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NON-TOXIC TITANIUM LEATHER TANNING AGENTS. PRODUCTION, PROPERTIES, APPLICATION.

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Abstract

Modern leather-producing enterprises operate on toxic chromium tanning agents. The environment contamination, caused by chromium(IV) escaping with effluents, can be eliminated by substituting, either totally or partially, the chromium tanning agents for non-toxic materials. A technology of a non-toxic titanium-aluminium leather tanning agent from titanite concentrate containing an alumosilicate material – nepheline – has been developed. The kinetic studies included the sulphuric acid processing of the concentrate, converting the acid-soluble components, titanium(IV) and aluminium in particular, into a sulphuric acid solution, from which a complex salt is crystallized, by using ammonium sulphate as a salting out agent. When dissolved, the salt forms metastable titanium-aluminium complexes enhancing the titanium stability and promoting its penetration into the leather collagen. Thus, the new tannin ensures diminishing of environmental loads without impairing the leather quality.

Key words: *titanium tanning agent, titanite, nepheline, titanium (IV) salt, eco friendly.*

1.INTRODUCTION

Leather is a unique material unmatched in properties by synthetics. Leather making is an environmentally challenged process. Tanning is the key process that renders stability to the skin matrix against microbial degradation, heat, sweat etc. Chromium (III) has been used widely in tanning for the excellent properties that it renders to the leather along with simplicity of operation. More than 90% of global leather production of 18 billion sq. ft is through chrome-tanning process currently. The conventional methods employed for tanning lead to significant material loss and serious environmental concern. The current chrome management options like high exhaustion tannage, chrome recycling and recovery–reuse methods, though offering improvements, do not provide comprehensive solutions (Sundar et all., 2002, Kolomaznik et all., 2008). During the tanning process, the exhaustion of chromium is between 40-70% only (Zaroual et all., 2009, Espinoza-Quinones et all., 2009). In specific environmental condition, chromium (III) can be converted to chromium (VI), (Fathima et al., 2001, Milacic and Stupar 1995, Chandra et all., 2005) resulting in skin allergy (Pederson, 1982), cancer (Hayes, 1982) and kidney necrosis (Dartsch et all., 1998). The recovery of solid wastes may also pose problems. One of them is chrome shavings, and this contributes to an extent of 10% of the quantum of raw skins/hides processed, amounting to 0.8 million ton globally (Rao et all., 2002). This waste is partly used in the manufacture of leather board, but most are deposited in landfill. This waste is classified as a category-one waste, one of the most dangerous and harmful wastes if discarded into the environment without any further treatment. Because of this, such a material needs a special disposal, which is very expensive (Nakajimaa and Babab 2004). Therefore searching for new, non-toxic,

tanning materials could tackle many of these challenges. Such materials have been a subject of several studies (see review of Sreeram and Ramasami, 2003).

Among the common metal salts with good tanning properties, titanium is abundant in nature, easily obtainable and non-toxic. Titanium tanned leather has better performance compared with other metal tanning agents (Heidemann, 1993). So, titanium tanning is one of the most promising replacements for chromium tanning in today`s leather industry.

As titanium tanning agents, titanium sulphate (Peng, et all., 2007) and ammonium oxotitanium sulphate $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$ (Motov, et all., 1976) can be used. However, a serious drawback in this case is the fact that tanning solutions hydrolyze during basification. If the solution pH is increased, the composition of the tanning complex changes. The oxo(hydroxo) titanium particles are fairly large and can hardly penetrate into leather, which both hinders the tanning rate and deteriorates the leather quality. To increase a titanium complex stability, masking agents are used, organic addends in particular (Chorles, 1960).

The stability of titanium tanning complex can be increased by producing a multicomponent agent, where tanning components are in a chemically bound state, for instance, a titanium-zirconium tannin based on oxotitanium ammonium sulphate (Motov, et all., 1986) and a titanium-aluminium one (Maslova, et all., 1997, Hinley, 1989). Unlike monocomponent agents, the multicomponent ones can interact simultaneously with several active groups of leather protein, i.e. collagen, facilitating the tanning process. For example, titanium mostly interacts with nitrogen-containing protein groups, whereas aluminium is weakly bonded with these groups while interacting with other functional groups, which increases the shrinkage temperature and hydrothermal stability of the leather (Covington, 1987). Aluminium enhances the titanium complex resistance to hydrolysis (Maslova, et all., 2001), promoting a better binding of components penetrating into the leather. Due to the combined action of aluminum, making the leather softer, and titanium compounds, increasing its strength and filling degree, such materials can be used in manufacture of different leather products.

