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Development and Application of Technologies for Producing Protein-Polymer Compositions from Strokes for the Process of Filling Skin

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ABSTRACT: This article provides the production of a protein hydrolyzate from skin wastes based on a protein hydrolyzate, a protein-polymer composition and a polymer group composition used in skin filling technologies.

KEYWORDS: collagen, protein hydrolyzate, tanning, filling, chrome shavings, mezra, split

I.INTRODUCTION

In leather and fur production, raw materials of biological origin are used, the main component of which are protein substances, or proteins - collagen of dermis and hair keratin [1].

Recently, much attention has been paid to collagen in physics as a fibrillar protein and a high molecular weight compound. Finally, collagen is also of industrial importance. The dermis of the skin of animals is the main substance for the development of a technical product - the skin. Glue and gelatin are prepared from collagen. Therefore, technologists are no less than other specialists interested in studying the structure and properties of collagen. This explains the large number of works devoted to the study of this protein [1].

Collagen in the animal body is very common: its content is 25-35% of all proteins. Therefore, it is natural that scientists in various specialties are involved in the structure of collagen. Collagen as an integral part of a living organism should be of interest to physicians - histologists, surgeons, rheumatologists, dermatologists, etc., biologists and biochemists [2].

II. SIGNIFICANCE OF THE SYSTEM

Collagen is the main connective tissue of the dermis used in the production of skin. To turn the dermis into skin requires treatment with electrolytes, enzymes and tanning agents. Only after such treatments and a number of mechanical influences is a technical product obtained - leather [3].

In the leather industry, low molecular weight inorganic substances are widely used as filler. However, during operation, these inorganic substances under extreme conditions easily migrate from skin products, are extracted, washed and the skin becomes loose, empty and brittle.

The introduction of high molecular weight compounds into the skin during the filling process leads to their reaction with collagen functional groups, as a result of which these polymers are transformed on the dermis fibers into water-insoluble compounds, which leads to an increase in the thickness of the peripheral regions. In this case, structuring occurs due to the transverse bonding of the collagen molecular chains.

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Wastes from tanneries in the form of peripheral parts of hides, skins, trimmings, substandard split can be used for the manufacture of gelatin, fodder flour and protein hydrolyzate[4].

III. LITERATURE SURVEY

Protein hydrolysates are used as feed for livestock and poultry, as foaming agents for fire extinguishers and when spraying plants with pesticides. Fats are used in perfumes for lipsticks, creams, soaps, proteins - for shampoos, gelatin - in the food industry for jelly, jellies and ice cream. Some waste after processing is also used as artificial fertilizer [5].

The protein hydrolyzate obtained by us is the processing of tanned and unkilled leather waste. Various amounts of wet mezra were mixed with chrome chips. In this case, a mixture resistant to rot and with a significantly increased viscosity compared to the starting products was obtained. The best performance was characterized by a composition consisting of 23-26% chrome shavings and 78-80% mezdra, the pH value of which was 7.5-7.8. The humidity of this composition was also in the optimal range. Thus, the ability of the components to leach decreased, and the composition can be stored for a longer time[6].

IV. METHODOLOGY

We assumed that with an increase in the pH value of chromium chips, unbound chromium compounds are released, and the product obtained after processing contains less leachable chromium salts. To increase the pH value of the chromium chip, Ca (OH) 2 was introduced into it, and after 10 min, water was added [7]. The composition was processed for 2 hours with constant stirring. The results of the analysis of the obtained product after processing the chromium chips Ca (OH) 2 in an amount of 5 and 10% are presented in table 1.

Table 1.
Physico-chemical characteristics of chrome chips treated with calcium hydroxide, depending on its concentration and duration of exposure

Indicators	Original Chrome Chip	Chromium shavings treated with Ca (OH) 2 - 5% after 2 hours		Chrome machined Ca (OH) 2 - 5%, 1 month. storage		Chrome machined Ca (OH) 2 - 10%, after 2 hours		Chrome machined Ca (OH) 2 - 10%, 1 month. storage	
		wet	dry	wet	dry	wet	dry	wet	сухая
Humidity	56,7	64,4	53,8	64,6	54,2	64,3	52,3	64,6	52,6
Cr + mg / kg	250	1,0	1,0	1,0	1,0	1,0	1,0	1,0	1,0
Content, g-total amount of soluble sulfate salts $(SO_4)^{-2}$	3,78 1,62	3,34 1,24	3,34 1,20	3,42 1,3	3,27 0,97	2,64 0,64	2,58 0,32	2,53 0,62	1,98 0,10
Value pH	4,6	8,0	8,2	9,8	10	11,8	11,6	11,9	11,5

As can be seen from the table, the humidity when adding Ca (OH) 2 to dry chrome shavings is 52-54%.

As a result of the studies, a protein hydrolyzate was obtained from the waste of chrome shavings and on the basis of which a new composition for filling the skin was obtained by chemical treatment with reactive monomers and polymers. The obtained protein hydrolysates, in addition, can be used for the manufacture of fibrous materials, artificial fertilizers, etc. [8].

