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The Influence of Tanning Method and Ph on the Morphology of Astrakhan Leather

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Abstract: The article examines the morphological structure of karakul fur depending on the type of tanning and pH of the environment. Micrographs of the cross-section, surface and hair layer of tanned karakul with glutaraldehyde in acidic, alkaline and neutral media were obtained. The process of sorption of water vapor at a temperature of 20 °C in karakul specimens, tanning with chromium salts and glutaraldehyde has been studied.
Key words: Karakul, glutaravic aldehyde, tanning, chromium oxide, pH index

Introduction

Aldehyde tanning has been known and used for over 70 years. But only formalin (40% formaldehyde solution) was used as an aldehyde [1].
However, as studies carried out earlier [2-4] have shown, during aldehyde tanning, bonds are formed not only with skin proteins, but also with hair proteins, so its use is promising for tanning skins with weak hair. These include substandard astrakhan fur skins with a burning defect. However, at present, aldehydes, in particular formalin, and glutaraldehyde are not used as a tanning agent for astrakhan fur, because The scientific and technological basis for carrying out this process has not been developed. Aldehyde tanning has a number of other advantages, as it produces a fairly plastic leather fabric, providing it with softness and low shrinkage. However, the disadvantage of aldehyde tanning is the low fullness of the leather fabric [5-6].

Experimental part.

Objects of research.

Glutaraldehyde - (glutaric dialdehyde, pentandial) - an organic compound, aldehyde with the chemical formula $C_5H_8O_2$. Transparent and colorless liquid, easily soluble in water, irritating to the eyes and lungs. Used as a tanning agent in leather production, also used in the textile industry and microscopy [7].
Broadtail - (Uzbekistan. karakulcha - diminutive of "karakul, Karakul sheep"; from Uzbek. Qorako'l "Black Lake", after the name of the city and locality in Uzbekistan) - fur made from the skins of premature lambs (miscarriages in the last period of pregnancy) or fruits (extracted from the womb of slaughtered queens for meat) of Karakul sheep, as well as products made from this fur [8].
Karakul is literally translated from Turkic, black as ash (karakul) - skin with fur, removed from lambs of the Karakul breed 1-3 days after birth, when their wool is distinguished by thick, elastic, silky hair, forming curls of various shapes and sizes [8].
In the **sorption** studies, the properties of the samples were studied at a temperature of 25 °C and a relative humidity of 0-100% on a Mc-Ben vacuum balance device with a quartz spring.

The methodological basis of the dissertation was the work of leading scientists on the technology and technology of tanning leather and fur production, methods and intensification of liquid production processes, standards, technological documentation, normative, encyclopedic and reference literature.

Standard and modern methods of investigation were used to determine the quality indicators of krakul semi-finished products: microscopic examination of objects, scanning electron microscopy, x-ray spectral microanalysis, and also standard methods for determining physical-mechanical and chemical indicators of krakul semi-finished products and the finished product.

Astrakhan fur after the soaking process was used as the object of study.

Selection of skins for analysis. To determine the chemical composition and physical and mechanical characteristics of astrakhan skins, 3 pieces were selected from a batch of up to 100 skins, 5 pieces were selected from over 100 to 625 skins inclusive, and from a batch of more than 625 skins, the number of skins selected for analysis determined by the formula $n = 0{,}2\sqrt{x}$, where x- is the number of skins in the batch, and n is not more than 15. The first object from the batch is chosen randomly, all subsequent ones - through a strictly defined number of objects equal to x/n.

Halves method. When conducting research in semi-production plants, the method of halves was used, in which a change in the quality indicator of interest is identified by comparing symmetrical halves of the same skins (or semi-finished product); in this case, one half is the control, and the second is the experimental one. Small batches (10-25 pieces) of experimental and control halves were selected, alternating the right and left halves. The control batch was processed according to standard methods, and the experimental batch was processed using aldehyde tanning. Since the comparison was introduced on the same astrakhan skins, deviations in the characteristics of the halves are due only to changes made to the technological process.

Results and its discussion.

Using a digital optical trinocular microscope (OTM) model KXL-2001 (with a 5 mR digital camera), internal structural changes were studied in samples of 1 - natural astrakhan untreated, 2 - astrakhan tanned with Cr2O3 with a basicity of 15-20% as a control, 3 - astrakhan tanned with GA in a slightly acidic environment, 4-astrakhan tanned with GA in a slightly alkaline environment, 5-astrakhan tanned with GA in a neutral environment as experimental ones.