The work demonstrates the possibility of producing a complex titanium leather tanning agent from multicomponent dressing wastes of apatite-nepheline ore (Russia) and methods of its application in leather tanning.

2. MATERIAL AND METHODS

The object of research was the current wastes of apatite-nepheline process with the main component contents given below, w/o:

titanite	nepheline	apatite	egirine
75-90	2-15	1-3	7-12

First, the material was ground in a vibratory mill. The fraction used for concentrate decomposition was less than 30 μm. The minerals were decomposed under conditions providing converting of titanium and aluminium from the minerals to solution (Gerasimova et al., 2008). The concentrate was batched into a sulphuric acid solution heated to 70-80°C at a concentration of 600 $g \cdot l^{-1}$ H_2SO_4. The ratio of the reagent volume to the concentrate mass was V_{acid}:T=3.5:1. In all the experiments, the acid volume was 2.5 times higher than its stoichiometric quantity needed to bond the acid-soluble components. The concentrate and sulphuric acid were left to interact under boiling and stirring for 7 hours. The suspension was then filtered, with the filtrate (sulphate titanium-aluminium solution) subsequently converted to a complex salt.

The tanning material was synthesized in the following way: the resulting sulphate solution containing TiO_2-80 $g \cdot l^{-1}$, Al_2O_3-10 $g \cdot l^{-1}$, free sulphuric acid H_2SO_{4free}-350 $g \cdot l^{-1}$ and 450 $g \cdot l^{-1}$, was gradually doped with a salting out agent – ammonium sulphate. The quantity of the latter was calculated so that its final concentration in a free state (unbound with titanium (IV) or aluminium) was $(NH_4)_2SO_{4free}$ – 60-300 $g \cdot l^{-1}$. After the reagent was added, the suspension was held for 2 hours under stirring and then left at rest to form a compound, i.e. a complex salt. The salt was then separated using filtration and washed with a saturated ammonium sulphate solution.

The solution's pH was measured with an Orion pH meter 611. The concentration of metal ions in solutions was determined using an AAS-300 atomic absorption spectrometer. The powder X-ray diffraction studies of samples were performed using a Siemens D 5000 diffractometer with a monochromatic Cu *K*α radiation (λ = 1.5418 Å). A scanning rate of 2.4º min^{-1} was used for a 2θ diffraction angle range of 10-60 degrees. Thermogravimetric (TG) and differential thermal analysis (DTA) of the samples were carried out in an argon atmosphere using a high-resolution thermogravimetric analyzer (Model Netzch STA 409/QMS) in a range of 25-900ºC at a heating rate of 10 ºC.min^{-1}. The morphologies of the samples were studied using a Philips XL 30 scanning electron microscope (SEM) equipped with a LaB_6 emission source. The sizes and shapes of titanium phosphate agglomerates were measured using a polarization microscope Leica DM 2500R.

An important factor, indicating the quality of the complex salt as leather tannin, is its basicity determining the content of free sulphuric acid in the tannin. Basicity is rigorously limited by consumers, because it affects both the leather quality and consumption of other ingredients in tanning. The higher the tannin basicity, the easier it is to raise the leather pH to the required value, and the better the tanning process occurs. Good tannin basicity values are in the range of 38-42%. Below 38%, the leather becomes acidified, which increases the consumption of basificating materials. At higher than 42%, the tanning process slows down due to hydrolysis of tanning components, as a result of which tanning components fail to fill the hide completely. The bacisity value was determined by the following formula:

$$X = \left[1 - \frac{C}{A \cdot 2{,}455 + B \cdot 2{,}882}\right] \cdot 100\%, \text{ where}$$

C – the content of active sulphuric acid, %;

A – TiO_2 content in the tanning agent, %;

B – Al_2O_3 content in the tanning agent, %.

