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Products Recycling Waste Fur Production: New Capabilities To Use.

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ABSTRACT

The article puts forward the thesis that the sustainable development of fur production directly depends on the recycling of its waste and their inclusion as secondary resources or auxiliary means of functional purpose in the process of manufacturing the main products. The authors note that the use of solubilized keratin as a recycling product can bring a tangible economic effect to the enterprise, as well as be very expedient from the standpoint of ecology. The results of studies aimed at obtaining solubilized keratin from some types of keratin-containing wastes of fur production are presented, the main indicators of chemical composition are studied, a detailed description of the physicochemical properties of this unique natural biopolymer is given. When evaluating the protective effect of the use of solubilized keratin in the process of dyeing a fur semifinished product, it was shown that an spreading method of applying this functional product on the scalp of a skin is preferable to adding it to the dyebath. The use of solubilized keratin in dyeing reliably increases the strength characteristics of the hair due to the formation of electrovalent bonds in the process of sorption and partial adhesion of this protein component on its surface, increases the resistance of the hair to abrasion.

Keywords: substances solubilized keratin, fur semi-finished product, dyeing, quality, recycling.

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INTRODUCTION

One of the current problems facing modern fur production and requiring urgent solutions is to find ways of rational and efficient use of a significant amount of waste in the form of wool and fur nozzle, flap, which is a rather powerful factor of negative anthropogenic environmental impact [3, 11, 12, 22]. Marketing research on the effective use of keratin-containing waste has shown that they are currently used in very small quantities, and most of them are taken to landfills and landfills, buried or burnt [2, 12]. At the same time, enterprises incur additional costs for the removal and disposal of waste, although they could receive income from the use of keratin-containing materials as secondary raw materials or functional aids that improve the quality of the fur semifinished product during the manufacturing of the main product [14, 22].

The main structural component of the above waste and by-products is fibrillar keratin. Modern innovative solutions in the field of recycling keratin-containing waste open up new opportunities and prospects for the use of this unique multi-biopolymer. Progress in this direction has been achieved thanks to technologies developed by domestic scientists to extract native keratin from wastes with preserved molecular structure and biological activity [6, 11].

Solubilized keratin, obtained by proprietary technologies from its fibrillary precursor, has now found its application and is in great demand in cosmetology [18, 19], medicine [14, 26, 27], biotechnology [3, 4, 9], fur farming [4, 24].

The use of this protein in fur production can and should be fully eligible, environmentally and economically viable.

Currently, fur semi-finished product as a unique natural material is widely used in the manufacture of various products. However, classical technologies for the production of semi-finished fur, when it is subjected to pickling, tanning, dyeing, bleaching, tinting and other types of processing, are associated with the use of various chemicals: alkalis, acids, alum, bleaching agents, salts, mordants and other chemically aggressive compounds, adversely affect the condition and quality of the hair coat fur products.

- The aim of the work is to obtain solubilized keratin from some types of keratin – containing waste and to evaluate the effect of its use as a protective agent at the stage of fur semi-finished product dyeing.
- Object of research. As objects of research used:
- substances of solubilized keratin derived from keratin-containing by-products and waste from fur production;
- fur semi-finished product of sheepskin, silver-black Fox and rabbit.

MATERIALS AND METHODS

Experimental studies were performed using standard methods and generally accepted methods, as well as methods modified by the authors in the course of research.

Substances of solubilized keratin from wool and fur nozzle and reindeer hair were obtained according to the method described in RF patent No. 2092072 "Method of Keratin Production" [16], modified by us with regard to the characteristics of the properties of the waste used.

The quality assessment of the obtained substances of solubilized keratin was carried out using organoleptic characteristics, such indicators of chemical composition as moisture content, protein, fat, minerals and sulfur in the dry residue, pH, density, dynamic and characteristic viscosity, molecular weight [5, 10].

When evaluating the protective effect of the use of solubilized keratin in the process of dyeing the fur semifinished product, we controlled the indicators of heat resistance, physicomechanical properties of leather and hair, resistance of colored hair to alkali, scanning electron microscopy [10, 12, 13, 20].

RESULTS AND DISCUSSION

Recycling of waste of modern fur production is becoming increasingly important due to stricter requirements for the environmental condition of the fur industry, the shortage of quality raw materials and the increase in its cost. Obtaining high-quality semi-finished products in the realities of modern fur production depends on whether the products of recycling its waste will become an integral part of the technological processes as reagents, the functional purpose of which is to protect products from the aggressive effects of the reagents used.

