THE ORGANO-MINERAL COMPOSITION FOR RETANNING-FILLING OF LEATHER SEMI-FINISHED ITEM

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The organo-mineral compounds with bentonite and lignosulfonats for retanning-filling leather semi-finished item were offered. The use of obtained organo-mineral compounds allows increasing the formation of derma volume and leathers resistance to mechanical actions.

Keywords: bentonite, lignosulfonats, organo-mineral compounds.

INTRODUCTION

The analysis of modern retanning-filling materials for leather semi-finished item treatment includes the broad spectrum of vegetable, polymeric and mineral compounds [1]. Recently the vegetable tannins have been the most important retanning agents. But the limitation of their extraction and high cost induced the development of synthetic compounds for leather retanning with the purpose of full elimination or partial replacement of valuable natural substances. But the information in scientific literature about compounds which could completely reproduce the retanning and filling effect on the structure of leather semi-finished item, analogous to the action of vegetable tannins, has not been found.

In this connection it is especially topical to develop the new retanning-filling composition for leather manufacture on the basis of lignosulphonate and highly dispersive minerals.

THE OBJECT AND METHOD OF INVESTIGATION

In order to obtain organo-mineral composition (OMC) bentonite of Dashukovskogo deposit (Ukraine) was used with the content of the main mineral – montmorillonite – 85% and technical powdered lignosulphonates.

The production of OMC used for retanning-filling of leather semi-finished item includes the following stages:

– obtaining Na-montmorillonite dispersion by means of bentonite dispersion treatment with carbonate natrium (consumption – 6.0% on dry mineral weight) with the aim of dispergation;

– obtaining Cr-montmorillonite by means of Na-montmorillonite treatment with the solution of chrome tannin (consumption 10.0% of Cr_2O_3) with the aim of zeolite softening of mineral particles surface;

– introducing lignosulphonate solution in the dispersion of Cr-montmorillonite (the content of tanning substances – 40% in technical product) with the aim of lignosulphonate adsorption on the surface of mineral particles and obtaining OMC.

For retanning-filling of leather semi-finished item the OMC, with different content of lignosulphonates, was used. The consumption of lignosulphonates made up 200-500% on dry mineral weight [2].

The properties of OMC were evaluated according to mineralogical composition and structural changes of mineral in the result of chrome salts and lignosulphonates adsorption. For investigation, Dron-3 X-ray diffractometer with filtrated Co Kα-radiation was used. The accuracy of determination of mass part of the components constituted ± 5%. The identification of mineral composition was carried out in conformity with the file of ASTM [3].

The structurizational influence of OMC on derma collagen was studied according to the changes of melting temperature of gelatin jelly after treatment by OMC. For this, the gelatin solution of 5% concentration was treated by OMC of various lignosulphonates content. After gelatinization of jelly thermostable test tubes were heated with the speed of 3ºC/min and melting temperature of gelatin jelly was fixed. The content of bentonite was 9.0% of mineral on dry protein weight.

The investigation of the efficiency of retanning-filling leather, with OMC application, was carried out using 5 groups with 8 samples in each group. The size of samples was 50×120 mm. The thickness of semi-finished item after shaving was 1.4-1.5 mm. The treatment of semi-finished item with the use of OMC was performed after retanning by chrome tannin, neutralization by bicarbonate, sodium formiate and washing. Retanning-filling of semi-finished item of the variants 1–4 were performed using OMC with the consumption of lignosulphonates – 200, 300, 400, 500% on dry mineral weight. Simultaneously, acrylic filling Tergotan PMB («Clariant», Poland) was introduced. The consumption of OMC and acrylic filling constituted, correspondingly, 2.5% (in terms of dry mineral) and 3.0% on shaved semi-finished item weight. After retanning-filling, the fixation treatment by aluminum potassium sulphonates and sodium formiate was performed with the consumption, correspondingly, of 1.5 and 0.5% on shaved semi-finished item weight. Variant 5 was a control one. The treatment of semi-finished item was accomplished according to the method of the manufacture of chrome leather for the uppers of shoes from raw cattle hides (LTD «Chinbar»).

After retanning-filling of control and experimental variants, the samples were fat-liquored, squeezed out up to humidity of 55-60%, dried on contact drier up to humidity of 26-28%, dried up in free state at the temperature of 35ºC, damped, stretched, dried in free state to humidity of 14-15%.