Continuing the study of the hydrolysis of chromium chips, the latter in a series of experiments was poured with a solution of hydrochloric acid and heated in a boiling water bath [9].

Physico-chemical characteristics of the finished protein hydrolyzate obtained from various leather chips, are presented in table 2.

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Table 2.
Physico-chemical characteristics of the protein hydrolyzate obtained from various tanned leather shavings

Indicators	Saddlery yuft chrome synthane tanning	Upper shoe chrome plant tanning	Leather for the bottom of the shoe	Chrome leather
Humidity, %	30	30	30	30
Fat content, %	6	26	4	7
Acidity, %	15	15	15	15
The content of impurities, %	1,5	1,5	1,5	1,5
Content Cr_2O_3 %	1,5	1,7	0,7	3,0

The yields of the hydrolyzate in the filtered solution were determined by the gravimetric method, and the amine nitrogen by elemental analysis. The molecular mass is on a Ubbelode viscometer. The results of the study are shown in table 3.

V. EXPERIMENTAL RESULTS

Table 3.
Physico-chemical characteristics of the protein hydrolyzate of chromium chips treated with 40% hydrochloric acid at a temperature of 800C and a liquid coefficient of 5.0

Indicators	Reaction time, h					
	1	2	3	4	5	6
The conversion of the hydrolyzate, % by weight of chromium chips	25,3	52,1	72,4	85,4	97,2	98,6
The content of amino nitrogen,%	0,65	0,66	0,85	1,23	1,54	1,67
Molecular Weight of Protein Hydrolyzate, $M10^3$	1,03	1,15	1,24	1,64	1,87	2,15

From the data of table 3 it can be seen that the destruction of chrome-plated skin wastes and the molecular weight of the protein hydrolyzate depend both on the amount of acid and on the time of hydrolysis. In this case, there is a correlation between the acid concentration, hydrolysis time, molecular weight and hydrolyzate conversion.

The data obtained also indicate a specific mechanism of the hydrolyzate, namely: hydrolysis is accompanied by a sequential detachment of fragments of polypeptides with a certain molecular weight from the chromium-plated collagen molecule. It can be seen from Fig. 1 that the hydrolysis of chromium chips and the obtained molecular weight of collagen depend on the ratio between the solid phase - chromium chips (CS), water and the concentration of the salt quota.

b) the ratio of chrome shavings CS: water 20:80, hydrochloric acid of various concentrations,%: 1 - 4 and 2 - 8.

With an increase in the amount of water to 80% (CS: water ratio of 20:80), the molecular weight of the hydrolyzed protein continues to slightly decrease, despite the achievement of almost complete hydrolyzate yield after 10-11 hours of hydrolysis.

From fig. 1 (b) it is also seen that the molecular weight of the protein formed as a result of the hydrolysis reaction depends on the amount of acid introduced into the reaction composition. With an increase in the amount of acid, a tendency to a decrease in the molecular weight of the hydrolyzate is observed. Thus, an increase in the water cut of the system leads to an increase in the hydrolysis of blocked fragments.

a) the ratio of chrome chips CH: water 80:20, hydrolyzed with a 5% solution of hydrochloric acid.

In this regard, we conducted experiments to obtain a protein hydrolyzate from non-standard leather raw materials and waste from this production by exposure to acid (H2SO4, HCl). To obtain a protein hydrolyzate, a digester was used. Water was collected into the digester with an LCD = 8, then the required amount of non-chrome leather waste was loaded. Then added sulfuric acid in an amount of 20-30 g/l with constant stirring with a mechanical stirrer.

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Then the temperature was gradually raised to 80-900C. The hydrolysis reaction of non-chromium raw materials and non-standard raw materials was carried out for 4 to 8 hours.

In this case, the main part of the raw skin of the dermis in the presence of sulfuric acid and vigorous mechanical action was completely destroyed and a viscous aqueous solution formed. Wool in connection with resistance to acid remained unchanged.

After settling, the resulting mixture was filtered from wool and various mechanical impurities. The filtered viscous solution was separated and the fat was separated, resulting in a protein hydrolyzate.

Based on the protein modifier we developed, from non-chrome-coated leather wastes, collagen-polymer derivatives, in particular protein-polymer compositions, were obtained from local raw materials. As you know, at present, in production conditions, when filling leathers, imported expensive starting products are used, and this is not economically feasible. In this regard, to fill the skins, we obtained and used protein-polymer compositions with hydrolyzed polyacrylonitrile locally produced. The composition of the obtained protein-polymer composition is shown in table 4.

At a ratio of cholesterol: water of 80:20 (parts by weight), the molecular weight after hours of hydrolysis reaches an almost constant value (Fig. 1a).