2.455 and 2.882 are coefficients for calculating the amount of sulphuric acid bound with titanium and aluminium, respectively.

3. RESULTS AND DISCUSSION

Interaction between the concentrate, activated through grinding, and acid-soluble titanite, nepheline, and some of the apatite, with sulphuric acid in the selected concentration range occurs by the following reactions (Lazareva et al., 2006):

$$KNa_3(AlSiO_4)_4 + 7H_2SO_4 = (KNa)_2SO_4 + 2AI_2(SO_4)_3 + \downarrow 4SiO_2 \cdot H_2O + 7H_2O \quad (1)$$

(nepheline)

$$CaSiTiO_5 + 2H_2SO_4 = TiOSO_4 + \downarrow CaSO_4 + \downarrow SiO_2 \cdot xH_2O + H_2O \quad (2)$$

(titanite)

$Ca_5(PO_4)_3(OH,F),+5H_2SO_4= 3H_3PO_4 + HF + 5CaSO_4$ (3)

(apatite)

Egirine does not interact with sulphuric acid, passing unaltered to the solid reaction products.

When interacting with acid, nepheline, as the easiest soluble component, enters into reaction already at the stage of concentrate feeding. From it, aluminum, sodium and potassium are leached to solution, their concentration varying depending on the nepheline content in concentrate. At the same time, titanium (IV) is converted from titanite. However, the rate of this process is much slower than that of nepheline: a fairly high level of titanium (IV) extraction to the liquid phase is achieved after 7 hours of boiling of the reacting mass (Table 1).

Table 1. Composition of sulphate solutions after leaching

Nepheline content in concentrate, %	Filtrate, $g \cdot l^{-1}$					
	TiO_2	H_2SO_4	Al_2O_3	Fe_2O_3	Na_2O	K_2O
0	126.7	580.2	-	1.8	-	-
1,5	120,5	574,6	4,76	2,71	1,6	0,57
3,0	120,5	553,4	5,93	2,91	2,1	0,78
5,0	107,8	542,7	9,07	3,3	2,5	1,0
8,0	114,1	532,7	7,63	3,49	3,6	1,4
10,0	101,5	530,7	15,26	3,86	3,7	1,7

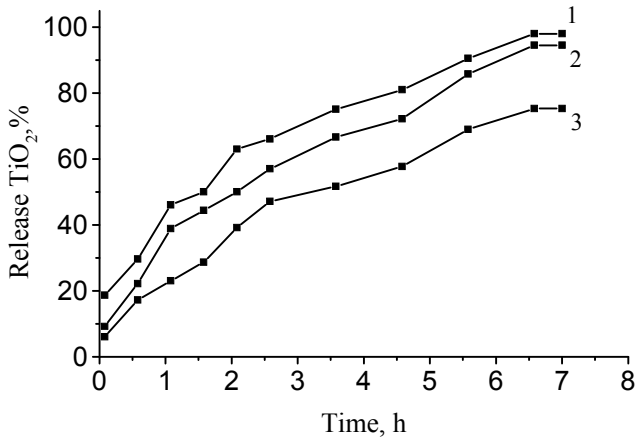

Fig.1 The level of titanium (in terms of TiO_2) release from concentrate depending on nepheline content, w/o: 1- 1,5%; 2 –5%; 3 – 10%. (Zero point is the onset of reaction mass boiling).

Kinetic studies of titanite decomposition in the presence of nepheline have revealed that the process of titanium (IV) leaching from titanite in sulphate solution decelerates with increasing salt contents. The relationship between the level of titanium (IV) release and nepheline quantity in the concentrate is presented in Fig.1.

