.e.* increasing seal temperature. Tannage increases dermis resistance to swelling in water that causes significant impact on performance properties of leather. It also increases dermis resistance to proteolytic enzymes, *i.e.* leather biostability increases. Moreover, the interaction of tanning substances with functional groups of dermis protein leads to increased elastic properties of collagen and, consequently, reduced deformation rate of moist dermis, reduction of leather shrinkage area and thickness when dried. Tanning compounds are intrinsically divided into two main groups: organic and inorganic. Inorganic ones are compounds of various metals: chromium, zirconium, titanium, iron, aluminum, silicon, phosphorus, etc., among which chromium compounds are of the prime importance. Organic compounds are natural tanning substances – tannides, synthetic tanning matters, aldehydes, water-soluble amino resins, and blubber oils [1].

Inorganic tanning matters. A large number of inorganic compounds possessing tanning properties are known. However, mostly chromium compounds are used as tanning matters, because they allow obtaining of high-quality leather good both in manufacture and operation and storage. Primarily, tanning chromium compounds were mostly applied to leather manufacture for shoe upper. At present, chromium compounds are used in manufacture of almost all kinds of leather, both solely or combined with vegetable tanning matters, with syntans and amino resins. Tannage consists in treatment of pelt by tanning chromium compound solution. Drums and worm apparatuses are used for tannage. When rotated in apparatuses, the semi-product is subject to quite intensive mechanical impact, because wooden wobblers or boards rise and drop the semi-product, which, along with continuous fluid mixing and temperature increase, accelerates tannage. Tannage starts with diffusion of compounds into dermis structure. Primarily, tanning matters penetrate into capillaries, wherefrom chromium compounds diffuse to direct response centers and link to functional groups of protein. Meanwhile, tanning agent penetration into the dermis depends on a number of factors:

- firstly, on sufficient separation of structural components, loosening of collagen in preliminary operations – the more loosened fibers, the higher the diffusion rate of chromium compounds into dermis;
- secondly, on tanning particle size – the smaller the tanning particles, the higher the diffusion rate.

Another important factor is pelt pH. It needs to be 4.5–5.5 to provide normal tanning matter diffusion into

the dermis. Chromium tanning compound diffusion is controlled by pelt section color change varied from white to blue or green. Resulting from these procedures, chromium tanned leather assumes exclusive properties. It is highly resistant to acids and alkali and has high seal temperature 413–423 K, high tensile strength (11 MPa), high softness and elasticity, and is resistant to higher temperatures (compared with vegetable tannage leather). Moreover, chromium tannage dried leather cannot be soaked again either in hot or in cold water. Although water penetrates easily into the chromium dermis, its structural elements remain waterproof [25].

These negative properties are explained by the nature of chromium complexes, type of bonds between them, functional groups of collagen and the strength of cross bonds between molecular chains forming bridges. The assumed features in turn explain sufficiently high bioresistance of chromium tanned leather. It is proven that tanned leathers are mainly impacted by microscopic fungi, because development of bacteria is hindered. However, it has been found that chromium tanned leather possess the highest resistance to molds because it is deeply impregnated by oils, wax and fats, and its fibers assume hydrophobic properties [21].

Moreover, chromium salts are weak antiseptics, which also play some role. However, despite relatively high resistance to biodamages of chromium tanned leather, danger of microorganism development is not completely eliminated. Biodamaging agents extracted from tanning solutions and from the semi-product surface may be bacteria *Bacillus mesentericus* and some fungi: *Aspergillus niger*, *Penicillium chrysogenum*, *Penicillium cyclopium*. At this stage, sodium pentachlorophenolate and chloramines B may be used as biocides [32].

Beside usage of chromium as the self tanning agent, it is also used for more intensive bonding of aluminum compounds with collagen. Aluminum tanning is one of the oldest tannage methods. Basic aluminum sulfate, chloride and nitrate are used as tanning agents. However, this method is applied restrictedly, because these aluminum compounds are unstably bound to dermis proteins. This bond breaks under the water effect and leather becomes detanned. Although aluminum tannage leather differs from other types of tannage due to higher softness and white color, it is undurable and due to aluminum compound washing out becomes wet rapidly and warps after drying [16]. These factors are significant for bioresistance of aluminum tanned leather; washing out of aluminum compounds makes semi-product and final product accessible for microorganism penetration into dermis and their active propagation in it. However, application of aluminum compounds for retanning of vegetable-tanned inner sole leather, for instance,

significantly increases its ability to resist mold development [14].

