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Study of bleaching with modified compounds of titan in white leather manufacturing

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Abstract. The process of semi chrome finished item bleaching by modified dispersions of titanium dioxide has been investigated. For the modification of the water dispersion of titanium dioxide, sodium polyphosphate was used with the aim of dispersion and activation of dispersion particles. It has been established that application of the modified dispersion for bleaching permits to increase qualitative and operational properties of bleached leathers, to rise the degree of leather surface whiteness and to decrease leather rigidity.

Key words: bleaching, titanium dioxide, sodium polyphosphate, wet-blue, modified dispersions, whiteness, white leathers.

1. INTRODUCTION

Leathers of white colour are in great demand nowadays. Leathers of such colour are in vogue not only for garment and haberdashery but also for upper leather for shoes. The main task, while producing white leathers, is to obtain homogeneous white colour all over the leather surface. In the process of exploitation, the leather must preserve colour, hue and tint and not yellow under light and oxidation action of fat materials.

The production of white leathers is very specific. Selection of chemical materials for the treatment of semi-finished items is of prime importance. Chemicals must be colourless or white and possess a number of characteristic properties:

- not to darken, but to bleach semi-finished items during different stages of treatment;

- to be resistant to chemical influence and not change the proper colour;
- to be light and heat-resistant during leather storage and sewing processes [1].

Semi chrome finished leather with bluish tint is used by the main Ukrainian tanneries for producing white leather. It complicates the obtaining of saturated leathers of white colour. Therefore aftertanning processes are very important and they are directed to whitening and bleaching of semi chrome finished leather. As to operational technology of white leather production from semi chrome finished leather, colourless synthetic tannins, acrylic copolymer compounds and water soluble resins are used for retanning and filling [2]. Titanium dioxide is employed for surface bleaching. The treatment is carried out in the process of fat-liquoring. As a result of it, the degree of leather grain whitening increases but certain defects appear. Firstly, the particles of titanium dioxide contain fat and during bleaching, in the process of fat-liquoring, they partly adsorb the fat substances on their surface [3]. This decreases the fat-liquoring effect and yield in leather area but increases leather density and obtained white leathers are more rigid. In order to remove these defects, it is necessary to increase the consumption of fat substances, but it is economically inefficient. Secondly, the particles of titanium dioxide with adsorbed substances usually settle on the grain and flesh surfaces. The diffusion into internal derma structure is not sufficiently intensive. Part of the titanium dioxide, adsorbed by the surface, is removed during washing, setting and squeezing. The remaining part of the titanium dioxide after drying performs the role of antiadhesive and as a result the grain becomes rather fatty. This decreases the quality of the following dyeing. Incomplete adsorption of titanium dioxide particles by the semi-finished item is probably connected with the deficiency in affinity of these particles to active centres of elements of the fibrous structure of leather and with the presence of large agglomerates, the size of which exceeds the diameters of interstructural capillaries of leather.

In this paper an attempt has been undertaken to eliminate a number of above mentioned defects by using auxiliary additives that modify and dispergate titanium dioxide particles. Due to modifications of water dispersions of titanium dioxide, stable water dispersion is obtained by means of dispersing agglomerations of titanium dioxide. It allows:

- to increase the degree of whiteness of semi-finished leather;
- to decrease the amount of coating dyestuff on the leather surface;
- to improve adhesiveness to derma surface;
- to increase leather softness and to increase the yield of leather area.

In this connection, the object of the work was to study the possibility of increasing the bleaching efficiency of semi chrome finished leather using modified water dispersion of the titanium dioxide.

2. EXPERIMENTS

2.1. Materials

For experimental investigation, semi chrome finished leather of light steers was used. Syntan Novoltan V (Clariant), fatty substance Provol VA (Clariant), potassium alum and titanium dioxide, modified with sodium polyphosphate, were used for aftertanning processes. Titanium dioxide, mark R-02 (State standard 9808-84) with medium particle size of 0.2 μm was used for semi-finished item bleaching.

