Resources-saving Chromium Tanning of Leather with the Use of Modified Montmorillonite

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It is described in the paper that twofold decrease in consumption of chromium tanning agent may be achieved by combined use of montmorillonite modified with hydroxychromium solutions and basic chromium sulphate at the following ratio: chromium oxide (III) : montmorillonite = 1 : 2. The semi finished item obtained exceeded reference samples by its physical-mechanical properties. The technology developed may be characterised as having better environmental efficiency and resources saving because of 3,2-4,6 times lower chromium oxide (III) content in the spent solution.

Keywords: hydroxychromium solutions, montmorillonite, modification, tanning, collagen, semi finished item

Chromium compounds of various chemical composition are widely used in the existing technology of leather manufacture [1-3], with around 90% [4] of the globally produced leather. Taking considerable toxicity of chromium compounds [5] into account, systematic scientific and technological researches are being conducted in order to select less harmful agents to replace the said ones. Despite of a considerable number of works in this field, because of a great amount of leather materials, it is still topical to continue with such studies. In this view, the development and use of materials that combine properties of both fillers and structure-forming agents [6-8] is deemed promising. That may be specifically true for the materials that are based on highly hydrophilic aluminosilicates distinguished with their high dispersion capacity in water. The use of such bi-functional materials may be efficient for hide and skin processing technologies.

Experimental part

The object is to study the leather semi finished product formation at tanning with the use of modified montmorillonite. The bentonite of Dashukivske deposit was used in the investigation (Ukraine), with the content of main mineral – montmorillonite (MMT). The montmorillonite modification includes the following stages:

-obtaining sodium montmorillonite (Na-MMT) dispersion by means of bentonite dispersion treatment with sodium carbonate (consumption 6.0 % on dry mineral weight) [9],

-obtaining hydroxychromium-montmorillonite (Hydroxy-Cr-MMT) by means of Na-MMT treatment with the solution of basic chromium sulfate (BCS) – $Cr_2(SOO_4)n(OH)_{6-2n}$ (Technical Conditions 2141-033-541386-2003), (consumption 10.0 % of Cr_2O_3) [10].

The adsorption of hydroxychromium complexes on the MMT was defined by means of comparison of the intensity of optical spectra absorption of initial and equilibrium solutions in the range of the wave length – 570-585 nm (Spectrometer Specord-UV-Vis (Germany).

The structural changes of MMT after modification by hydroxychromium complexes were studied with X-ray diffraction (DRON-3 with filterted CoKα - radiation). Specific surface areas of Hydroxy-Cr-MMT were determined by nitrogen adsorption at liquid nitrogen temperature using a gravimetric procedure (BET method).

Obtained Hydroxy-Cr-MMT was used for chromium tanning of pelts by following plan. Pelt obtained with the help of technology [2] was treated in 4 Treatments (table 1). Pelt was tanned with BCS and added Hydroxy-Cr-MMT. Before tanning the pelt was treated by the following solution, in mass. % of the pelt weight: sodium chloride - 6, formic acid - 0.2, duration 10 min. Treatment 4 was set as a control one with the use of 2.0 % chromium oxide (III) [2]. Two samples were taken in each of the groups, and their hydrothermal resistance was measured. The technological solutions were analysed after tanning for residual chromium oxide concentration (III) and *p*H.

Table 1
CHARACTERISTICS OF TANNING

Treatment	Cr_2O_3, in %% of pelt weight		Hydroxy-Cr-MMT, in %% of pelt weight	pH after 12 hr tanning	Increase in basicity			
	BCS	MMT			Na_2CO_3, %	pH after 40 min.	Na_2CO_3, %	pH after 2 hr
1	0.9	0.1	1	3.6	0.2	3.9	0.2	4.2
2	0.8	0.2	2	3.6	0.2	4.0	0.2	4.2
3	0.7	0.3	3	3.8	0.2	4.1	0.2	4.2
4	2.0	0	0	2.8	0.3	3.8	0.3	4.2

workers [13, 14].