The precipitates contained the following solid reaction products: calcium sulphate (anhydrate), amorphous silica, and particles of undecomposed titanite and egirine. Using TGA analysis (Fig.2), it was found that mass losses up to 200°C, are mostly caused by the loss of crystallization water becoming higher as the nepheline content increases. When the content of nepheline concentrate achieves 10%, the amount of water increases by an order of magnitude compared with the experiment, where nepheline was absent. This fact can be accounted for by increasing quantity of amorphous silica in the solid. Further, up to about 1000°C, the mass loss for Precipitate 1 is 2%, a low-intensity effect, probably caused by calcium compounds desulphatization, being noted at 806°C. For Precipitate 2, the mass loss was 6%. Two effects up to 300°C, and two at 530°C and 683°C, must have been caused by crystallizing of amorphous titanium phosphate, precipitating in the process of titanium (IV) interaction with phosphoric acid formed by Reaction 3.

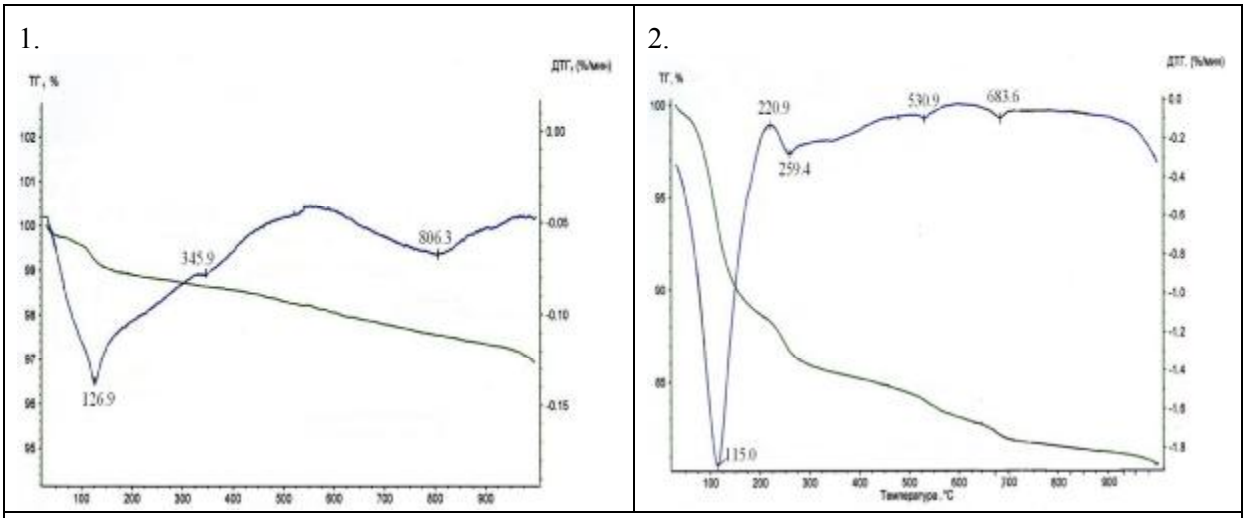

Fig. 2. TG and DTA analysis of solid phases after decomposing of concentrate without nepheline (1) and 10% of nepheline (2)

The kinetics of phase formation in a sulphate titanium-aluminium system involves a latent period lasting until achieving an ammonium concentration necessary to bind the main components (titanium and aluminium) into a solid phase. As shown by XRD analysis (Fig.3), the solid phase is represented by two crystalline compounds: ammonia alum $NH_4Al(SO_4)_2 \cdot 12H_2O$ and ammonium oxotitanium sulphate $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$.

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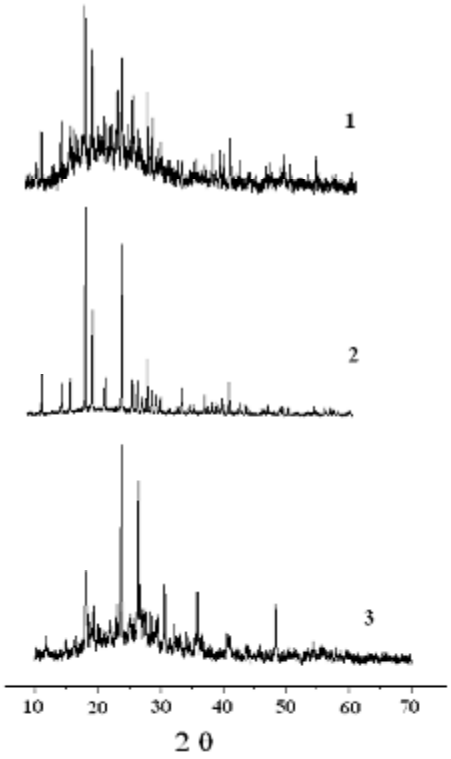

