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Tanning of nutria skins based on interpolycomplex and its effect on the physic-chemical and mechanical properties of fur

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ABSTRACT: General information about the nutria animal, such as reproduction statistics, skin weight, area, coat color, etc., are given. The technological sequence of synthesis of interpolycomplex and the technology of fur production in the tanning process, the chemicals used in the tanning process were studied. In the course of the research, instead of the imported chemical additives, the additive technology was created using local additive chemicals. To compare the results of the experimental test with each other, two identical grade II standard nutria skin raw materials were selected, and these skins were treated with the traditional tanning method and interpolycomplex tanning process. By these methods, the results were obtained on the standard plots of furs and these results were compared with each other. Changes in the process-dependent hydrothermal destruction of nutria furs tanning based on the traditional tanning method and the interpolycomplex tanning agent have been presented. The results of fat content, minerals and moisture content of fur, strength limit, and elongation at break were determined by experimental tests.

KEYWORDS. nutria, interpolycomplex tanning agent, tanning, derm, collagen, wool, epidermis, leather, fur, hydrothermal destruction, oil, chromium, mineral matter, moisture, maximum elongation, strength, fluidity coefficient.

I. INTRODUCTION

Leather is the outer layer of the animal that protects the animal body from the external environment: mechanical, hot, cold, moisture, etc., leather and fur products are made as a result of leather processing [1]. Tanning is one of the oldest crafts of mankind, and the use of leather in archaeological excavations and rock paintings is a clear example of this. Tanning was casual and gradually turned into a craft in the Middle Ages. Scientific research on tanning began in the nineteenth century and, with the development of machinery and the Industrial Revolution, progressed to modern tanning technology. Remains of durable leather were found that were worked by the Egyptians 3000 years ago and are still in good condition, and according to the results of analysis, they were found to be enriched with oil [2].

The nutria is a rodent native to South America and has been farmed in most parts of the world since the early 1900s, initially mainly for its fur. The nutria is a large (over 6 kg) semi-aquatic rodent with a good appetite and high reproductive potential. The nutria appeared in the swamps of Louisiana in the 1930s. Due to their adaptive lifestyle, the number increased to approximately 20 million animals in less than 20 years. Their most important impact is habitat modification and, in many cases, habitat destruction. The first nutrias suitable for keeping in cages were brought to Europe from Argentina in the 1930s, and since then, nutrias have been bred in many European countries. In particular, from 1930 to 1940, about 100 000 nutria furs were produced annually in Germany. There were about 1000 nutria farms. The State Sanitary Inspectorate of the Ministry of Health of the USSR dated April 25, 1961, and the General Directorate of Veterinary Control of the Ministry of Agriculture of the USSR dated June 30, 1969, allowed the use of nutria meat in

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nutrition [3]. An important part of tanning agents refers to compounds that form complex bonds with the active groups of collagen. These are mainly inorganic substances related to basic salts (chromium, aluminum, zirconium) or poly- and heteroacids of tungsten, molybdenum, and silicon.

The study provides an overview of the current state of fur tanning processes, development trends, and prospects of the fur industry. Domestic and foreign market preparations used in fur production are reviewed [4]. Chitosan is an amorphous transparent substance with a structural unit similar to the polysaccharide structure of the extracellular matrix, which has good antibacterial, biocompatible, and degradable properties. It is important in fur production, water purification, medicine, food, and other fields, so chitosan and its modified products have received wide attention. In this study, the preparation methods of chitosan-based antibacterial composites including chitosan/collagen, chitosan/graphene, chitosan/tannic acid, and chitosan/polyethylene glycol composite materials were reviewed in recent years, their modification methods and antibacterial mechanisms were studied in detail, and antibacterial auxiliaries in the fur industry, and its use as antibacterial adsorbent materials for water purification is discussed. Finally, the future development and challenges of chitosan-based composite materials in the fur industry are projected [5].

As an alternative to the chromium tanning method, the use of humic acids from brown coal is proposed. Humic acids are aromatic hydroxycarboxylic acids that can be used as emulsifiers due to their emulsifying properties. The growth properties of sulfogumic acids converted to water-soluble sodium sulfogumat were studied, and the temperature of hydrothermal destruction of semi-finished products reached 65-80 °C [6].