Organic tanning agents. Organic tanning agents are simple and complex by structure. Simple tanning agents are mostly aliphatic compounds: aldehydes and some kinds of blubber oils (tanning oils). Complex tanning agents are aromatic derivatives and some heterochain polymers: vegetable tanning agents (tannides), synthetic tanning agents (syntans), synthetic polymers (mostly amino resins). Tannides are substances contained in various parts of numerous plants, are extracted by water and capable of transforming dermis into leather while interacting. With regard to species of plants tannides are accumulated in their different parts: cortex, wood, leaves, roots and fruits. In this case, tannide content may vary in a very broad range, from parts to tens of percents.

Leather formation during rawhide tanning by complex organic compounds is the result of permeation of these substances into the semi-product and their bonding with broadly developed inner surface of particular structural elements of collagen via both thermodynamic adsorption and chemical interaction with amino groups and peptide groups of protein, with formation of cross bonds of electrovalent, hydrogen and, apparently, covalent type [13].

Semi-product seal temperature increases during tannage by tannides. This is explained by the fact that collagen has a multistage structure, and tanning particles having large size are incapable of penetrating into the smallest structural elements of the protein. These particles can easily be washed off, accompanied by simplest phenols and acids, which reduce the seal temperature. Moreover, similar to collagen, tannides have many reaction groups. As located on the collagen structure surface, tannide particle reacts with several structural elements of collagen forming cross bonds between them, which, in turn, increases the seal temperature (up to 341–363 K).

It is desirable to use tannage by tannides in cases when volume, hardness and rigidity are to be imparted to the leather or to increase its size stability in case of humidity variations, and when leather with high friction coefficient is required. However, such leather has low tensile strength, because when large tannide particles permeate into fibers they expand them and reduce the number of protein substance per specific cross-section. It should be noted that biostability and performance characteristics of such leather and articles from it abruptly decrease with increasing tannide concentration. In this case, tannides represent nutrition for microorganisms and manifest their impact in the form of hydrolysis of tanning agents, pigment spots, grain roughness [12].

However, tannides that represent phenols derivatives possess some bactericide and fungicide action. Fungicide effect of vegetable tanned leather on

Trichophyton genus fungi is shown. Synthetic tannins (syntans) are also available and are of two types: (a) substitutes for vegetable tannins, which are produced from naturally-occurring phenols and which provide some protection against biodamage to the leather; and (b) auxiliary syntans, which are used in combination with other tanning agents. These syntans are hydrocarbons (petroleum and gas refinery products), and have no biocidal properties. Instances of severe damage to semi-finished leather by mould fungi have been reported after using syntans prepared from hydrocarbon material in the absence of any other tanning agent.

Thus neither organic, nor inorganic tanning compounds have the properties of the ideal biocide which, along with providing biostability, would impart the desired physical, mechanical and chemical properties to the finished leather [21].

2.4. Fur Skin Structure and Properties Changes by Microorganisms

Microbiological stability of fur skins at different stages of manufacture by the standard technology (tannage, greasing) was assessed on the example of mink skins (rawhide and semi-products). Mink skins as rawhides, chrome non-oil and ready (*i.e.* greasy) semi-product were studied. Mink skin samples matured under conditions favorable for microorganism development showed clear sensory determined signs of degradation – leather tissue samples became fragile and hairs slipping of the fur was observed.

Data on the influence of microorganisms, spontaneous microflora, on such physical properties of materials, as thickness, density and porosity are represented in Table 1.

As follows from the data obtained, both rawhide and non-greasy and ready semi-product demonstrate density increase resulted from the spontaneous microflora effect.

Such change of the leather tissue density is apparently associated with the fact that molecular weight of collagen decreases and denser packing of structural elements (frequently, more ordered) becomes easier. This is testified by observed increase of real density of the leather tissue and abrupt reduction of its porosity with increasing duration of microbiological impact on both leather tissue of the rawhide and tanned semi-product. The system packing observed leads to leather tissue thickness reduction [10].