Fig.3. XRD powder patterns for $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$ (1), $NH_4Al(SO_4)_2 \cdot 12H_2O$ (2), $NH_4Al(SO_4)_2 \cdot 12H_2O$+ $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$ (3)

These compounds are identified by using an optic microscope (Fig.4). The particles of Phase 1 are large crystals of 20 to 50 μm in size. Particles of the titanium phase (2) are aggregates with sizes varying between 5-7 μm. The bulk of the aggregates have a shell.

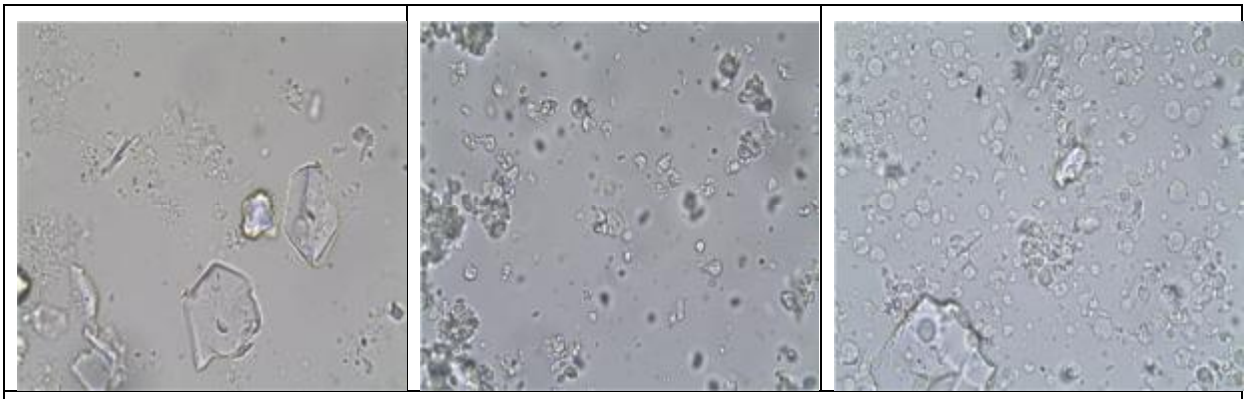

Fig. 4. The results of crystallooptic analysis. Magnification 200.

$NH_4Al(SO_4)_2 \cdot 12H_2O$ (1)	$(NH_4)_2TiO(SO_4)_2 \cdot H_2O$ (2)	$NH_4Al(SO_4)_2 \cdot 12H_2O$+ $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$ (3)

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Fig.5 demonstrates the SEM images of the complex phase (1) and the titanium phase (2). It can be seen that single particles within the titanium phase aggregates in the complex salt are much smaller than the monosalt particles. This indicates the formation of predominantly phase $NH_4Al(SO_4)_2 \cdot 12H_2O$ at the first crystallization stage and of ammonium oxotitanium sulphate $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$ (AOS) – at the second stage.