It is no exaggeration to call our age the age of polymer composite materials due to the range of materials used in all fields today. The importance of polymers in human life is so great that it is difficult to imagine people's lifestyles without these materials. As you know, there is a sharp difference between polymer substances and polymer materials. For the polymeric substance to transfer to the material, in most cases it is necessary to add various chemical additives to it. It helps to improve the physical and chemical properties of compounds, and substances, stability to heat and light, mechanical strength and climate resistance, water resistance, and other properties. Usually, the properties of the material are changed by adding an inorganic filler to many polymer materials [7]. Several characteristics of polyelectrolytes consisting of mixtures of acid-base polymers deviate from additivity. The resulting interpolymer complexes are close to amorphous polymers in terms of their physical properties. The thermal conductivity value obtained in this case is free of the relaxation contribution and indicates pure molecular thermal conductivity [8]. The study [9] continued the study of water-soluble fluorescent polymers of polyacrylamide and polyacrylic acid derivatives, which can be used as a working additive to polyacrylamide industrial samples. Partially hydrolyzed polyacrylamide or polyacrylic acid has been used for effective and reliable control of residual polyacrylic acid content in working mixtures, wastewater, etc.

Previously [10], conditions for precipitation polymerization and copolymerization of acrylamide with phosphorus monomers were studied. The optimal use of polar aprotic solvents with a boiling point of at least 70 - 80 ºC has been determined. Most of the syntheses have been carried out by researchers in dioxane or ethyl acetate at 70 - 80 ºC, leading to the formation of polyacrylamide and its modification in good yields. In this study, the results of the study of water-soluble fluorescent polymers of polyacrylamide and polyacrylic acid derivatives, which can be used as working additives for partially hydrolyzed industrial samples, are presented. The content of residual polyacrylic acid in polyacrylamide working mixtures or wastewater, etc. can be controlled with high efficiency and reliability.

For better placement of aluminum complexes in furs, compositions based on condensation products of formaldehyde with acryl sulfone and acrylic acid derivatives, as well as copolymers of unsaturated mono- or dicarboxylic acids or their hydro compounds have been developed [11].

Reactive organic compounds, aliphatic aldehydes, methylol derivatives of amino acid compounds, oxazolidines, etc. can interact with functional groups of collagen. When supplemented with these compounds, the hydrothermal stability of the skin is in the range of 75-85 °C [12]. This study used tetrahydroxyethylenediamine, an interaction product of monoethanolamine, formaldehyde, and urea.

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A multi-component composition of natural biopolymer rich in natural oil antioxidants (liposomes and niosomes) capable of forming chitosan, phospholipids, silicone polyethers, and nanovesicle particles has been created. The created composition [13] not only restores and stabilizes, but also ensures the preservation of the properties of the fur product over time. However, such a composition is very susceptible to biodegradation and the effects of insecticides. In the fur growing process, 10,0 to 90,0 % by mass of raw materials were treated with compositions from 1,0 to 30,0 % based on polymers based on one or more carboxyl mixtures.

To increase the water resistance properties of chromium-enriched leather, foreign researchers treated it based on an emulsion consisting of a mixture of triethanolamine, carbonic acid, alkane polymer, sulfurized synthetic ether, and sulfosuccinic acid with paraffin [14].

II. MATERIALS AND METHODS

Taking into account the above-mentioned research, we have set ourselves the task of synthesizing a new generation tanning agent with complex properties and using it in the process of dyeing nutria skins.

In solving this problem, the sequence of the tanning agent synthesis process is performed as follows [15-16], bentonite as a mineral preservative, polyacrylamide as an acrylate polymer, and leather dust or glycerin components as a reducing agent were formed in a certain ratio according to the technological scheme shown in Fig. 1, %.