Table 1 summarizes the results of studies on organoleptic evaluation of the quality of substances solubilized keratin obtained from certain types of waste fur production.

Table 1: Comparative evaluation of the organoleptic characteristics of solubilized keratin substances

Indicators	Substances of the solubilized keratin (SSK) from		
	wool comb	fur comb	reindeer hair
Appearance	homogeneous, dense, finely dispersed mass, without residues of wool, hair		
Colour	white with a slight cream shade	various shades of brown	light gray
Smell	low peculiar smell of sulfur		
Consistency	homogeneous		
Transparency	opaque		

According to the results, the organoleptic properties of the studied SSK slightly differ in color depending on the source material and the content of the hair pigment. The data characterizing the chemical composition of SSK are presented in table 2.

Table 2: Chemical Composition of SSK Samples (n = 5)

SSK from:	Dry residue, %	Content,% of absolutely dry matter			
		Minerals	Fatty substances	Protein substances	Total sulfur
wool comb	5,8±0,2	0,21±0,03	0,81±0,01	98,7±0,08	2,89±0,02
fur comb	4,6±0,1	0,68±0,01	0,34±0,05	98,4±0,07	2,52±0,03
reindeer hair	3,7+0,1	0,90±0,01	0,52±0,01	97,9±0,06	2,05±0,03

Dry residue and components included in its composition are the main criteria characterizing the quality of any finished product. As can be seen from table 2, the dry residue in the obtained SSK is represented by three main components: mineral, fat and protein. At the same time, the total content of mineral and fat substances found in SSK from wool and fur was slightly more than 1%, from the hair of an adult reindeer - 1.42%. Therefore, the lower the ash and fat content, the better the finished product is cleaned. The established fact indicates that the solubilized keratin obtained from wool and fur comb is the most purified from the accompanying substances keratin-containing product. The highest protein content was recorded in SSK, obtained from wool and fur combs-98.7% and 98.4%, respectively. The lowest protein content in SSK from reindeer hair (97.9%) is due to its histological structure, namely with a high core content (up to 90%) [17]. The presence of sulfur-containing amino acids is an identifying indicator for keratin.

Solubilized keratin is a very specific protein product. In order to estimate its molecular weight, it is necessary to know such indicators as the dry residue content, pH, density and dynamic viscosity of solutions, without which it is impossible to calculate it. These data are presented in table 3.

Table 3: Physico-chemical indicators of substances solubilizing keratin (n = 5)

SSK from:	pH	Density, kg / m³	Dynamic viscosity, 10^{-4}Pa·s	
			according to Goppler	according to Ubbelode
wool comb	7,16 ± 0,03	1,0150 ± 0,0005	23,0 ± 0,5	21,5 ± 0,4
fur comb	7,14 ± 0,03	1,0100 ± 0,0004	52,0 ± 0,7	51,0 ± 0,6
reindeer hair	7,10 ± 0,02	1,0060 ± 0,0003	38,5 ± 0,6	40,0 ± 0,6

As can be seen from table 3, the average pH for each type of solubilized keratin is in the neutral region of the scale. The second indicator was the density of keratin-containing substances-a value measured by the mass of the substance per unit volume. The maximum value of the density index was set for the SSK obtained from the woolen comb and the lowest value for the SSK obtained from the reindeer hair. According to the data obtained, the highest viscosity was SSK, obtained from the fur comb, and then, in descending order, SSK from the hair of the reindeer and from the woolen comb. The absence of a direct relationship between the values of density and dynamic viscosity can be explained by the fact that the viscosity of colloidal solutions depends primarily on the structure and size of colloidal particles and the nature of their interaction with the dispersed medium [5]. The obtained results on the viscosity of SSK allowed us to proceed to the calculations of their molecular weight. Although viscometry can not be considered as an absolute method of measuring molecular weight, however, it is widely used for this purpose in the study of protein products.

Depending on the method of preparation, and sometimes due to the influence of subsequent processing, the degree of molecular heterogeneity (polydispersity) of the colloidal substance can have different values. Indeed, substances solubilized keratin are a mixture of inhomogeneous largest colloidal particles, and therefore, the molecular weight determined by any method, will be a certain average value. To calculate the molecular weight, the values of the characteristic viscosity of SSK from each type of waste were used (figure 1).