Consistently, all samples of skins were placed on the Tostem and microphotographs of their hair surface and the side cut of the end were taken.

Table 1

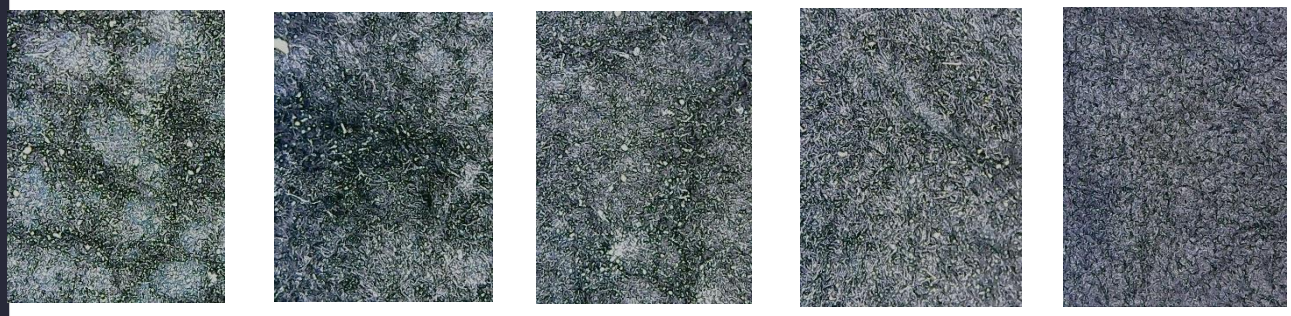
Characteristics of the appearance properties of samples of original and tanned astrakhan fur with glutaraldehyde depending on the pH of the environment

№	Skin samples	Type of processing	Characteristics of the appearance of astrakhan fur
1.	1- astrakhan	Natural astrakhan unprocessed original control	White-matte, not smooth, heterogeneous weaving with invisible mesh of tufts
2.	2- astrakhan	Karakul tanned with Cr^2O^3 with basicity 15-20%	Light green, smooth, smoothed, uniform fabric with an invisible mesh of tufts
3.	3-	Karakul tanned with GA in a	Relatively homogeneous with smoothed

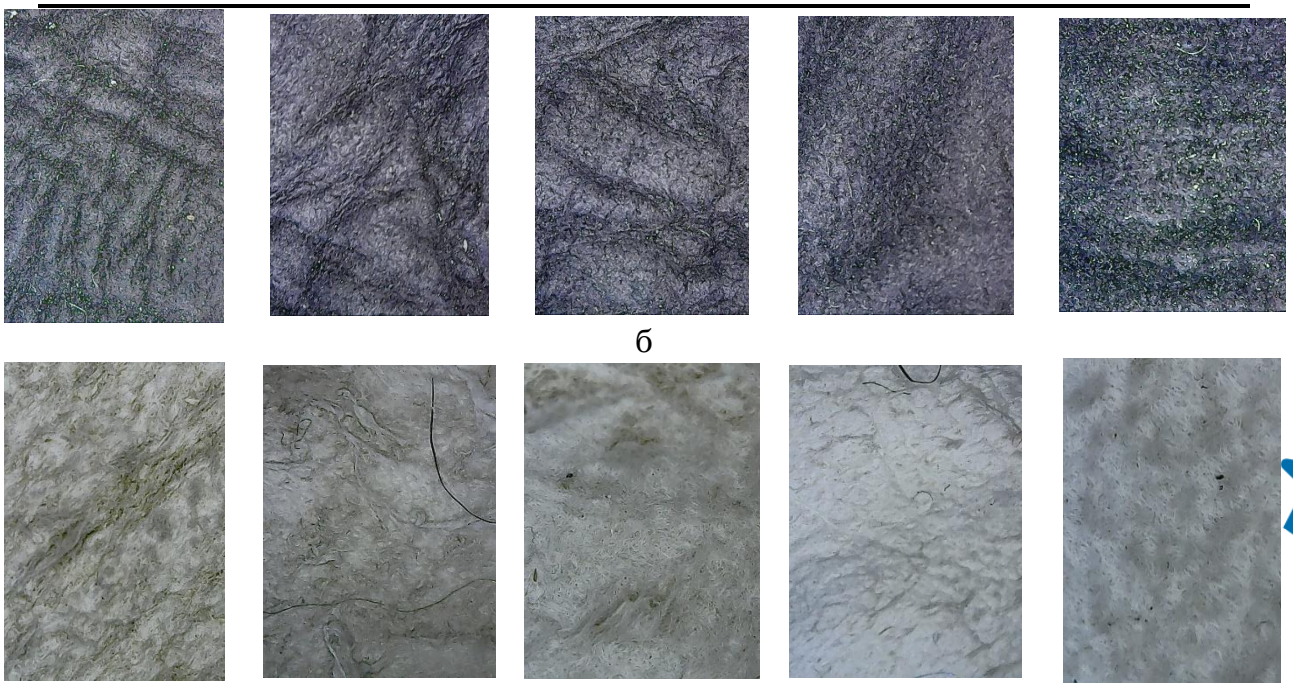
	astrakhan	slightly acidic environment	areas of macrotufts and thickenings
4.	4- astrakhan	Karakul tanned with GA in a slightly alkaline environment	Quite uniform, light yellow tissue with shiny, smoothed areas and uniform bundles of mycofibrils
5.	5- astrakhan	Astrakhan fur tanned with GA in a neutral environment	Light white skin, less uniform, with a noticeable network of white tufts