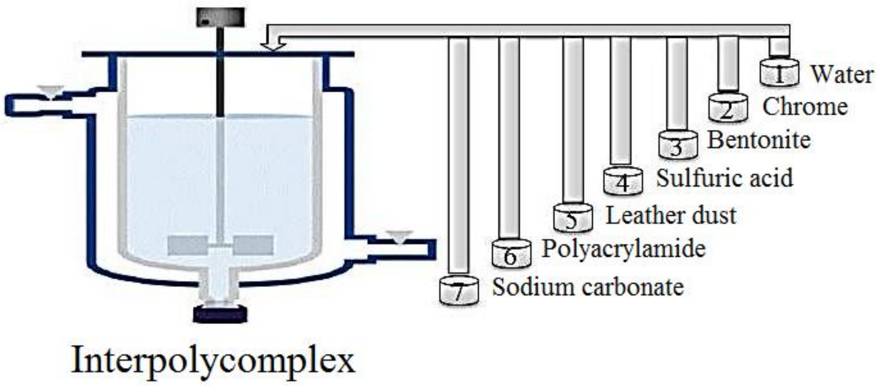

Figure 1. Technological scheme of synthesis of interpolycomplex enhancer.

A suspension of potassium dichromate and bentonite dissolved in water was poured into a reactor equipped with a mechanical stirrer. Sulfuric acid was slowly poured over it in portions. Leather dust or glycerin was added portion-wise to convert the mixture into a basic chromium (III) complex. When the mixture heated to a vigorous boil and evolved a rapid gas, the mixture was cooled and then continued. Continuing the process, the color of the mixture's solution starts to change from reddish-yellow to purple and then to green. When further portions of leather dust or glycerine are added, the chromium mixture decreases in boiling point and stops completely, indicating that the chromium has been completely reduced to the III-valent state.

A calculated amount of polyacrylamide was then added, and an appropriate amount of sodium carbonate was added to increase the tanning agents's stability and raise the pH as a correction. The difference is that bentonite was used instead of sulfuric acid and alumino-potassium caustic stone. Polyacrylamide, a product manufactured at "Navoiazot" HJ, was added to the reaction products' composition during the tanning synthesis. The tanning catalyst was then neutralized with sodium carbonate. The tanning of bentonite and polyacrylamides to the composition of the resulting additive creates an interpolycomplex of a cationic nature and provides additional mineral and polymer filling, saturation, and hydrothermal stability of the fur.

The formation of this interpolycomplex additive can proceed according to the following reaction:

$$7K_2Cr_2O_7 + 21H_2SO_4 + 3C_3H_8O_3 \rightarrow 14CrOHSO_4 + 7K_2SO_4 + 9CO_2 + 26H_2O$$

$$ad_{\text{degree of basicity}} = \frac{1}{3} \times 100 = 33{,}3\ \%$$

From these equations, it can be seen that 12,2 % leather dust and 7,5 % sodium carbonate are required to reduce 35 % potassium or sodium dichromate. In fact, in this reaction, several substances are formed from the complete deoxidation of leather dust and sodium carbonate, for which it is necessary to obtain more organic substances for the reduction of chromium. Experiments show that it is desirable to get 3,0-4,0 % more leather dust in practice. It can also be seen from these reactions that the reduction reaction takes place in an acidic environment. It is used for the formation of acid-base chromium compounds and potassium sulfate. The degree of basicity depends on the amount of acid in the system, and the equation for obtaining a chromium interpolycomplex extract with a basicity of 66,6 % is as follows.

$$4Na_2Cr_2O_7 + 8H_2SO_4 + C_6H_{12}O_6 \rightarrow 4Cr_2(OH)_4SO_4 + 4Na_2SO_4 + 6CO_2 + 6H_2O$$

$$ad_{\text{degree of basicity}} = \frac{2}{3} \times 100 = 66{,}6\ \%$$

In the preparation of chromium salts with a base of 33,3 %, 3 moles of acid are used for 1 mole of chromium, that is, 4:12 or 1:3. In the preparation of chromium salts with a basicity of 66,6 %, 1 mole of chromium requires 2 moles of acid, that is, 4:8 or 1:2. Sulfuric acid is used not only in the formation of chromium extracts but also in the formation of neutral salts. From the reaction we have considered, it is known that the chromium extract prepared from bichromate also contains neutral salts. If there is an excess of alkali in the technical monochromate, in addition to neutralization, acid is consumed, which in turn leads to an increase in neutral salts in the extract.