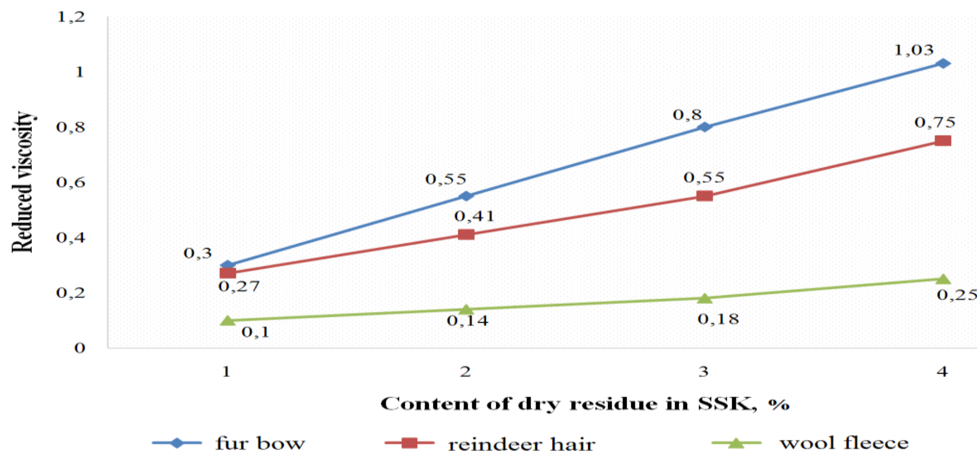


Figure 1: Characteristic viscosity of keratin-containing substances

The characteristic viscosity was determined by graphical extrapolation of the reduced viscosity to the zero concentration of the substance.

The result graph was obtained the following values of intrinsic viscosity: wool flock - 0,045 DL/g, fur flock - 0,060 DL/g and hair of the reindeer - 0,100 DL/g. According to the calculations, the approximate molecular weight of the obtained substances solubilising keratin from the wool of the flock was– 61644.e. (carbon units) from a hair reindeer - 91104.e. fur flock – 70711.e.

The obtained substances of solubilized keratin according to their quality indicators corresponded to the data published in the domestic and foreign scientific literature [16, 23, 25, 26, 27] in the characterization of keratin solutions used previously in various sectors of the economy. The above gave us the basis for studying the possibilities of using SSK in the technology of obtaining fur semi-finished product.

In matters of assessing the quality of the finished fur product properties of selected skins occupy a Central place, as they determine the technology of its manufacture. Despite the external beauty and apparent, at first glance, simplicity of form, fur is one of the most complex materials of processing, whose properties depend both on the chemical nature of the raw material, and on the impact on it of the whole set of chemical, physico-chemical and mechanical processing during dressing [15, 21].

As you know, finishing operations are the final cycle of dressing, it is at this stage that the final formation of the properties of the fur semi-finished product and quality indicators of the finished product from it. In particular, the dyeing of semi-finished fur is one of the most important finishing operations in its production. Finishing operations are divided into two groups: liquid, which are based on chemical and physico-chemical phenomena that change the properties of semi-finished products and operations, which are based on mechanical effects on the semi-finished product (shearing, to comb, pinch, etc.) [1, 15, 21]. In our work, we paid special attention to such a process, which is included in the first group of finishing operations of fur semi-finished products, as dyeing.

For example, dyeing is a complex set of different chemical effects on the fur semi-finished product, including such processes as neutralization, etching, bleaching, dyeing itself, etc. [1, 7, 15].

Due to the fact that the semi-finished fur is often subjected to dyeing, it was of interest to study the protective effect of the use of solubilized keratin at this stage of finishing processes. The results of determining the quality indicators of dyed fur semi-finished products are presented in tables 4-6.