Further, leather performances were determined. Chemical analysis and physico-mechanical indices of the finished leather were determined according to the methods [4]. The error of determination did not exceed 5% for physico-mechanical tests, 3% for chemical analysis.

RESULTS AND DISCUSSION

The data of X-rays analysis indicate that, in natural form, bentonite contains quarts, calcite, kaolinite, anatase, crystabolite. On the whole, collateral rockforming components make up 15-20%. The basic rockforming mineral is montmorillonite. It was confirmed by basal reflexes at 15.60 Å; 5.04 Å; 4.48 Å; 2.56 Å; 1.49 Å (Figure 1a).

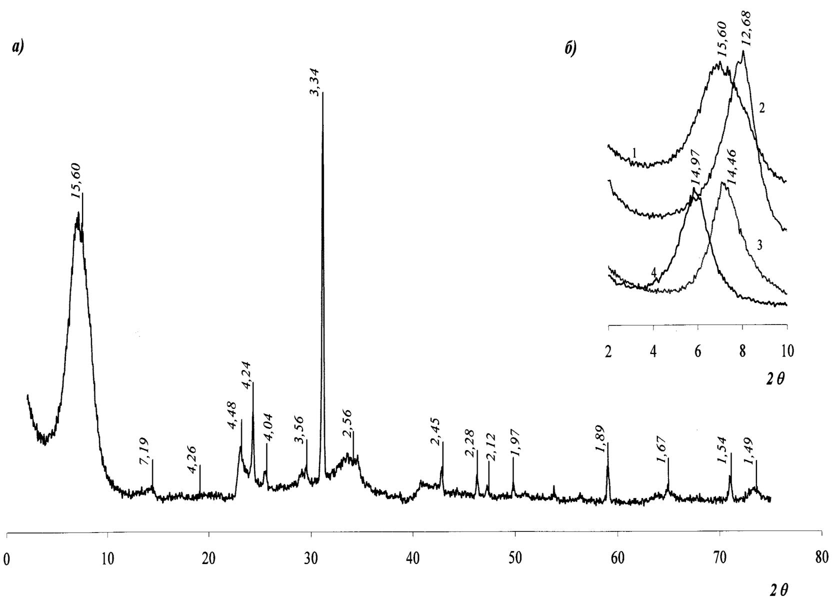

Figure 1. X-ray grams of bentonite (a) and basal interlayer space distances (b) of inlet montmorillonite (1), Na – montmorillonite (2), Cr- montmorillonite (3) and OMC (4)

The characteristic feature of Na – montmorillonite is a decrease of the intensity of the first basal peak to 12.68 Å (Fig. 1b$^{(2)}$). It testifies about the conservation of montmorillonite structure.

For Cr–montmorillonite only the first basal peaks can be exactly defined. The rest peaks were washed out and this is connected with the redistribution of water between the layers of mineral structure. The increasing of the first basal reflex from 12.68 to 14.46 Å (Fig. 1b$^{(3)}$) points out the propagation of chrome polyoxycations in interlayer space. According to literature sources [5], aquahydroxycomplexes are polymerized in interlayer space and compensate the interlayer charge. The characteristic peculiarity of OMC is that even negligible value increasing of the first basal peak – to 14.97 Å (Fig. 1b$^{(4)}$) and its shift testify about the expansion of interlayer mineral space and interlayer adsorption of lignosulphonate in Cr–montmorillonite structure.

The treatment of gelatin jelly by OMC promotes the increase of hydrothermal stability (Fig. 2).