It has been recognized by fur manufacturers that chromium extract from monochromate is inferior for tanning to chromium extract from dichromate. Based on the resulting interpolycomplex, collagen was processed. Interpolycomplex (3,5 % by collagen mass) was exposed to a 10 % collagen solution for 3 hours at a temperature of 20 °C. Films from a 6.0% solution (pH = 5,3) were poured onto mercury in a Petri dish. To remove the adsorbed and non-interacting agent on the surface of the film, they were repeatedly washed with distilled water in several portions and then dried. The result of the interaction between the interpolycomplex enhancer and the collagen was evidenced by the significant difference in the spectra of the initial and interpolycomplex-treated collagen.

It is known that fur skins are required to have a high level of softness and plasticity. After tanning, the skin must have partial elasticity, and during the tanning process of the fur, its plastic properties must be preserved. Therefore, these skins are well saturated with acid during pickling. In this kind of pickling, the skins have plasticity and elasticity properties at the required level.

When tanning fur, it is necessary to take into account that it is difficult for the tanning agents to pass from the epidermis to the dermis. The dermal filler diffuses through different layers of the skin. This can cause chromium compounds to spread unevenly across the layers of the skin, reduce plasticity, and tear strength, and stretch across the area. In addition, it is necessary to take into account the characteristics of the interaction between the tanning agent and the wool, because determining the quality of the fur can change the appearance of the wool cover. The interpolycomplex tanning agents have a high tanning capacity combined with a good tanning property, as well as a good curling of the fur. It is possible to actively change the specific areas of the fur by changing the ratio of the curing components [17].

Nutria skin collagen processed based on the synthesized interpolycomplex was analyzed and the results revealed that the interpolycomplex has a high causticity. Taking into account the results, the interpolycomplex tanning agent was synthesized according to the percentage of the component. The consumption of components is as follows in Table 1, %:

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Table 1

The general composition and quantities of the interpolycomplex tanning agent

№	Components name	Percentage of components, in %	
		a	b[15]
1	Chromic (potassium or sodium dichromate)	18,2	25,0-35,0
2	Sulfuric acid	14,5	10,0-15,0
3	Bentonite	1,8	7,5-10,0
4	Leather Dust/Glycerine	5,4	10,0-12,5
5	Sodium carbonate	4,9	5,0-7,5
6	Polyacrylamide	6,0	10,0-12,5
7	Water	The rest	

The standard nutria skins were selected to obtain reliable results, and the change in the required quality indicators was determined by comparing the results of skins of the same type, of which b-control, and a-experiment samples were used. The selected skins were sampled using the traditional method of control samples, and the experimental samples were modified, based on the improvement process, i.e. interpolycomplex, which leads to the improvement of leather quality. When increasing the experimental samples of the research work, at a liquid coefficient (LK) of 9, the consumption of interpolycomplex is 7,5 g/l, salt (NaCl) – 40,0 g/l and sodium carbonate (Na_2CO_3) – 0,3 g/l, at a temperature of 32,0-36,0 ^oC. During 20-22 hours, the heating process was carried out until the hydrothermal destruction exceeded 60,0 ^oC. All other processes were carried out according to the traditional method. The effectiveness of the tanning process was evaluated by changing the hydrothermal chemical and physical-mechanical indicators of the skin tissue and the finished product [17].

In continuation of the research work, a control sample of nutria hides [18] was treated in a mixture of 50 g/l NaCl, 25,0 g/l alumino-ammonium bitumen at a LC of 10,0 and 35,0 ^oC, and after 2 hours with the addition of 5,0 g/l Moutotan. mixed and after 4 hours 2,0 g/l tanning assist B. was added and the liquid medium was monitored with constant stirring for 1 hour. Tanning oil G. was added in the amount of 2,0 g/l when the liquid pH was 3,6-3,7, and the increase process was continued with constant stirring for 0,5 hours. All the above-mentioned pre- and post-increase processes were carried out without modification in the experiments.

Technological processes of processing nutria skins were carried out according to the following scheme:

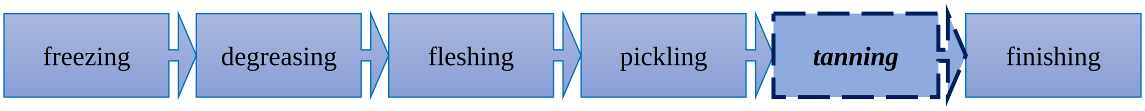

Figure 2. Scheme of technological processes of processing nutria skins.