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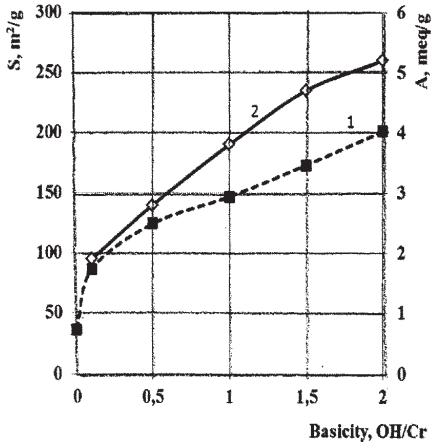

Fig 1. The colloid-chemical characteristics of Hydroxy-Cr-montmorillonities

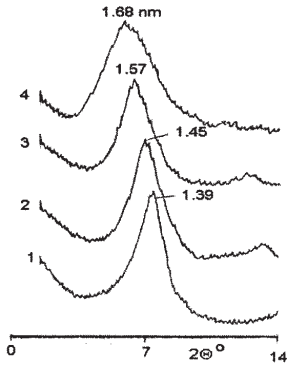

Fig 2. Diffractograms of Na-MMT modified by 0.1 M solutions of hydroxychromium complexes with different basicity:OH/Cr=0.1 (1), 0.5 (2), 1.5 (3), 2.0 (4)

After 24 h holding of tanned samples, they were neutralized with the use of sodium bicarbonate and sodium formiate, 0.8 and 0.5 %, respectively. Then, fat-liquored was performed with the use of 6.0 % «Provol BA» (weight on chromium semi finished item) recalculated for technical product of "Zimmer & Schwarz" (Germany). The experimental samples were slimy and plastic, whilst the control sample was darker and coarse at the face.

After washing and squeezing out up to humidity of 55-60 %, the samples were dried free at 20-23°C. After moistening up to 30-32 %, and malaxing/stretching, and re-drying free to 14-16 %, the samples were ironed at 70-80°C. The experimental samples were more smooth and light-colored at the face, and stretchable. The control samples were harder to iron and smoothing, and shown higher shrinkage as compared to the experimental tested samples.

The chemical composition and physical-chemical indicators of semi finished item samples obtained were studied, and the waste solution was analysed for chromium oxide content (III) [11].

Results and discussions

Modification of montmorillonite by hydroxychromium complexes may yield new applications such as new leather materials for tanning.

The adsorption of polymeric hydroxychromium cations (A) (fig.1 curve 1) depends upon the basicity of chromium solution and is able to exceed the exchange mineral capacity by 2-5 times. Figure 1 shows, that if relationship of OH/Cr=0, then the adsorption of hydroxychromium cations only slightly exceed the capacity of Na-MMT exchange (0.72 meq/g). With the increase of the degree of solution basicity chromium solution from 0 to 0.1, chrome adsorption on Na-MMT sharply grows. It is connected with the appearance of polymeric forms of chrome in solution (dimers, tetramers etc) [12]. As it is seen from figure 1 (curve 2), Hydroxy-Cr-MMT obtains the highly developed surface (S).

The analysis of diffractograms of Hydroxy-Cr-MMT (fig. 2) suggest that hydroxochromium cations of various degrees of polymerization and sizes are intercalated into the interlayer space of MMT crystals increasing d_{001} to 1.68 nm. The variations in the basal spaceings (fig.2) can be attributed to differences both in the nature and the orientations of the interlayer species [13, 14].

Apparently, in the process of drying bevelling of silicate layers occurs mainly along the edgy sections of packages because of non-homogeneous splitting of layered structure by hydroxychromium cations of various sizes. Hydroxy-Cr-MMT acquires highly developed micro- and mesoporous turbostratic structure. This is confirmed not only by the breadths of diffraction maxima but also by the sharp increase of accessible specific surface area of Hydroxy-Cr-MMT, which ranges from 95 to 260 m^2/g (fig. 1).