Table 4: Indicators of physicomechanical properties of dyed fur semi-finished product

Analyzed indicators	Processing option	Type of semi-finished product		
		fur sheepskin	silver black fox	fur rabbit
Leather (n=10)				
Temperature of welding, ° C	control	82,4±0,6	68,4±0,6	74,1±0,6
	1	82,8±0,4	68,2±0,9	73,9±0,5
	2	81,5±0,5	67,8±0,6	73,6±0,5
Explosive stress, MPa	control	127,2±6,4	28,8±0,6	20,9±0,9
	1	130,2±6,6	30,1±0,6	21,3±0,6
	2	127,1±6,1	29,8±0,4	20,8±0,8
Elongation at break,%	control	37,2±1,9	33,6±1,0	34,6±0,9
	1	37,1±1,5	35,2±0,9	33,4±1,0
	2	36,2±1,6	33,4±1,2	33,2±1,1
Hair coat (n=100)				
Explosive stress, MPa	control	139,34±5,3	150,6±6,2	128,2±5,2
	1	159,81±6,5	175,9±7,2	142,6±5,8
	2	162,83±6,7	178,2±7,3	153,6±6,3
Relative extension, %	control	30,1±0,7	29,2±0,5	28,5±0,6
	1	31,6±0,6	30,8±0,5	31,3±0,6
	2	32,8±0,6	31,8±0,6	32,8±0,5

Note: * control - without keratin, 1 - solubilized keratin was added to the dyebath, 2 - keratin was applied to the hair of the skins.

According to the data (table. 5), an indicator of the thermal stability of the samples is fur sheepskin equal to the average of 82,2 °C, which corresponds to the standards GOST 4661-76 "Sheepskin fur crafted. TU" (not less than 70 °C). Significant difference between the average values of the indicator of the thermal stability of the samples the three options of dyeing is not established (P=0,95 t_f0,55;1,15 <t_{st}2,4). The heat resistance index of semi-finished silver-black Fox averages 68.1 °C, rabbit-73.9 °C, which meets the regulatory requirements (not less than 65 °C).

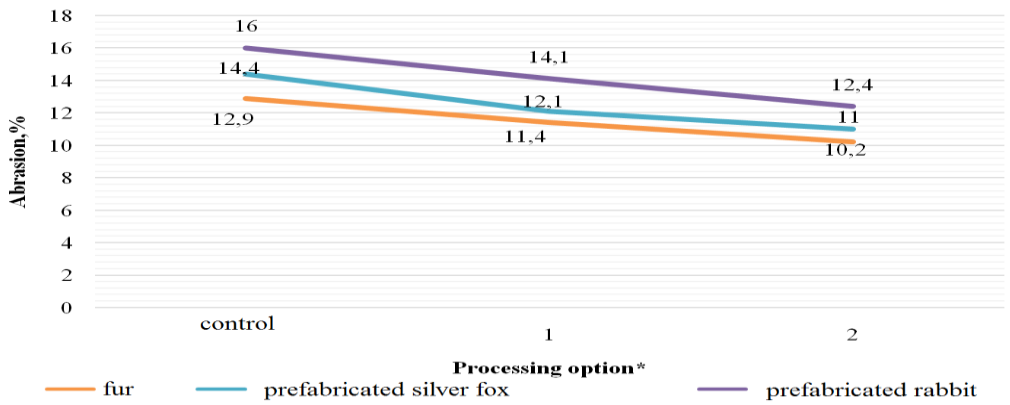
The indicator of the tensile stress of the skin tissue of fur sheepskin after dyeing is 127.2±6.4 MPa, when adding solubilized keratin to the dye bath, it was slightly different from the values of the control sample and the sample treated with 2 variants ($P=0,95 t_f 0,33; 0,01 < t_{st} 2,4$). Differences in the values of different types of fur semi-finished products are due to such properties of the skin tissue as thickness, density in different topographic areas of the skin, etc.According to the obtained data, the index of the tensile stress of the skin tissue of the control samples of silvery-black Fox and rabbit was 28.8±0.6 MPa and 20.9±0.9 MPa, respectively. Depending on the method of use of keratin, there are slight differences in the average values of the studied indicator of the skin tissue of silvery-black Fox, but the difference between them is not reliable ($P=0,95\ t_f 1,53; 1,39 < t_{st} 2,4$). A similar trend is observed for rabbit skins ($P=0,95\ t_f 0,08; 0,37 < t_{st} 2,4$).

The relative elongation, characterizing the elastic-plastic properties of the semi-finished product, for fur sheepskin is 37%, for silver-black Fox and fur rabbit-34%. The data obtained indicate a good stretch of leather fabric fur semi-finished product and indicate the prospects of their use in furry production.

It should be noted that the studies revealed no significant difference in the values of the studied parameters of the skin tissue of the control and experimental samples of semi-finished Fox, rabbit and fur sheepskin. Keratin adhesion mainly occurs in the upper layer of dead keratinized epidermal cells. In the pre - treatment of keratin hair with subsequent dyeing (option 2) is to minimize the destructive effects of coloring solutions on the skin tissue, due to the fact that it mainly interacts with the structure of the hair cuticle by adsorption.