Table 2
Characteristics of the front surface and end of the DOM photographs of samples of original and processed astrakhan skins

№	System	Rank	Sample	Characteristics of skin appearance
1.	1- astrakhan	5	Front surface	More heterogeneous, coarse, coarse-grained, fibrils are unevenly located, densely packed (90-170 μm)
			Torest	Heterogeneous, non-smooth, fibrous, not loose, densely packed, gaps (60-150 microns)
2.	2- astrakhan	2	Front surface	More homogeneous, smoothed, less pronounced depressions, less granularity, sparse fibrous elements, there are gaps (8-20 microns)
			Torest	Fibrous, looser, packed, spaces (15-30 μm)
3.	3- astrakhan	4	Front surface	Homogeneous, smooth, granular, shifts, rounded areas like hills (35-60 μm)
			Torest	Fibrous, less loose, not tightly packed, spaces (22-58 microns)
4.	4- astrakhan	1	Front surface	Very homogeneous, there are smoothed areas with macro and micro fibers, firills in smooth areas, granular, without depressions (5-10 μm)
			Torest	More fibrous, highly loose, not packed, spaces (6-12 microns)
5	5- astrakhan	3	Front surface	Heterogeneous, unsmooth, granular, rounded shear areas, depressions (72 – 125)
			Torest	Less fibrous, less loose, spaces not tightly packed (36-114 μm)



a



б

в

Fig. 1 Digital microphotographs of the surface of the original, control and experimental samples of natural astrakhan fur. Magnification: a-50; b-100 and c-200 times