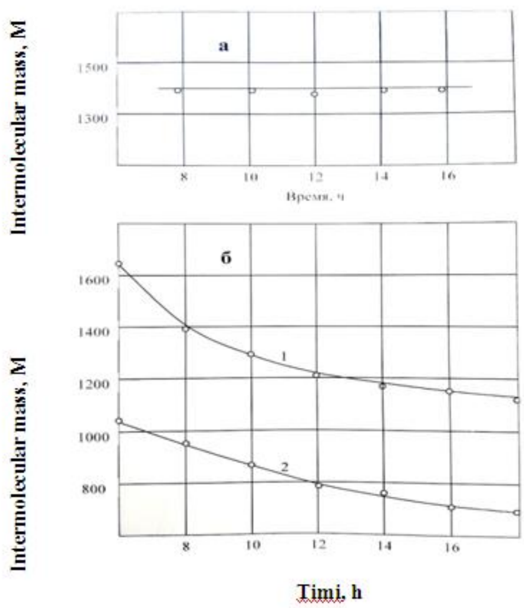

Fig. 1. Dependence of the molecular weight of the hydrolysis of chrome-plated leather wastes on the duration.

The results of studies of the dependence of the destruction and destruction of chromium chips on the length of time are presented in Fig. 2.

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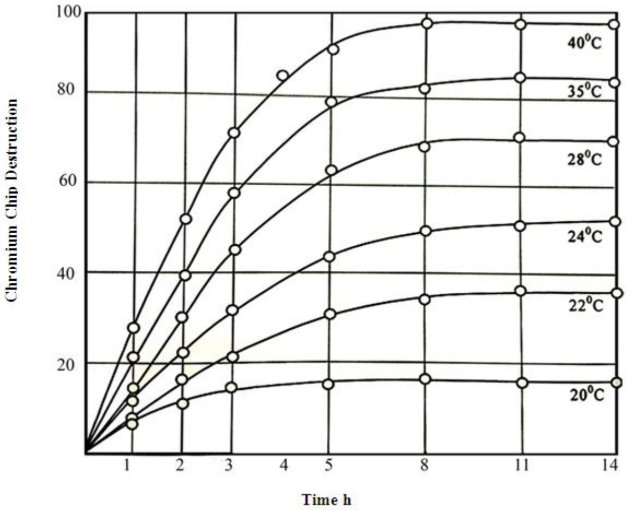

Fig. 2. The dependence of the destruction of chrome chips on the duration

Table 4.
The composition of the protein-polymer composition for filling the skin

№	Name of source components	Mass part	kg
1.	Protein Hydrolyzate	40	150
2.	Hydrolyzed Polyacrylonitrile	30	112,5
3.	Technical ammonia water	3	11,25
4.	Surfactant (OP-10, OP-7)	2	7,5
5.	Water condensate	25	93,75
	Total	**100**	**375**

Protein-polymer composition was prepared as follows. In a reactor equipped with a mechanical stirrer 40 mass. including 52.3% protein hydrolyzate of chromium chips, 30 mass. including hydrolyzed with sodium hydroxide polyacrylonitrile with a degree of saponification of 40%, 3 wt. including ammonium hydroxide -25%, 25 wt. including water condensate and 2.0 mass. including non-ionic surfactant (OP-10) with vigorous stirring was heated with compressed steam through the jacket of the reactor to a temperature of 55-700C for 3-4 hours. As a result of the reaction, a homogeneous protein-polymer composition with a dry residue of 20.4% and a pH of 8.2 was formed. According to this method, in a production environment, the yield of the protein-polymer composition was 375 kg.

Further experiments were aimed at using the obtained protein-polymer composition in the skin filling technology. For this, after the tanning process, the chrome semi-finished product was loaded into the drum, where the filling process was carried out. At the stage of the filling process, fillers were fed through the hollow axis of the drum at a rate of 100 m2. The composition of the filler is shown in table 5.

Table 5.
The composition of beokovo-polymer composition for filling leather

The name of the fillers	Consumption per 100 m2			
	By known technology, control		Experienced technology	
	%	kg	%	kg
MX-30	2,5	2,49	1,3	1,29
BN-30 K-2	0,6	0,51	0,2	0,17
Protein-polymer composition	-	-	2,5	1,18

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After adding fillers, the LC = 1.0-1.2 was adjusted and the drum was rotated for 60-60 minutes at a temperature of 60-650C. After filling the semi-finished product, all finishing processes and operations were carried out according to the production method.

Next, we studied the physical and mechanical properties of the finished experimental and control skins. The data obtained are presented in table 6.

The table shows that in the experimental samples the physico-mechanical properties of the skin do not deteriorate compared to the control. An organoleptic evaluation of the skin showed that the skin becomes soft, full, especially in loose areas. At the same time, physical and mechanical indicators throughout the area become the same. Skin developed using protein-polymer compositions are well filled, especially in the peripheral areas, have a silky front surface.

Table 6.

Physico-mechanical properties of experimental and control leathers treated with a protein-polymer composition

Name indicators	Experienced		Control	GOST 292277-92
	1 option	2 option		
Tensile Strength, kgf \ mm	2,41	2,43	2,23	н\м 2,0
Relative extension, %	28,5	28,3	29,9	н\б 35
Moisture content,%	55,9	56,1	51,4	н\б 65
Stiffness, kg	48,6	48,7	47,4	н\м 45

This shows that the obtained protein-polymer composition can be used in a certain amount instead of the expensive imported components of the skin filling compositions.

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