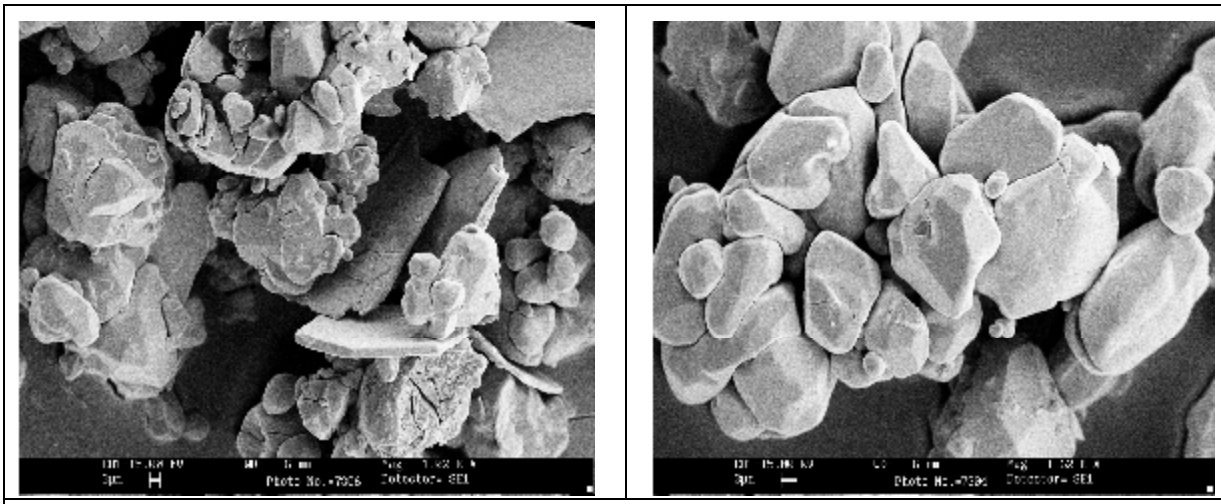

Fig 5. SEM images of solid phase particles

$NH_4Al(SO_4)_2 \cdot 12H_2O$+ $(NH_4)_2TiO(SO_4)_2 \cdot H_2O$.	$(NH_4)_2TiO(SO_4)_2 \cdot H_2O$

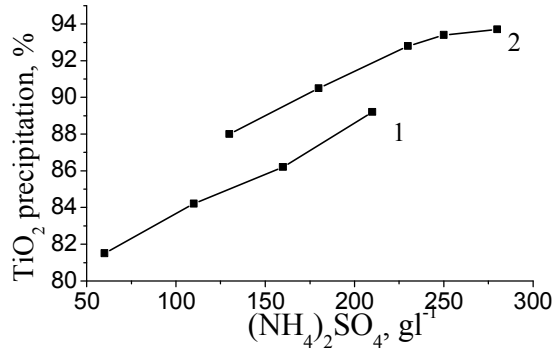

Fig. 6. The effect of ammonium sulphate on titanium(IV) precipitation during desalination:1-$[H_2SO_4]_{free}$– 450 g·l^{-1}, 2--$[H_2SO_4]_{free}$ – 350 g·l^{-1}.

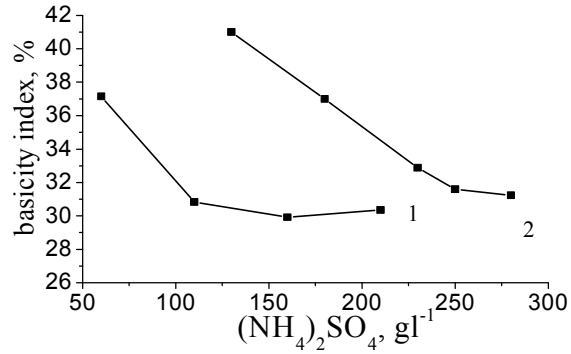

Fig. 7. The effect of ammonium sulphate on the complex salt basicity:1-$[H_2SO_4]_{free}$ – 450 g·l^{-1}, 2--$[H_2SO_4]_{free}$ – 350 g·l^{-1}

Diminishing of the titanium phase particles size is probably due to the slow rate of dozing of the salting-out component, which fails to create a concentration necessary for building up the AOS particles.

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Inquiry into the effect of ammonium sulphate concentration on the degree of titanium(IV) release to the solid phase from sulphate titanium-aluminium solutions at its acidity: 1- 450g·l^{-1}; 2- 350 g·l^{-1} has revealed that increasing ammonium sulphate concentrations initiates the crystallization process due to increased salting mass that diminishes the titanium(IV) solubility (Fig.6). Decreasing of the H_2SO_4 concentration has led to greater titanium (IV) precipitation during the crystallization process. Greater ammonium sulphate and sulfuric acid consumption results in diminishing of the basicity index (Fig.7).

The properties of the salt isolated from sulphate titanium solutions with different aluminium contents are shown in Table 2.