Data on the structure density increase resulting from microbiological impact are confirmed by the data obtained by EPR spectroscopy by radical probe correlation time [1]. The radical probe mobility decreases with the increase of microbiological impact duration. This

may testify to packing of the leather tissue structure as a result of microflora impact on the material.

Analysis of the chemical composition of mink's leather tissue before and after impact of microorganisms testifies to reduction of the quantity of fatty matter with simultaneous relative increase of collagen proteins and mineral substances quantity (specifically observed in the raw material) (Table 2).

One may suggest that affected by the microflora, non-collagen proteins degrade and are "washed off" from

the structure. In this connection, relative content of collagen proteins in the leather tissue increases.

Thus, observed reduction of organic matter content (fats, non-collagen proteins) is obviously associated with the change of leather tissue structure. The destructive effect on the structure of studied materials may also cause alkalinity of the medium, which, as known, increases at natural proteins degradation [32]. Table 3 shows data of pH change of water extract of initial and test samples. In all cases, system alkalinity increase was observed.

Table 1

The change of mink leather thickness, density and porosity under the effect of spontaneous microflora
($T = 303\text{--}305\text{ K}$; $\varphi = 100\%$; $n = 10$; $P \leq 0.93$)

Sample	Exposure time, days	Thickness, mm	Density, kg/m ³		Porosity, %
			real	seeming	
Rawhide	init.	0.42	1336	701	47.5
	7	0.41	1340	719	46.3
	28	0.40	1345	747	44.5
Tanned semi-product (non-greased)	init.	0.4	1342	647	51.8
	7	0.37	1357	681	49.8
	28	0.33	1363	719	47.2
Prepared semi-product (greased)	init.	0.58	1353	632	53.3
	7	0.55	1355	755	44.3
	28	0.45	1366	825	39.6

Table 2

Chemical composition of mink fur's leather tissue before and after spontaneous microflora impact
($T = 303\text{--}305\text{ K}$ and $\varphi = 100\%$)

Material	Impact duration, days	Humidity, %	Substance content, in % of abs. dry substance			
			fatty	mineral	collagen protein	non-collagen protein
Raw material	Init.	12.3	10.15	2.28	76.39	11.18
	7	12.8	7.25	2.53	83.06	7.16
	14	14.3	7.14	2.69	84.28	5.29
Tanned semi-product (ungreased)	Init.	9.7	2.99	5.88	90.08	1.15
	7	10.1	2.78	6.11	90.10	1.01
	14	10.8	2.58	6.49	89.98	0.95
	28	11.3	2.03	6.67	90.37	0.93
Ready semi-product (greased)	Init.	8.2	13.63	6.54	78.83	1.00
	7	9.8	9.99	6.88	82.14	0.99
	14	10.5	7.62	7.06	84.37	0.95
	28	11.1	6.61	7.06	85.42	0.91

Table 3

Water extract pH of mink's leather tissue at different stages of their manufacture before and after spontaneous microflora impact ($T = 303\text{--}305\text{ K}$; $\varphi = 100\%$; $n = 10$; $P \leq 0.93$)

Mink's sample	Water extract pH			
	Microflora impact duration, days			
	0	7	14	28
Raw material	5.76	6.40	6.30	Not determined
Tanned semi-product (ungreased)	3.84	4.27	5.24	6.40
Ready semi-product (greased)	3.91	4.83	5.92	7.23