The next turn of research was focused on studying the physico-chemical properties of nutria skins and finished products. The formation of properties of nutria fur, their quality, and quantitative values are mainly determined by the type and nature of chemical materials. Currently, among such chemical materials, we use interpolycomplex (chromic, sulfuric acid, bentonite, leather dust or glucose, sodium carbonate, polyacrylamide) and salt in our experimental samples for leather enhancement. For our control samples, based on existing technology, chemical materials such as salt, aluminum-ammonium caustic stone, Moutotan, Tanning Assist B., and Tanning Oil G. were used.

III. RESULTS AND DISCUSSION

It should be noted separately that all the listed chemical materials have solid, emulsion, liquid, dissolved, plasma, and other states of aggregation. We know that the physico-chemical properties of the fur produced by us must meet the requirements of the relevant standard GOST. Therefore, taking into account the above, the experiments were carried out and the results were presented by taking samples of the standard fields of fur for testing the main physico-chemical parameters of the experimental and control samples (Table 2).

Table 2
Dependence of consumption of different additives on physico-chemical properties of nutria fur

№	Sample	Amount of minerals, %	Fat content, %	Moisture content, %
5	a	6,8217	14,985	13,42
6	b	6,2919	13,036	13,47
GOST 12133-86		Not less than **1,0**	Not more than **20,0**	Not more than **14,0**

Where, a-experimental and b-control sample.

As can be seen from the results, the moisture content of the samples is almost the same, the amount of fat is 14,98 % in the experimental sample and 13,04 % in the control version. The amount of mineral substances in fur is 6,82 % in the experimental sample and 6,29 % in the control sample. These indicators were compared to standard GOST 12133-86, checking their reliability, and we witnessed that all indicators corresponded.

Continuing the research work, the hydrothermal destruction temperature, which is one of the main indicators that quantitatively describes the tanning process, was determined based on a known method and the results were presented in the table.

Table 3
Hydrothermal destruction of nutria fur on a standard plot

Samples	**Hydrothermal destruction, °C**
a	85,3
b	73,0
Standard according to GOST 12133-86	Not less than 60,0

When the control and experimental nutria fur samples were compared, the hydrothermal destruction temperature of the experimental sample, increased based on interpolycomplex, was 85,3 °C, and it was found to be 73,0 °C in the control sample based on the experimental test results. It can be seen from the result that the experimental sample is 12,3 °C higher than the control sample.

It is known that hydrothermal destruction is one of the main parameters describing the level of fur, and this parameter changes in each process. To study the importance of processes in fur production, the effect of pickling, tanning, oiling, and drying processes on hydrothermal destruction was studied. In this case, grade II, moderately defective nutria skin was selected and divided into two from the spine area, samples were processed according to technology in traditional and experimental methods. The kinetics of changes in hydrothermal destruction of nutria skin depending on the processes are shown in Fig. 3.

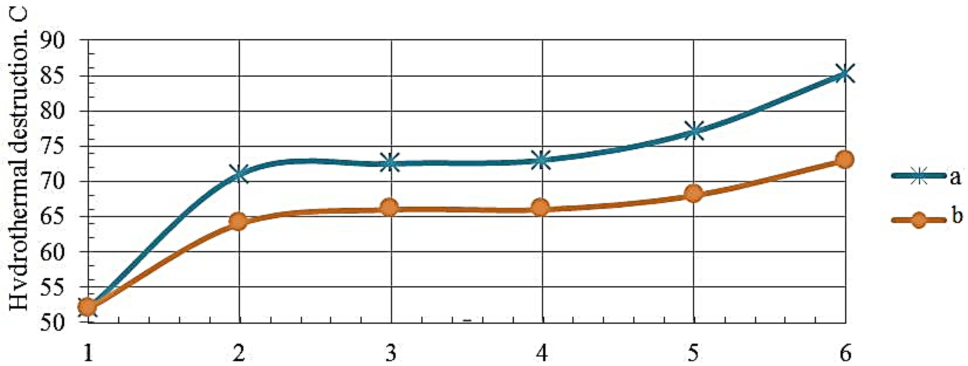

Figure 3. Variation of hydrothermal destruction of a-experimental and b-control sample depending on the processes. Here it is after 1st tanning, 2nd tanning, 3-7 hours of laying, 4th after oiling, 5-6 hours of drying, and 6th after finishing (unpainted).

