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New technologies for skin impregnation using collagen-polymer systems

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Abstract

The article analyzes the use of new collagen-polymer impregnants for leather finishing.

Keywords: *collagen, modification, vinyl monomers, impregnant..*

In the manufacture of leather, the finishing process is one of the most important processes. In many countries, different synthetic substances in the composition of the primers are used to finish the skin. The field of creation and application of new collagen-polymer systems in soil compositions for leather finishing has not been thoroughly studied. According to modern methods, research into the modification of polymer molecules interacts with the active groups of those sections of the polypeptide chains that form regions of the disordered structure of collagen. Which are more accessible for the penetration of modifying substances into them than the regions of the ordered structure of collagen. It should be noted that under the development conditions, the issue of rational use of secondary resources occupies a special place, including the search for new technologies for processing collagen-containing wastes of the leather industry and the creation of new collagen-polymer impregnants based on them for leather finishing, which is a very urgent scientific and technological problem.

The aim of this work is the synthesis of new collagen-polymer systems for impregnating the skin in finishing processes. Our research has obtained a new collagen-polymer system based on a natural high-molecular compound by modifying it with vinyl monomers of the acrylic series and developed production technologies. Collagen-polymer impregnants were used to impregnate the skin in finishing processes.

Based on the studies of collagen-polymer systems for skin impregnation, we obtained important experimental data for the development of a very effective technology. In fig. 1. presents a flow chart of the preparation and impregnation of leather.

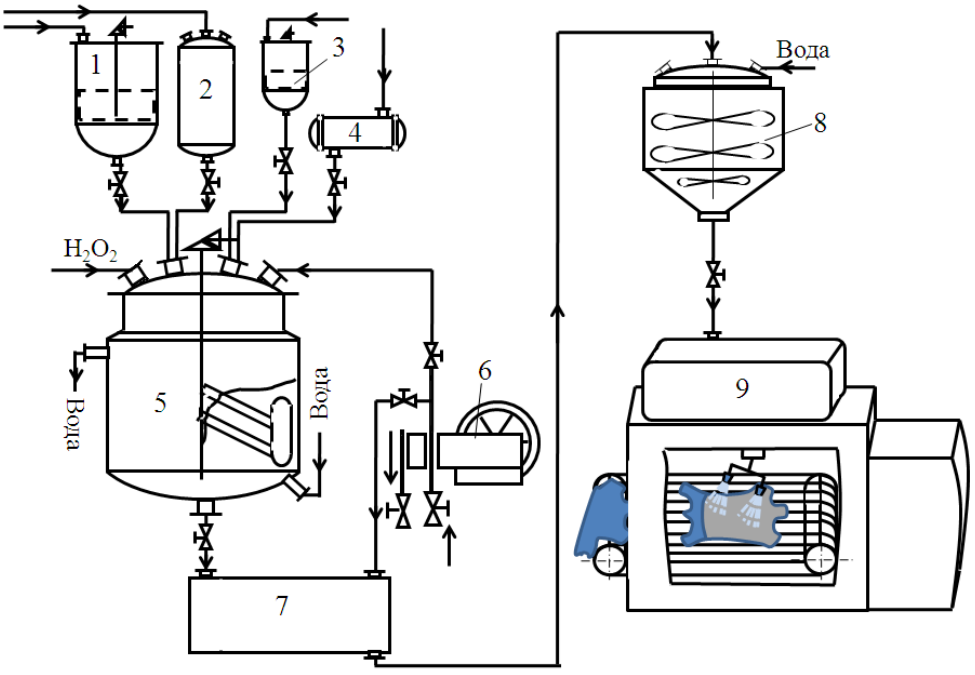


Fig. 1. Schematic diagram of the preparation and impregnation of leather. 1-capacity for collagen dissolution products; 2- capacity for acrylic acid solution; 3- capacity for nitrile of acrylic acid; 4- capacity for penetrator; 5 - reactor for the preparation of collagen-polymer impregnant; 6- compressor; 7- storage tank for the assembly of collagen-polymer impregnant; 8- mixer for adjusting the collagen-polymer impregnant to the required viscosity; 9- spray unit for impregnating leather with a collagen-polymer system.