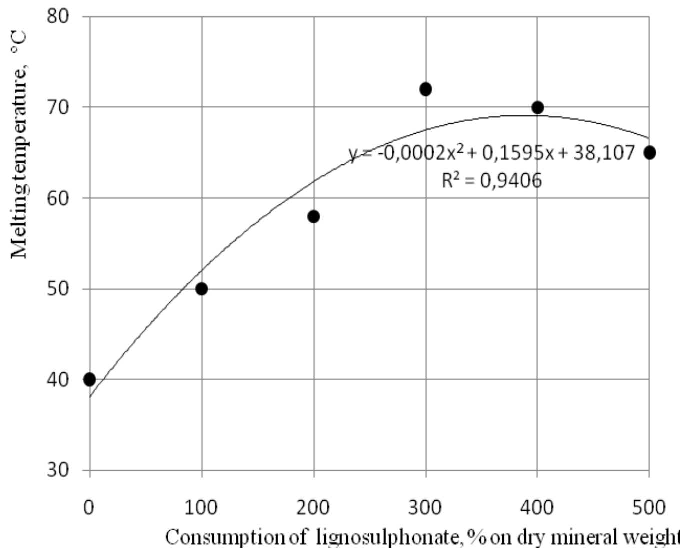

Figure 2. The influence of lignosulphonate sodium in the composition of OMC on melting temperature of gelatin jelly

The maximum rise of melting temperature (70-72ºC) corresponds to the consumption of lignosulphonate natrium in the composition of OMC equal to 300-400% on dry mineral weight. The further increase of lignosulphonate natrium consumption results in partial decrease of melting temperature of gelatin jelly. This is conditioned by availability of free, unfixed lignosulphonates in the composition of OMC which divide gelatin structure at heating. On the whole, lignosulphonates in OMC composition are able to structurized derma collagen in the result of interaction and fixation of active protein groups.

The further investigation of the efficiency of OMC application in aftertanning processes confirmed the positive influence of composition on leather quality. According to the organoleptic estimation all leathers were filled, soft, plastic, elastic, with volumetric and grained surface. The indicators of forming derma volume are presented in Table 1.

Table 1. The indices of forming leather structure

Index	Variant of treatment				
	1	2	3	4	control
Yield of leather, % of control:					
as to thickness	96.5	100.5	102.5	101.9	100.0
as to area	100.8	104.9	106.5	105.6	100.0
Volume yield, cm3/100 g derma	241.0	250.0	260.0	256.0	246.0
Apparent specific gravity, g/cm³	0.638	0.621	0.611	0.615	0.645
Shrinking temperature,ºC	111	114	115	114	112

The samples of variants 3 and 4 (consumption of lignosulphonate in OMC constituted 400-500%) differ from control leather samples by greater yield of area, volume yield and less apparent specific gravity. The indices of physico-mechanical tests and rigidity of experimental and control samples are practically identical (Table 2). But it is necessary to point out the increase of shrinking temperature, greater content of mineral substances and chromium oxide in experimental samples.

Table 2. Indices of physico-mechanical tests and chemical analysis of the finished leathers

Index	Variant of treatment				
	1	2	3	4	control
Rigidity, 10-2 H	24.2	23.2	22.0	21.8	23.0
Tensile strength, 10×MPa	2.21	2.38	2.45	2.39	2.25
Elongation at stress 10 MPa, %	26.6	29.2	29.9	27.5	27.8
Content per absolutely dry substance, %:					
mineral matter	7.2	7.5	7.7	7.8	6.6
chromium oxide	4.6	4.6	4.6	4.5	4.4
substances extracted by organic solvents	6.4	6.3	6.3	6.5	6.5

Taken as a whole, the results of research testify about positivity of using OMC with the consumption of lignosulphonate – 400-500% for retanning-filling of leather semi-finished item. It will give the possibility to substitute usage of vegetable tannins in leather manufacture, to combine the processes of retanning-filling and to produce leathers possessing highly formed structure and efficient performances.

CONCLUSIONS

Organo-mineral composition, on the basis of bentonite and lignosulphonates, has been obtained with the aim of using it for retanning-filling of leather semi-finished item. The investigation of the properties of obtained OMC have shown that in the result of montmorillonite modification by chromium compounds and lignosulphonates, structural changes of mineral occur and high level of lignosulphonates adsorption and their fixation with mineral are ensured. Obtained OMC, with the consumption of lignosulphonates – 400-500%, assists in increasing hydrothermal stability of gelatin jelly at 32-34ºC. The application of OMC for retanning-filling of leather semi-finished item confirmed the positive influence on the effectiveness of derma structure formation and obtaining leathers with high performances. At the same time, yield of leather as to the thickness increases by 1.9-2.5%, area yield by – 5.6-6.5%, volume yield by 4.1-5.7% but leather rigidity decreases. The obtained leathers are characterized by softness, smoothness, elasticity, plasticity, pliability and grain filling.

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