As a result, Hydroxy-Cr-MMT obtains external surface and adsorptive capacity relatively to collagen of derma for tanning.

The stabilization and formation of derma collagen structure at tanning stage is determined, to a great extend, by chemical composition of the functional system used [15]. With this, both chemical compound and physico-chemical properties of hide leather semi finished item changes considerably. In particular it is proved with combined use of Hydroxy-Cr-MMT and BCS.

As it is shown by the obtained results (table 2), the increase in of Hydroxy-Cr-MMT content in leather semi finished item is accompanied by an extreme dependence

Index	Variant of treatment			
	1	2	3	4
Moisture content in leather, in %	13.7	12.7	12.4	12.9
- chromium oxide*	2.1	2.5	2.4	4.3
- mineral substances*	5.6	6.7	7.8	5.7
- substances that can be extracted by organic solvents *	6.6	6.5	6.3	6.8
- protein substance	73.9	73.9	72.7	74.3
Cr_2O_3 content in spent solution, g/l	2.1	1.4	1.5	6.5

Note. The parameters marked * are calculated for the weight of absolutely dry substance

Table 2
CHEMICAL COMPOSITION OF CHROMIUM-MONTMORILLONITE TANNING SAMPLES

Index	Treatments			
	1	2	3	4
Hydro-thermal resistance , °C	92.0	94.0	88.0	100.0
Tensile strength, MPa	24.0	29.0	27.0	25.0
Face layer strength, MPa	16.0	21.0	19.0	16.0
Elongation at 9,8 MPa load, %	18.0	24.0	26.0	29.0
Specific elongation at rupture, %	44.0	52.0	54.0	58.0
Residual tensile strain, %	11.5	12.0	11.0	14.0
Specific elastic elongation, %	32.5	41.0	43.0	44.0
Apparent specific gravity, g/sm^3	0.638	0.627	0.610	0.685
Volume yield, sm^3/100 g derma	215.0	218.0	226.0	194.0
Yield of leather area, %	102.0	105.2	103.1	100.0

Table 3
PHYSICO-CHEMICAL PROPERTIES OF HYDROXY-CR-MONTMORILLONITE TANNING SAMPLES

on the chromium oxide content (III) in its structure, which confirms an effective influence of modified montmorillonite on chromium compounds interaction with the active groups of collagen macromolecules.

This effect can be explained as structure-forming and plasticizing influence of hydrophyllic aluminosilicate on the availability of ionized carboxylic collagen groups for reaction with hydroxychromium complexes, where the content of the latter decreases in tanning system. Thereby, hydroxyl groups of montmorillonite situated in the internal sphere of hydroxychromium complexes are being replaced by more active ionized carboxyl collagen groups. As soon as the ratio Cr_2O_3 : MMT = 1 : 2, hydroxychromium complexes efficiency in the system drops dramatically. With this, as mineral substance content increases in the semi finished item structure, a decrease in proteic substance in the latter is being observed. The advantage of developed technology over the control one is a considerable decrease of chromium oxide content (III) in spent solutions.

It is worth to mention the effective combined use of Hydroxy-Cr-MMT and BCS in structure-forming and derma collagen stabilization in comparison with the standard use of chromium compounds. Even with twofold dropdown in tanning substance consumption in the first case, rather high values of the semi finished item hydro-thermal resistance were observed, the former increses up to 94 °C in the tanning system of the second type of semi finished item treatment (table 3).

Studies of physico-mechanical properties of semi finished item obtained by means of developed technologies show that semi finished item parameters reach extreme in tensile strength and face layer quality, the extreme being 16 and 31 times higher, as compared to the control treatment, whil the deformation parameters of studied samples have smaller values, and they increase with increasing content of modified montmorillonite. It may be explained by lower shrinkage due to plasticizing effect of Hydroxy-Cr-MMT.

The depth of modified montmorillonite microparticles diffusion into inter-microfibrillary gaps is conductive to efficient splitting up of collagen structure and its protection after the moisture has been removed, providing for increase in volume yield of semi finished item and for extreme yield of leather area. This effect is explained by structural specifics of derma collagen, the former be related to the tilt angle of fibre bundles towards leather surface.