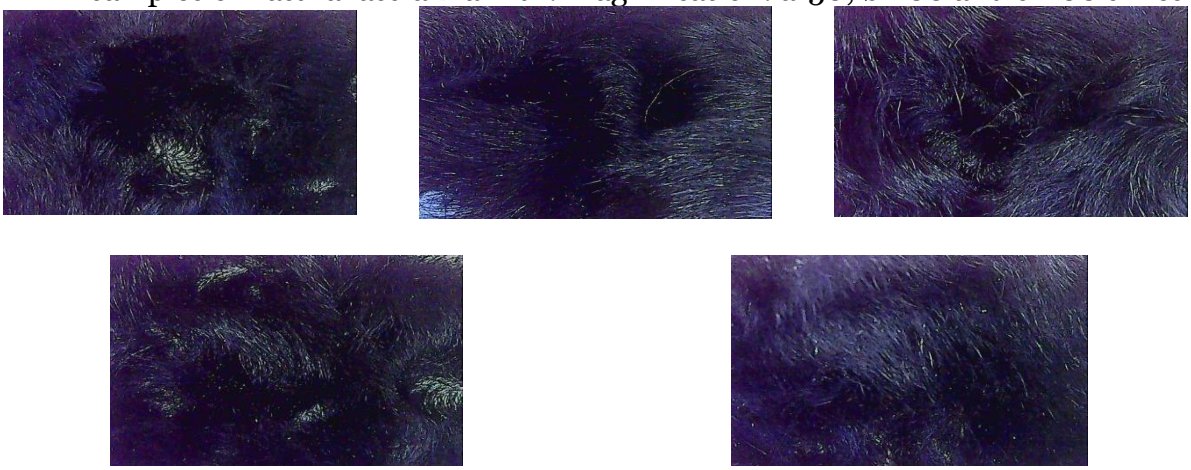
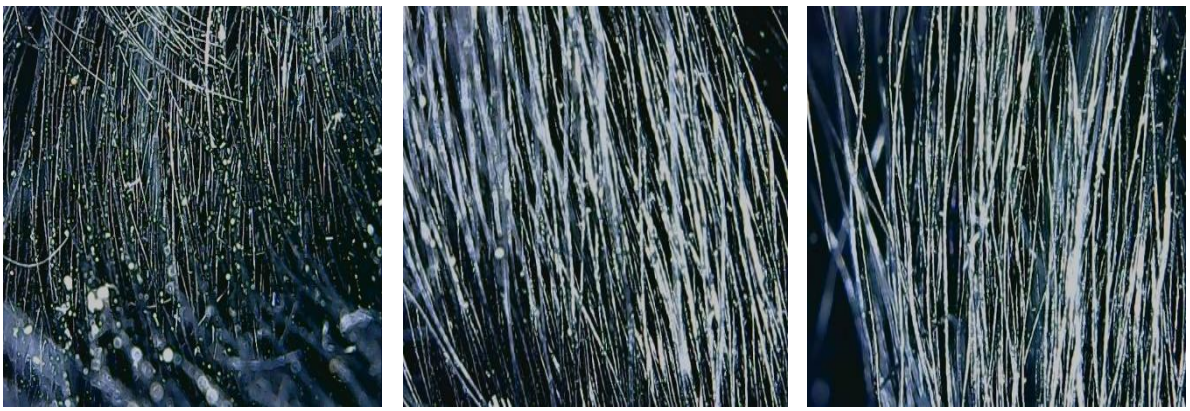


Fig. 2. Digital microphotographs of the hair of the original, control and experimental samples of natural astrakhan fur. Magnification x200 times



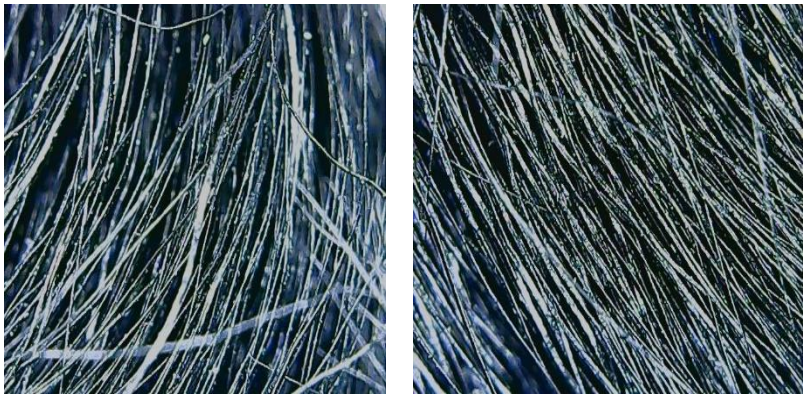


Fig 3. Digital microphotographs of wool of the original, control and experimental samples of natural astrakhan fur. Magnification x200 times

The front surface (hair) of astrakhan skins changes more significantly and depends on the type of tanning component and the pH of the environment.
There are areas unevenly smoothed with macrotufts and rough granular, dense, glued with packings and areas without depressions, which could be expected in advance without the degree of change in the structural properties.
After processing astrakhan skins with GA in a neutral environment, it also appears uniformly granular with smoother rounded areas (in the form of hills).
Thus, when processing astrakhan skins with HA in a slightly acidic environment, the front surface and end, as one would expect, practically do not change, only becoming less loose with smaller intervals, possibly due to the acidic swelling of the fibers during processing.
Treatment with chrome tanning agent gives a more uniform surface structure, which becomes smoother with less pronounced depressions and graininess, and contributes to the appearance of fibrous-plate elements.
Finally, the greatest changes in skin structure are observed when treated with GA. On experimental samples of astrakhan skins treated with HA, the structure is very homogeneous, there are smoothed areas with macro and micro fibers, firills in smooth areas, granular, without depressions (5-10 μm). At the same time, the change in the structure of krakul skins occurs more intensively in the following row, depending on the type of processing:
1- astrakhan < 5- astrakhan < 3- astrakhan < 2- astrakhan < 4- astrakhan
It can be concluded that the study of samples of the original, control and opalized samples of skins showed that processing it with GA leads to some structuring properties and to uniformity of the structure.
Digital microscopy micrographs have established that the uniformity of the internal distribution of GA in the structure of the dermis of astrakhan skins is due to the deposition of colloidal aldehyde particles at the intervals of fiber bundles, in the form of blocks and arrays, which leads to a sharp decrease in the effective pore radius, which can lead to an increase in the performance properties of finished products.
Studies have also been carried out on the processes of adsorption of water vapor from astrakhan skins. Since the skin, being a hydrophilic material, is very prone to absorbing moisture from the environment, and moreover, it is highly wettable.
In this regard, further research was aimed at adsorption processes running through the internal-spatial circumference of the dermis structure of astrakhan skins.