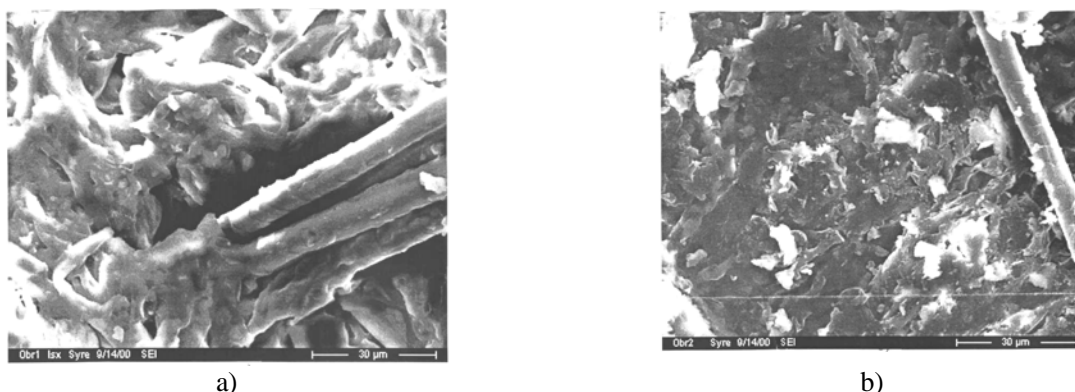


Fig. 1. Microphotographs of the leather tissue of mink's rawhides (1000x): initial sample (a) and 14 days after spontaneous microflora impact (b)

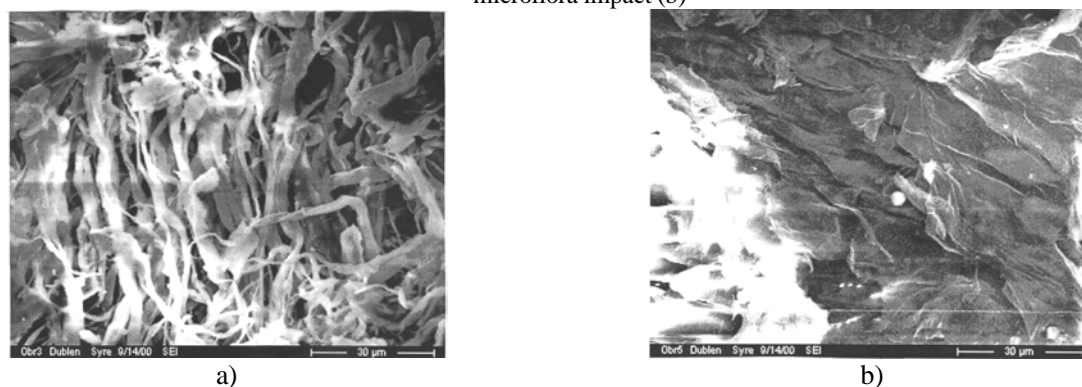


Fig. 2. Microphotographs of mink's fur leather tissue, both tanned and greased (1000x): initial sample (a) and 28 days after spontaneous microflora impact (b)

Table 4

The change of physico-mechanical properties of ready mink semi-product before and after impact of microorganisms ($T = 303\text{--}308\text{ K}$; $\varphi = 100\%$)

Kind of impacting microflora	Exposure time, days	Breaking strain of leather tissue (σ_p), MPa	Change to init., %	Relative elongation at rupture of leather tissue (ϵ), %	Change to init., %	Hair bonding strength with leather tissue (σ_p), $1 \cdot 10^{-4}\text{ N}$	Change to init., %
Spontaneous microflora	7	11.5	-10.9	50.4	-12.0	64.4	-11.2
	14	11.0	-14.7	45.3	-20.9	53.3	-26.5
	28	9.8	-24.0	37.7	-34.2	34.1	-52.9
<i>Asp. niger</i>	7	9.6	-25.6	48.3	-15.7	57.5	-20.7
	14	4.7	-63.6	43.5	-24.1	45.4	-37.4
	28	2.4	-81.4	35.6	-37.9	29.3	-59.6
<i>Bac. subtilis</i>	7	7.5	-41.9	47.1	-17.8	53.5	-26.2
	14	2.6	-79.8	41.5	-27.6	40.3	-44.4
	28	1.9	-85.3	34.3	-40.1	26.7	-63.2

Microscopy study results testify to the fact that observed changes in the material properties are caused by the change of supermolecular structure are electron.

Figs. 1 and 2 show electron microscopic images of the leather tissue sample surfaces (raw material and ready semi-product) before and after spontaneous microflora impact.