From the data of table 5 it can be seen that the value of the tensile stress of a single fiber of fur sheepskin dyed with keratin, 7-8 MPa significantly higher ($P=0,95; 5,76; 9,19 \geq t_{st} 2,1$), in comparison with data on the semi-finished product painted on control option. A similar trend is observed for the skins of silvery-black Fox and fur rabbit: the highest strength of the hair is observed in the case where keratin is directly applied to the hair, the value of this indicator is 178.2±7.3 MPa and 153.6±6.3 MPa, respectively. Perhaps, in the process of dyeing with the use of solubilized keratin in the structure of the hair, additional electrovalent bonds are formed, which cause an increase in strength characteristics.

The results of the stability of the hair cover of the fur semi-finished product to mechanical effects on abrasion are shown in figure 2.



*** control - without keratin, 1 - solubilized keratin was added to the dyebath, 2 - keratin was applied to the skin of the skin**

Figure 2: Abrasion of hair of various types of semi-finished fur,%

The resistance of the hair to abrasion proves that the highest percentage of weight loss is characteristic of the samples painted on the control version. This figure is averaged for fur sheepskin 12,9±0,2%, of the skins of silver-black foxes - 14,4±0,2% rabbit -16,0±0,2%.To a lesser extent, samples of fur semi-finished products painted with the use of solubilized keratin were subjected to abrasion, as evidenced by the values of the hair stability index, which is lower by 12-24% compared to the control samples.

Evaluation of the stability of the fur semi-finished product after dyeing with and without keratin is shown in table 5.

Table 5: Resistance of hair color to dry friction and the effect of light fur semifinished

Processing option	Analyzed indicators					
	Color stability to dry friction, score			Resistance of color to light, score		
	fur sheepskin	silver black fox	fur rabbit	fur sheepskin	silver black fox	fur rabbit
1	4	4	4	5	5	5
2	4	4	4	5	5	5
3	4-5	5	5	5	5	5
Requirements of GOST 4661-76, 6803-72, 2974-75, not less	4			5		

According to the obtained data, the used acid dyes are well adsorbed by the hair and are resistant to dry friction (not less than 4 points). When applying solubilized keratin directly to the hair of the test samples of fur semi-finished product was assigned the highest score (5) in terms of "resistance to dry friction." The resistance of the hair to the action of light corresponded to 5 points, which meets the requirements of the standard for the studied species. The data obtained confirm the fact that the dyeing was carried out in accordance with the requirements for this type of fur processing. They indicate the strength of the dye connection with the hair, which in the future should ensure the safety of the color of fur products during operation.

To determine the chemical resistance of hair were used two independent methods of estimation: for the weight loss of hair after treatment with alkali and using the modified methodology for the determination of the value of the optical density of the resulting filtrates (table. 6).

Table 6: Resistance of hair coat of colored fur semi-finished product to the action of alkali (n = 10)

Analyzed indicators	Processing option	Painted semi-finished product		
		fur sheepskin	silver black fox	fur rabbit
Weight loss of a hair sample,%	control	13,2±0,6	19,2±0,6	22,5±0,4
	1	10,3±0,4	16,6±0,5	19,1±0,5
	2	9,7±0,4	14,7±0,5	17,3±0,4
Optical density of filtrates, unit of optical density	control	0,59±0,11	0,58±0,09	0,45±0,07
	1	0,37±0,09	0,39±0,06	0,28±0,06
	2	0,32±0,09	0,37±0,06	0,25±0,08

Note: * control - without keratin, 1 - solubilized keratin was added to the whitening bath, 2 - keratin was applied to the hair of the skin.

As can be seen from the presented results, the chemical resistance of the fur sheepskin hair to the action of alkali (0.1 N sodium hydroxide solution) in terms of weight loss is in the range of 9.7 – 13.2%. In the case of the introduction in the composition of the dye bath solubilising keratin, as well as when directly applied it on the scalp, this figure was significantly lower at 22-23% ($P=0,95$; $t_f 4,02; 4,85 \geq tst 2,1$).