From the tank - 1 is fed into the reactor -5, 30 -% product of collagen dissolution (in terms of dry residue), in an amount of 60% by weight of the total number of ingredients, and mixed. Constantly mixing with the anchor stirrer of the reactor - 5, technical acrylic acid (in terms of 100%) in the amount of 20% by weight of the total number of ingredients and technical acrylic nitrile in the amount of 10% by weight of the total number of ingredients are lowered from the tank - 2, 3 . 0.5 hours after the supply of all the ingredients, a penetrator prepared according to our method [3], 10% of the mass of the total number of ingredients, is introduced into the reactor - 5.

After this, mixing continues for another 1.5 hours, i.e. until a homogeneous substance is formed. Preheating the reactor to 65-70 ° C, 60% is introduced into the reaction mixture — hydrogen peroxide (five-fold diluted) in an amount of 0.05% by weight of the composition, over a period of 0.5 hours. Note that after the introduction of hydrogen peroxide, mixing continues for 1.5-2.0 hours.

At the end of the process, a sample is taken to control the quality of the obtained product (for viscosity, pH, high-quality reaction to bromite-bromate).

The finished product is a viscous-flowing homogeneous emulsion of light yellow color. Ultimately, the product should have an intrinsic viscosityη = 160,46 ± 8,5 MPa, pH = 6,0-6,5 and bleach of the bromine water by quality reaction.

Thus, the prepared viscous-flowing consistency of the collagen-polymer impregnant is lowered into the storage tank - 7, through the nozzle, with the help of compressed air created by the compressor - 6.

In conclusion, the required amount of collagen-polymer impregnant, again using compressed air from compressor 6, is transported to a mixer 8, where the impregnant is diluted with water to a density of 1.08 g / cm3.

The prepared collagen-polymer impregnant by gravity enters the spray -9 unit, where the skin is impregnated with a collagen-polymer system.

For processing leathers with a natural front surface, a semi-finished product was uniformly colored by drum dyeing. The product with a fairly dense structure is perfumed, having a small number of facial defects.

- the impregnating impregnating composition was applied once on the front surface of the leathers on a spray. Impregnant consumption 80 ± 10 g / m^2.
- Hydropress pressing with a smooth plate. Temperature 70 ± 5.0 ° C, pressure 9.0 ± 1.0 MPa.
-applying pigmented soil (2 times) with a brush. Ground consumption 130 ± 10 g / m^2.
- applying topcoat on the sprayer 3-4 times (before shelter). Paint consumption 160 ± 10 g / m^2.
- first coating fastening once. Fixer consumption 40 ± 5 g / m^2.
- hydropress pressing. Temperature 80 ± 5.0 ° C, pressure 15.0 ± 1.0 MPa.
- the second fixing coating 1-2 times. Fixer consumption 100 ± 10 g / m^2.

Application of fixatives is carried out using a spray gun with drying at a temperature of 45 ± 5.0 ° C, for 35 ± 5 min.

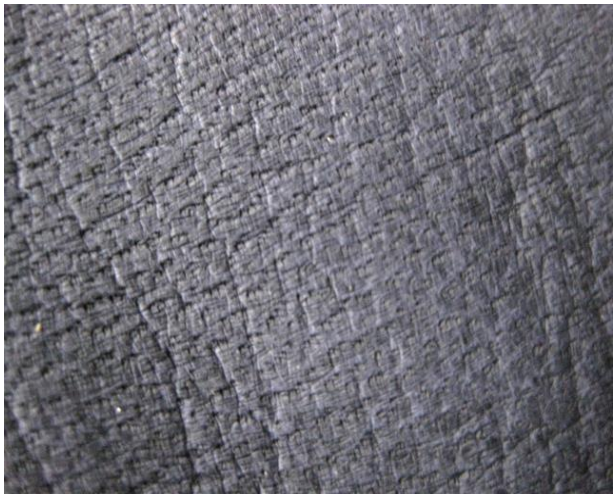
Table 1.
Physico-mechanical properties of impregnated skin with modified collagen