Table 2. Composition and basicity of the salts

№	Content of main components, w/o					Basicity,%
	TiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	
1	21,6	0.3	0,09	0,10	0,06	42,3
2	15,6	3,0	0,12	0,25	0,14	40,1
3	12,3	5,9	0,19	0.31	0,20	38,4

Test results on the stability of tanning solutions are presented in the Table 3. Basicity of the tanning salts in all experiments was 40.1%. The stability index was the time interval before the onset of titanium (IV) hydrolysis. This index is essential for the leather tanning process (Table 3).

Table 3. Stability of complex salt solutions

Solution composition, g·l^{-1}			Time before hydrolysis, h
TiO_2	H_2SO_4	Al_2O_3	
20	25	-	0.5
20	30	-	1,0
50	62,5	-	1,4
50	75	-	2,0
50	75	3,0	6,0
50	70	6.0	9,0
50	70	12.0	3,75
70	87.5	3,0	15,0
70	87.5	6,0	18,0
70	98	6,0	More than 24
70	98	12,0	20,5

As the sulphuric acid and titanium (IV) concentrations in solution are increased, the solution stability increases correspondingly. The presence of aluminium, up to a certain concentration, also promotes

stability owing to the formation of a metastable titanium-aluminium complex (Maslova et al., 2001). However, at higher than 10-12 $g \cdot l^{-1}$ Al_2O_3, the solid phase crystallizes in the form of ammonia alum.

Our research has resulted in developing of the most favorable parameters and process regimes for nepheline-containing titanium concentrate, yielding a complex salt with a composition and properties acceptable for leather tanning. The technology has been patented (Gerasimova et all, 2010) and tested on an experimental-industrial scale.

Samples of the titanium-aluminium tanning agent were tested in laboratory on raw cattle hides. The soaking and other pre-tanning processes and operations were carried out in a conventional way. For pickling, sodium chloride and sulphuric acid were used in amounts of 6% and 0.7%, respectively, of the raw hide mass. At the end of pickling, the titanium-aluminium tanning agent was added to the bath (at 3.9% of the hide mass, in terms of titanium and aluminium oxide sum). The concentration of titanium-aluminium tanning agent in the tanning chamber was 20 $g \cdot l^{-1}$ in terms of titanium and aluminium oxides.

The fact of tannin penetration into hides was evaluated by their yellow colouring when treated by 3% hydroxide solution. The shrinking temperature was recorded after 1, 2, 3 and 5 hours. Besides, the hides were tested for the tanning agent's penetration in terms of titanium and aluminium oxides, the tanning salt content in the spent bath, and the physical-mechanical properties of the leather.

Table 4. Test results

Indices	Sample №1	Sample №2	Sample №3	Standard
Contents of titanium and aluminium dioxides in spent solution, $g \cdot l^{-1}$	6,2	5,0	5,4	—
Tannin penetration into hides, %	75	95	100	—
pH of the solution during tanning	1.92	1.85	1.51	—
Shrinking temperature of the leather after basification	78	84	87	100
Ultimate tensile strength, 10 MPa	1,6±0,5	2,0 ±0,5	1,7	1,8
Specific elongation at 10 MPa, %	15,2±1,0	19,2±1,1	18,5±1,0	15-35

CONCLUSIONS

The conditions of a sulphate titanium-aluminium solution production from a concentrate containing nepheline and titanite have been investigated. It has been shown that the presence of nepheline hinders the titanium leaching to solution due to the formation of an amorphous silica shell on the surface of titanite particles. The optimal nepheline content in the concentrate was found to be not higher than 3% in terms of Al_2O_3, providing both stability for the solution and a technologically attractive level of releasing main components.

Studies of the process of solid phase crystallization from sulphate titanium-aluminium solution by adding ammonium sulphate as a salting-out agent have led to establishing of a relationship between the agent consumption and the degree of components precipitation at different levels of initial acidity.

The crystallization kinetics and properties of solid phases, consisting of ammonium sulphate oxotitanate and ammonia alum, have been investigated.

On the basis of our findings, a technology of a nontoxic titanium-aluminium tanning agent has been created and successfully tested in a specialized company.

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