The images clearly show the fibrous structure of initial samples. Fibrous yarns (within $20\text{--}40\text{ }\mu\text{m}$ in diameter), separate filaments forming yarns (up to $20\text{ }\mu\text{m}$ in diameter) and collagen fibrils ($0.1\text{--}20\text{ }\mu\text{m}$) are distinguished in collagen. Dermis represents an irregular three-dimensional entanglement of fibers and their yarns, which is clearly seen in the images of initial samples of

both mink's raw skins and ready semi-product. Collagen yarns with clear contours are seen, fibers in yarns being higher structured for the semi-product [21].

Samples affected by microorganisms show destruction of fibril formations and their transformation to laminated structures. Hence, it is noted that the leather tissue porosity was slightly reduced as a result of microorganism impact.

Physicomechanical properties, first of all strength and deformation characteristics of the leather tissue, as well as hair connection strength with the leather tissue, are the most important fur properties.

Table 4 shows results of our study of physicomechanical property change of ready mink semi-product (with greasing) impacted by microorganisms – spontaneous microflora, micromycetes *Aspergillus niger* and bacteria *Bac. subtilis*.

The investigation has determined that the highest reduction of the breaking strain, leather tissue elongation at rupture and hair bonding strength with the leather tissue is observed under the impact of bacteria *Bac. subtilis*.

Thus it is observed that the properties of both rawhide and ready semi-product leather tissue change under the impact of microorganisms. Meanwhile, the true density increases, and porosity decreases due to degradation processes, which simplify packing of structural elements into more ordered formations as a result of steric hindrances reduction. The tensile strength, leather tissue elongation at rupture and hair bonding strength with the leather tissue are also reduced [6, 7].

2.5. The Methods of Leather Preservation against Microorganism Impact

2.5.1. Rawhide and cured raw leather protection

To increase biostability of leather and articles from it, it is recommended to protect leather against microorganisms at all stages of its treatment, starting with the rawhide.

Due to termination of oxygen delivery and metabolism, tissue degradation in just flayed hides is accelerated. The medium response reaches its optimal value for protease action. First breakdown of proteins forming the hide base is initiated and then carbohydrates, fats and other organic compounds degrade. As a result, chemical composition and the structure of tissues change. As impacted by microorganisms and enzymes, rawhides go bad rapidly at the temperature above 291 K, and tissue putrefaction starts [4].

At further development of putrefaction process, epidermis is destroyed and delaminated, and “damaged grain”, the absence of grain in some areas, occurs.

Putrefactive microbes damage subcutaneous fat. Then occurring in the reticular dermis, they rapidly spread in the interfascicular space, and then degrade collagen and elastin fibers. Due to these processes dermis delaminates which, in turn, leads to complete destruction of leather [2].

To preserve high quality of the raw material at this stage and to make it stable to putrefactive microbe impact the hide has to be thoroughly cured, *i.e.* all contamination, slices of fat and meat, has to be removed, and proper curing has to be performed. As mentioned above, rawhides are cured by three methods: flint-dried, dry salting and wet salting. The main substance used for curing is sodium chloride. Common salt microflora is represented by microbes developed in salt solutions – brines, and microbes occurring in salt during its production and transportation.

Under natural conditions, this salt possesses microbes of the halophobe group, as well as salt-tolerant species. Moreover, salt contains representatives of sporous microflora, yeasts, mold fungi spores, micrococci, variously dyed bacteria of *Flavobacterium* genus. When occurring on hides with salt during curing, microorganisms induce various defects; therefore, antiseptic agents are formed alongside with sodium chlorides. They possess bactericide, fungicide, bacteriostatic and fungistatic properties. Antiseptic agents used for curing must be toxic for microorganisms, well-soluble in water and in sodium chloride solution, cause no negative effect on the hide quality and leather semi-products. In this connection, paradichlorobenzene and sodium silicofluoride are most widespread [1].

When affected by paradichlorobenzene, some microbes developing in the wet-salt rawhide die and development of others is terminated. Hence, gaps between hides are filled with vapors of this substance. These vapors are heavy, slowly removable and hindering microorganism propagation for a long time. Some part of antiseptic agent is dissolved in fat and penetrates into the dermis; therefore, its typical odor is preserved for a long time. Sodium silicofluoride is quite effective. It possesses high bactericide properties and causes no negative effect on dermis. Rawhides brining with simultaneous treatment by sodium silicofluoride ensures long, (over a year) storage of hides without additional salting. However, this antiseptic agent is poisonous and care should be taken when operating it.