Indicator	Options						ГОСТ 29277-93
	Experienced					Control	
	I	II	III	IV	V		
TensileStrength, 9.8 MPa	2,85	2,87	2,96	3,15	3,20	3,10	2.0 noless

Resistance to repeated bending, points	3,74	3,88	3,94	4,20	4,15	3,98	2.0 noless
Resistance to wet friction, rpm	71,20	71,60	71,80	72,11	72,05	71,93	50,0 noless
Waterpermeability, %	49,54	49,12	48,85	48,74	48,10	49,20	65,0 noless
Vaporpermeability, %	47,14	46,72	46,30	45,12	45,50	46,83	53,0 noless
Heatresistance, °C	143	152	156	160	165	158	notstandard ized

Next, trimming the edges of the skin, measuring the area and studying the physico-mechanical properties.
In the table. 1. shows the physical and mechanical properties of the control and experimental samples of finished leathers treated with an impregnating impregnating composition based on collagen.
The developed technology of skin impregnation and the use of a new impregnating impregnating composition, based on a collagen derivative, provides skin with high strength, resistance to wet friction and a decrease in water permeability.
From the above data it should be concluded that the impregnating impregnating composition can be used for finishing leather for upper shoes, in combination with polymer film-forming materials.
The technology for using the impregnating impregnating composition obtained using collagen dissolution products is similar to the above. In the work, it was determined that using collagen dissolution products, instead of rigid-chain polymer film-forming agents, skin samples with good appearance and improved film quality can be obtained. The resulting coatings have high physical and mechanical properties. The finishing method developed by us can also be applied to leathers with a refined front surface.
The relatively high degree of interaction of the impregnating impregnating composition based on the products of collagen dissolution with the skin can be explained by both adsorption and diffusion factors. In this case, chemical modifications may take place. It must be assumed that the carboxyl groups present in the protein part of the coating can enter chromium complexes in the skin.
Studies of the structure of collagen dissolution products and the materials obtained from them have shown that they differ significantly from the structure of water-soluble acrylic dispersion and emulsion polymers used to finish the skin. In particular, globular-shaped structures were discovered that are not capable of forming continuous film coatings.