Conclusions

The effect of montmorillonite modification with hydroxychromium complexes on the structural properties of mineral dispersions was investigated. It is proved that with increasing the level of basicity of chromium compounds the adsorption of polynuclear complexes of chromium on montmorillonite increases and the volume of the cation exchange capacity of the mineral exceeds by 2-5 times. Modification of montmorillonite is accompanied by expansion of the crystal lattice d001 to 1.68 nm.

The high sorption ability and specific surface Hydroxy-Cr-MMT has a positive effect on the collagen structure formation in during of chrome tanning.

Joint application of Hydroxy-Cr-MMT and BCS made provision for production of chromium-tanned semi finished product containing 1.7-2.0 times less amount of chromium oxide (III) with two times smaller amount of chromium tanning agent required. The use of Hydroxy-Cr-MMT solutions enables efficient control over reaction between chromium compounds and functional collagen groups due to its reactive-plasticizing action. Resulted semi finished item exceeded control samples by its physico-mechanical properties.The technology developed may be characterised as of having better environmental efficiency and resources saving because of 3.2-4.6 times lower chromium oxide (III) content in spent solution.

References

1.DANYLKOVICH, A., GRYSHCHENKO, I., LISHCHUK, V. The innovative technology of leather and fur materials and products: Monograph, Kiev, Phoenix, 2012. - 344 p.

2.DANYLKOVICH, A., MOKROUSOVA, O., OKHMAT, O. Technology and materials of leather production, Kiev, Phoenix, 2009. – 578 p.

3.DANYLKOVICH, A., Ukr. Ch. J., **68** (8), 2002, p. 78.

4. SLAATS, H., World Leather, **12** (7), 1999, p. 37.

5.DANYLKOVICH, A., ZHYHOTSKYY, A., Proceeding of SIET 12-02 «Modern information and energy save technologies», **12**, 2002, p. 51.

6.MOKROUSOVA, O. The organo-mineral composition for retanning – filling of leather semi-finished item, Proceedings of the 3rd Internatioal conference on advanced materials and systems, Bucharest : ICPI, 2010, p. 85.

7.MOKROUSOVA, O., DANYLKOVICH, A., Scien. Proc. of Riga Technical

University. Material science and applied chemistry, **1** (14), 2006, p. 83.
8.MOKROUSOVA, O. Technological ways for use of the mineral dispersion in leather manufacturing. Monograph: Innovative materials & technologies in made-up textile articles and footwear, Lodz : Wydawnictwo Politchniki Lodzkiej, 2008, p. 146.
9.MOKROUSOVA, O., MORARU, V., Effect of inorganic alkaline reagents on the dispersity and deflocculation of clay minerals dispersions apply to the leather fillers, Book of abstracts of XIV International Clay Conference "Micro et Nano Scientiale Mare Magnum", Castellaneta-Marina, ONLUS, 2009, p. 80.
10.MOKROUSOVA, O., MORARU, V., The effect of montmorillonite modification by Cr(III)-compounds on its microcrystalline structure and electrosurface properties. Proceedings of XIX congress of the Carpatian-Balkan Geological Association, Thessaloniki, Aristotle University of Thessaloniki, 99, 2010, p. 281.
11.DANYLKOVICH, A., Workshop on Chemistry and Technology of Leather and Fur, – K. : Phoenix, 2006. – 338 p.
12.LASWICK, J., PLANE, R, J. Amer. Chem. Soc., **81**, 1959, p .3564.
13.BRINDLEY, G., YAMANAKA, S., American Mineralogist, **64**, 1979, p. 830.
14.MELVILLE CARR, R., Clays and Clay Minerals, **33** (4), 1985, p .357.
15.PLAVAN, V., VALEIKA, V., KOVTUNENKO, O., ŠIRVAITYTE, J., J. Soc. Leath. Tech. Ch., **93** (5), 2009, p. 186.

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