Due to the fact that the hair coat of fur sheepskin is represented by only one morphological type of fibers, namely down, the studied indicator of this sample is less than that of skins of silvery-black Fox and rabbit, due to the presence in their hair cover in addition to down, guard and transitional hair types, which have a well-developed core layer, less resistant to chemical When working with semi-finished silvery-black Fox, painted without the use of keratin, it was found that the indicator of "hair mass loss under the influence of alkali" is 19.2%, and with the use of keratin in both treatment options, its value is significantly less by 14-23% ($P=0,95$, $t_f 3,33;5,76 \geq t_{st} 2,1$). A similar trend is observed for semi-finished rabbit: the highest percentage of weight loss of hair under the action of alkali is revealed after dyeing on the control version (22.5%), after experimental dyeing, this figure is significantly reduced, especially in the third embodiment of treatment by an average of 24%, which indicates the protective effect of keratin ($P=0,95$, $t_f 5,31;9,19 \geq t_{st} 2,1$).

The developed technique is based on the registration of differences in the optical density of filtrates obtained after dissolution of experimental and control hair samples in alkali. According to our data, the filtrates obtained by dissolving the hair treated with solubilized keratin, the optical density decreases by about 1.5 times. The proposed method allows to reduce the time of obtaining results by 6 times.

In the process of dyeing, which has a destructive effect on the hair, the presence of a protective agent – keratin not only reduces the solubility of the hair, but also increases its strength due to sorption and partial adhesion of the protein component.

Previous studies [6, 7] comparative microscopic analysis showed that when dyeing fur semi-finished product solubilized keratin protects the hair, filling and cementing the damaged areas of the hair (Fig. 3-5).

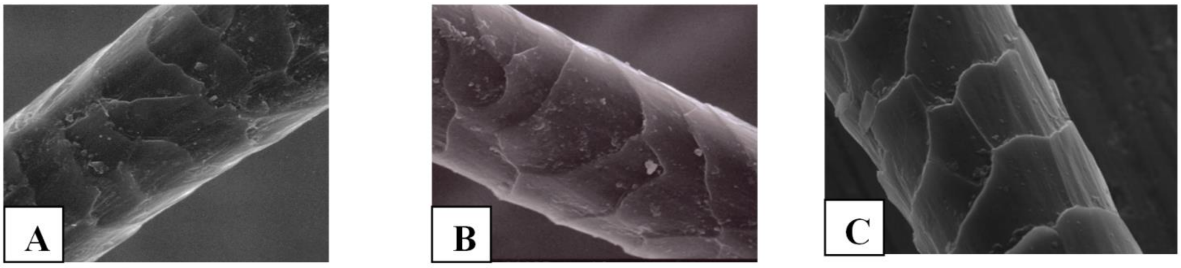


Figure 3: Micrograph of a fur sheepskin hair after dyeing according to: A - the control variant, B - with the addition of keratin in the coloring bath (option 1), C - preliminary application of keratin on the hair coat (option 2) (magnification x 1000)

On the surface of the scaly layer of fur sheepskin hair, painted on the control version, there is a partial exfoliation of cuticle scales from the surface of the hair, the presence of cracks, irregularities, resulting in a kind of notches on the scales, there is their destruction and deformation. When processing samples with dye reagents according to experimental variants (with the addition of keratin), no noticeable damage was found.

A similar trend can be observed in hair samples with semi-finished silver-black Fox and rabbit (Fig.4 and 5), where it can be noted a significant improvement in the state of the cuticle layer of the guard and down hair: cuticle scales have a smooth optical edge and fit tightly to each other along the entire length of the hair.