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Table 3 shows the results of a study of water vapor sorption of control and experimental samples of krakul skins.

Table 3

Sorption of water vapor of control and experimental samples of astrakhan skins.

Temperature 20 °C

Relative humidity of the system, %	Sorption of water vapor by control and experimental samples of astrakhan skins, in%				
	Tests		Experienced		
	Natural astrakhan unprocessed original control	Karakul tanned with Cr^2O^3 with a basicity of 15-20%	Karakul tanned with GA in a slightly acidic environment	Karakul tanned with GA in a slightly alkaline environment	Astrakhan fur tanned with GA in a neutral environment
	1- astrakhan	2- astrakhan	3- astrakhan	4- astrakhan	5- astrakhan
10	6,43	4,74	5,86	3,58	5,12
30	19,38	9,37	15,62	8,05	11,04
50	26,28	11,89	22,26	10,14	15,68
70	32,16	14,46	26,42	11,36	20,37
90	36,49	15,83	29,06	12,25	22,35

Research has found that the morphological and adsorption characteristics of karkulids also significantly depend on the type of tanning and pH of the environment.

Table 4

Specific surface area, volume and radius of control pores and experienced tanned astrakhan skins

№	Indicators	Samples				
		Tests		Experienced		
		Natural astrakhan unprocessed original control	Karakul tanned with Cr^2O^3 with a basicity of 15-20%	Karakul tanned with GA in a slightly acidic environment	Karakul tanned with GA in a slightly alkaline environment	Astrakhan fur tanned with GA in a neutral environment
1	Specific surface (S_{sp}), m^2/g	113,712	280,324	178,467	308,514	257,123
2	Pore volume (Wo), sm^3/g	0,473	0,265	0,412	0,238	0,358
3	Pore radius (rк), nm	4,18	2,93	3,624	2,48	3,058

Thus, the ability to sorption of water vapor is reduced under all types and conditions of tanning. Maximum sorption is observed in untreated control initial astrakhan, then in astrakhan tanned with HA in a slightly acidic environment. The minimum

absorption of water vapor was noted on a test sample of astrakhan fur tanned with HA in a slightly alkaline environment, then in astrakhan fur tanned with Cr2O3 with a basicity of 15-20%

If for a test sample of astrakhan tanned with GA in a slightly alkaline environment at 70% relative humidity, sorption is 11.36%, then when treated with Cr2O3 it is 14.46%, with GA in a neutral environment 20.37%, with GA in an acidic environment 26.42 %. This phenomenon is also accompanied first by an increase in the specific surface area while maintaining the volume and pore size for astrakhan fur (m2/g) tanned 257.123 with HA in a slightly acidic environment 178.467, then tanned with HA in a neutral environment 257.123, and then with a significant increase in the specific surface area when tanning astrakhan fur with Cr2O3 and especially, a sharp increase in the surface area for tanned with HA in a slightly alkaline environment 308.514 compared to the control sample. 113.712.

Also, there is also a loss of pore volume (cm3/g) for astrakhan tanned with HA in a weakly alkaline medium of 0.265 compared to astrakhan Cr2O3 0.265 with a subsequent decrease in the effective pore radius (Table 4).

Conclusions.

Thus, it has been established that, in comparison with astrakhan fur tanned with GA in a slightly acidic environment, leather samples tanned in a neutral environment, with Cr^2O^3 and tanned with GA in a slightly alkaline environment are resistant to water. This is apparently due to the possible chemical interaction of the active groups of collagens with the carbonyl groups of GA.

To confirm this assumption, it was of interest to study the original and tanned collagen with GA IR spectroscopy. The data obtained correlate to a certain extent with the results of IR spectroscopic studies.

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