As can be seen from the graph, the main change was related to the 2nd area after the tanning process. We can see that the hydrothermal destruction remained almost unchanged in the other processes, i.e. after 7 hours of deposition, lubrication, and after 6 hours of drying. We can conclude from this that we once again witnessed that the main process that serves to improve hydrothermal destruction in fur processing processes is tanning.

Of course, one of the main indicators for evaluating the quality of fur is its strength and elongation at break. Because the produced furs are required to be strong and elastic. Therefore, the tensile elongation and tensile strength of the control and experimental samples of the increased nutria fur were determined using a Japanese WDW-5E shearing machine with the standard samples cut. For this, experimental and control samples were selected, and to increase the accuracy of the results, 4 standard samples were cut from each sample, and the average value of the results is presented in Figure 4.

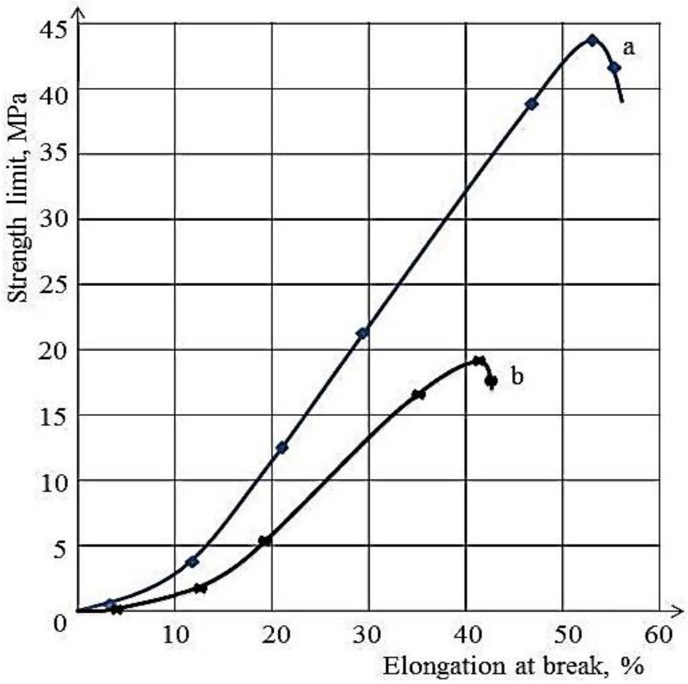

Figure 4. Graph of relationship between elongation at break and strength limit of a- experimental and b-control samples.

In this case, the average value of the elongation at the break of the experiment-a sample was 54,1 % and the strength limit was 43,9 MPa. In the control-b sample, the average elongation at break is 41,2 %, and the strength limit is 18,7 MPa, these results are consistent with GOST 12133-86 based on experimental tests. Based on the above results, we can conclude that polyacrylamide, which is part of interpolycomplex, gives softness to the fur and improves its elongation at break, and other substances included in the additive have a positive effect on its hydrothermal destruction and strength limits by forming complex bonds in the dermis.

IV. CONCLUSIONS

Thus, for the first time, the possibility of using interpolycomplex to increase nutria skins was studied. Physico-chemical and mechanical properties of nutria fur were determined, and the results were cited and discussed. From the results, it was found that the amount of fat, mineral substances, and moisture in the samples is by GOST 12133-86, and hydrothermal destruction in the experimental sample is 85,3 ^{o}C and 12,3 ^{o}C higher than the control sample. According to the results of the analysis of the dependence of hydrothermal destruction on the processes, it was found that the highest indicator belongs to the process of tanning. Strength limit and elongation at break, which are one of the main parameters of fur, were found to be 25,2 MPa and 12,9 % higher in the experimental sample compared to the control sample, respectively. By comparing the results of physical and mechanical tests, it was noted that the furs tanned with the presence of interpolycomplex have high hydrothermal stability, strength, and elongation at break indicators. It can be concluded from the results that nutria fur tanned based on interpolycomplex has complex properties.

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