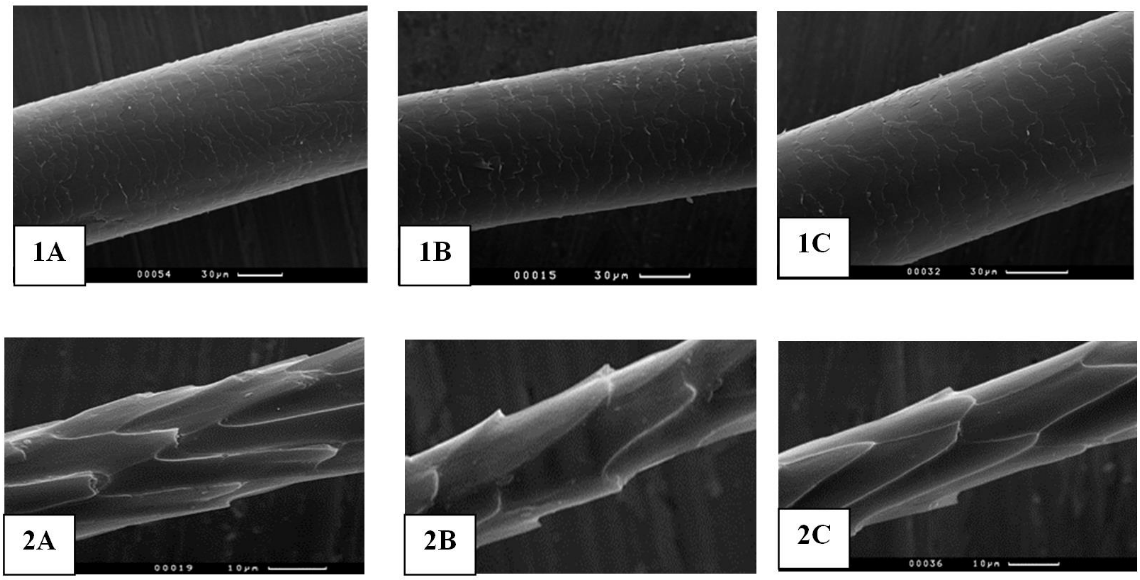


Figure 4: Micrograph of the guard (1) and down (2) hair of a silver-black fox after dyeing in: A - the control variant, B - with the addition of keratin in the coloring bath (variant 1), C - preliminary application of keratin on the hairline (variant 2) (magnification x 1000; x 1500)

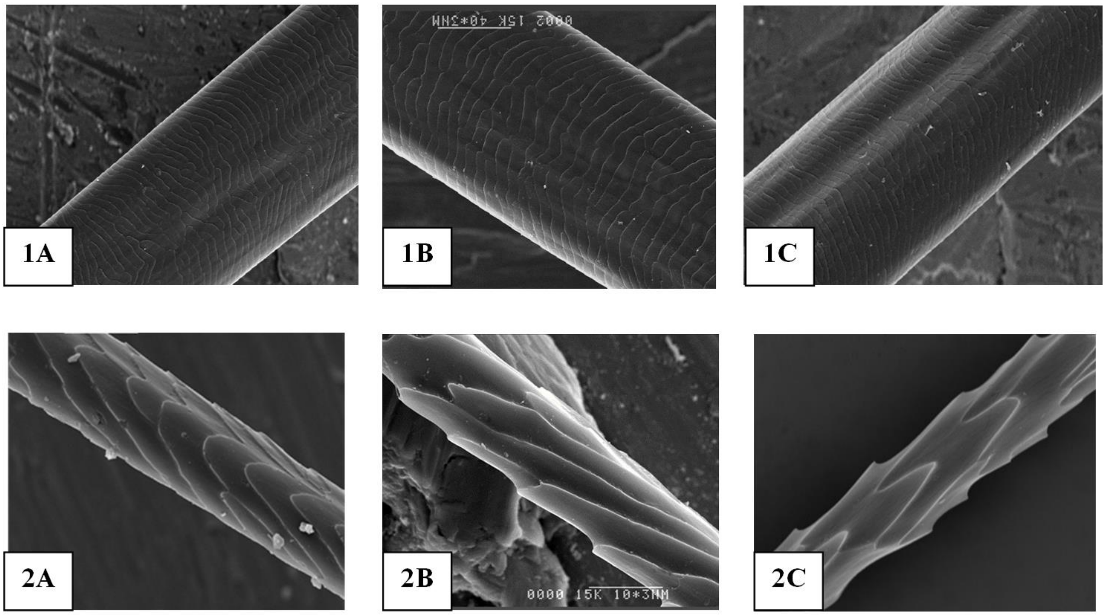


Figure 5: Micrograph of bristle and down hair of a rabbit fur after dyeing according to: A - the control variant, B - with the addition of keratin in the coloring bath (option 1), C - preliminary application of keratin on the hairline (option 2) (magnification x 1000)

The result of the interaction of solubilized keratin with hair (variants 2 and 3), as we have previously established [6, 7, 8], is an increase in its strength characteristics. In this regard, we adhere to the opinion of a number of authors that keratin, in this case, cements the surface of the hair, increasing its resistance to aggressive environment in the process of dyeing.

CONCLUSIONS

The results obtained indicate the feasibility of using solubilized keratin to protect the fur of the fur semifinished product at the dyeing stage and suggest the use of a spreading method for this purpose.

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