I


II

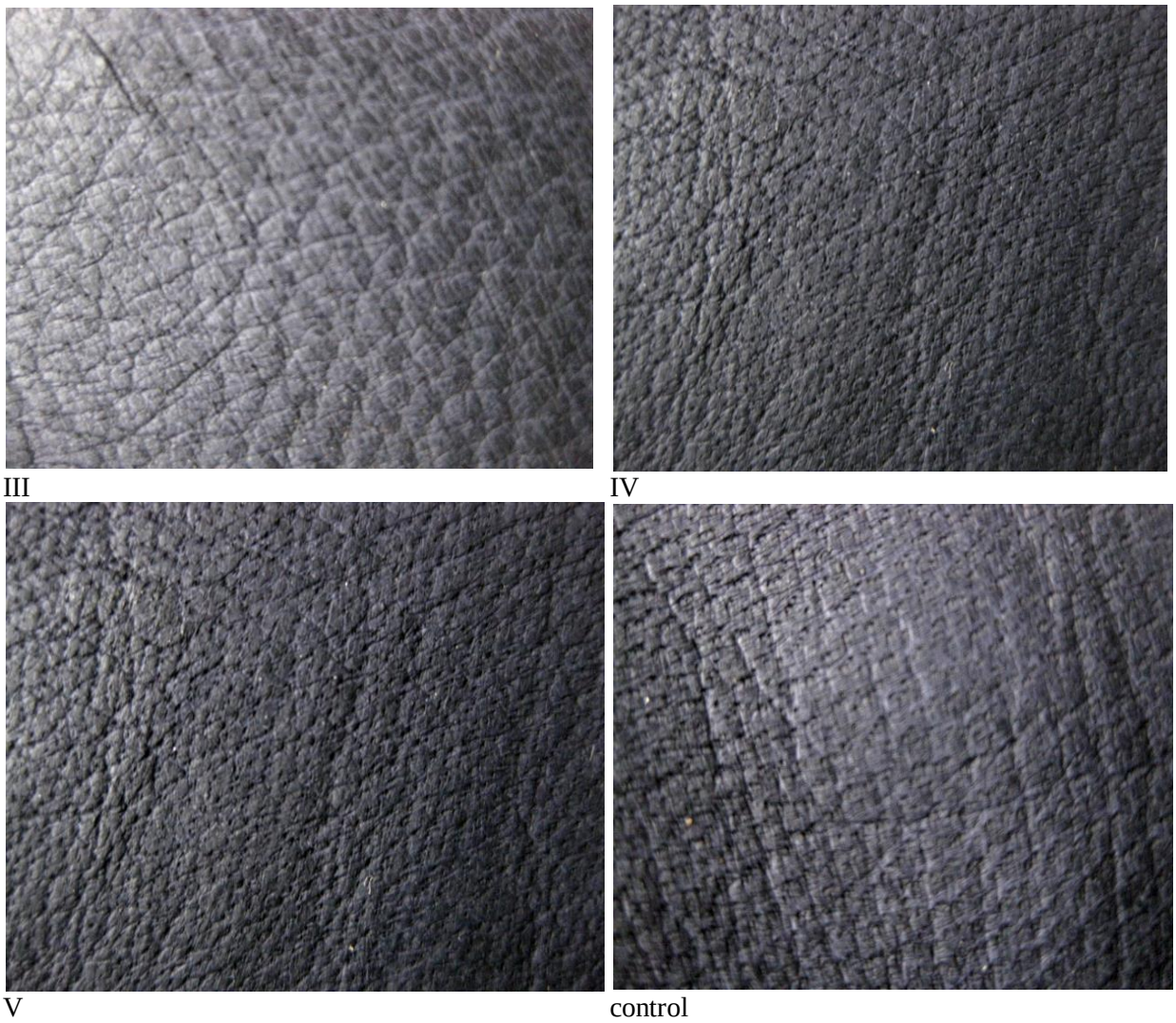


Fig. 2. Microphotographs of free films impregnated with polymer impregnants of experimental (I-V) and control skin options. Increase350^{x10}

Comparative microscopic studies of coatings on the skin, obtained on the basis of collagen dissolution products, showed that the complete replacement of imported dispersed acrylic emulsions (Fig. 2) makes it possible to obtain a protein-polymer impregnating impregnant on the skin that does not give cracks during a single tensile deformation - reduction by 20% from the original length of the sample. It was found that in the presence of an acrylic emulsion A and dispersion MX-30, this leads to the formation of cracks.

The above results on differing microstructures obviously indicate conformational differences in protein macromolecules found in collagen dissolution products. It can also be noted that the impregnating impregnant on the skin, obtained on the basis of collagen dissolution products, creates the prerequisites for obtaining a film with the necessary mechanical properties and elasticity.

Based on the results achieved, it can be assumed that the additional plasticization of collagen dissolution products, which is contained in the penetrator, allows to obtain coatings on the skin that have good "performance" when stretched and to wet skin friction, especially during wear. Further, it should be pointed out that the impregnant obtained in the case of the use of collagen dissolution products occupies an intermediate position between the coatings of the first type (elastic or film) and coatings of the second type (inelastic). This is due to the fact that they form a continuous, fairly flexible film, firmly retaining their high hygienic properties.

Studies were conducted to establish the possibility of using collagen dissolution products as a binder and film former, an impregnating agent in combination with dispersions of other polymer film former. Protein-polymer impregnating impregnant on the skin, which were obtained using collagen dissolution products, allows the formation of a film with sufficiently high mechanical properties and elasticity.

Features of the physicomechanical properties of the impregnating impregnant on the skin, modified products from collagen dissolution, are determined by the conformation of their main structural units - three-helix particles and a high degree of asymmetry of these particles.

Based on the results of comprehensive research, we can conclude that it is advisable to replace the traditionally used acrylic emulsions. These products, like microheterogeneous systems, can be used to finish chrome tanned leathers from cattle hides. It should be noted that collagen-polymer impregnants can eliminate defects of crease and stillness, as well as improve the quality and improve the performance properties of the coating film. The resulting leather in all qualities meets the requirements of the guest.

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