It is found that antiseptic agents also give strong effect when combined with each other. Moreover, goods results are reached by application of sodium hypochloride, boric acid, sodium borate, zinc chloride, sodium fluoride, benzene and phenol chlorine derivatives, antibiotics and other antiseptic agents to rawhides curing.

However, beside chemical means of the raw material protection against microorganisms, meeting

conditions and technology of curing is of importance. If the raw material was tainted when cured then despite the absence of tissue destruction the microflora of such raw material is richer. The presence of a great layer of reticular dermis, musculature and especially fat inclusions hinders diffusion processes, decelerates curing, has negative impact on the raw material quality and promotes development of microbes [30]. Moreover, the rawhide of flint-dried and dry-salt curing requires ideal conditions during transportation and storage, because high humidity forms favorable conditions for bacterium and mold development [21].

2.5.2. Protection of leather and leather articles against biodamages

The problem of biological damaging of natural materials, especially upper leather for shoes used in increased humidity conditions, is of great importance. Alongside with direct action associated with leather structure damage, microorganisms also manifest indirect adverse effect on the leather articles. Microscopic fungi promote leather hygroscopic property increase. As a result, relative humidity inside the shoes increases. This causes untimely wear of joints and development of pathogenic microorganisms inside the shoes [17].

In the world practice, rawhide and ready leather is widely protected by the following compounds: phenylmercury, bromo-acetophenone, *n*-chlor-*m*-creosol, alkyl naphthalene-sulphodiacid, sodium borate, zinc oxide, 2-oxydiphenyl, salicylanilide, and some other. However, a wide application of some biocides is restricted by specific requirements to leather protection: biocides must be soluble in fats, thermostable at stuffing temperature and compatible with other components used for leather treatment [15].

It has also been found that most of the above biocides do not provide a long-term antimicrobial action, because the antiseptic agent injected at the oiling stage is evacuated with fat during the use, and frequently, the fungicide simply evaporates. The optimum protection may be provided by biocides introduced into the finish coating composition and by compounds which are capable of bonding chemically with collagen. In this regard, β -naphthol and β -oxy-naphthaldehyde have been shown to be effective if injected into leather when finishing. Catamine AB, a quaternary ammonium compound, prevents the development of microscopic fungi on the surface of tanned leather. It links to collagen by coordinate or salt and adsorptive bonds.

Among microorganisms, mold fungi from *Aspergillus* and *Penicillium* genus are the most active and widespread destructors of the real leather. To eliminate mold development much can be done by the temperature

regulation and leather humidity decrease below 12 % with the help of hygroscopic agents (e.g. silicagel). However, such regulation is not always practical. The most effective means to eliminate mold development on the leather is the use of chemical agents [15, 17, 21, 30].

It is found that natural fungus resistance of the leather is increased by using materials based on organochlorine products; leather with fungicide properties can be obtained by using sulfochlorinated paraffins during stuffing. Both semi-products and the ready leather are effectively protected by benzoguanamine formaldehyde resins (BGAF). These compounds containing 40 % of the basic substance are water-soluble, which allows their application at all stages of leather manufacture process.

The ability of BGAF-resins to suppress mold micellium growth was also determined, the resin with higher content of sulphosalicylic acid having higher fungicide activity [32].

3. Conclusions

The paper presents the information about biodamages and protection of leather and fur. The contributors put a special emphasis on rawhide microflora, putrefied hide microflora, effect of prior operations on bioresistance of leather, interesting facts, fur skin structure and properties changes by microorganisms and the methods of leather preservation against microorganism impact.

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БІОПОШКОДЖЕННЯ ТА ЗАХИСТ ШКІРИ І ХУТРА

***Анотація.** Приведено дані стосовно біопошкодження і захисту шкіри та хутра. Особливу увагу приділено мікрофлорі сирової шкіри, процесу біорозкладу натуральної шкіри, впливу мікроорганізмів на різних стадіях вичинки шкіри, зміні структури шкіри і хутра під впливом мікроорганізмів та методам захисту натуральної шкіри.*

***Ключові слова:** біопошкодження, захист, хутро, шкіра, біологічний опір.*