As a modifying additive, inorganic polymer of sodium polyphosphate or sodium hexametaphosphate (State standard 20291-80) was used. Sodium polyphosphate is able to dissolve precipitations, to dispergate, to deflocculate suspended particles, to be adsorbed on the surface (as a result of polymeric structure) and to stabilize systems.

Fat emulsion was used for fat-liquoring. It was obtained by means of emulsification of fatty material Provol VA (Clariant) and non-ionic SAS – savenol.

Titanium dioxide was modified by sodium polyphosphate before bleaching. For that sodium polyphosphate in soluble state in the amount of 10% of titanium dioxide weight, was introduced into water dispersion of titanium dioxide with a concentration of 100 g/l. The obtained dispersion was mixed for 10 min and further used for bleaching.

2.2. Bleaching trials

For bleaching investigation, 4 batches of semi chrome finished items of light steers from butt were used. Each batch included 3 wet-blue samples of the size 15×15 cm. One batch was for control and 3 were experimental. The thickness of wet-blue samples after shaving was 1.4–1.6 mm. The raw material treatment was performed according to traditional technology of chrome leather for the upper of shoes production used by Limited Joint Stock Company "Chinbar".

While processing the controllable batch, the method of obtaining white leather from wet-blue was taken as a basis which provides bleaching with titanium dioxide in the amount of 2.5% of the shaved leather weight [4]. Bleaching is performed in the process of fat-liquoring.

The experimental batches were bleached with modified water dispersion of the titanium dioxide in the amount of 1.5, 2.0 and 4.0% titanium dioxide of shaving leather weight and 10% of sodium polyphosphate of titanium dioxide weight for modification. Preliminary data confirmed that the usage of 2.0% of modified titanium dioxide dispersion is optimum for obtaining sufficient level of wet-blue samples bleaching and in the following it will be used. The details of the control and experimental processes are given in Table 1.

Table 1. The details of control and experimental processes

Process/chemicals	Amount of the chemicals in shaved leather, weight %	Duration	T°C	Remarks
Control process				
Retanning–fat-liquoring–bleaching				
Water	150		55	
Novoltan V	6.0	60		
Provol VA	8.0	40	60	pH was 4.1–4.2
TiO_2	2.5	60		
Washing				Bath was drained
Water	200	10	25	
Experimental process				
Retanning–bleaching				Bath was not drained
Water	150		45	
Modified compounds of titan	1.0	5		
Novoltan V	3.0	30		
Novoltan V	3.0	60		
Fixing				
Potassium alum	2.5		45	
Sodium formate	0.5	30		
Fat-liquoring–bleaching				Bath was not drained
Water	150		60	
Provol VA	6.0	40		
Modified compounds of titan	1.0	30		
Provol VA	2.0	30		
Fixing				
Formic acid	0.2	10	40	pH was found to be 4.0–4.1

Commercial products used: Provol VA (Clariant), Novoltan V (Clariant).
The leathers were dried completely and coat dye was sprayed.

2.3. Examination with scanning electron microscope

The modifying action of sodium polyphosphate on the dispersion of titanium dioxide was studied with the help of scanning electron microscope BS–340, which was completed with digital system of picture analysis for studying the size distribution of the particles. The results of the analysis are presented as histograms of distribution of titanium dioxide particles in the dispersion. By experiments the modified dispersion of titanium dioxide was used. Before investigation, the modified dispersion of titanium dioxide was additionally dispersed for 10 min under ultrasonic action with the frequency of 22 kHz by 40 W. Then the dispersion was placed on a silicon plate and sprayed with gold (h = 200 Å) to remove the electrostatic charge.

The degree of whiteness of the bleached semi-finished item and leather after coat dyeing was determined with the help of Tseisa leucometre [1]. Whiteness was determined following the standard [5]. The coefficients of light ray reflection from the surface of the bleached semi-finished item were measured in blue spectrum at ~430 nm and in red spectrum at ~670 nm.

The whiteness was calculated according to the Stephenson formula

$$W = 2 * R_{430} + R_{670},$$

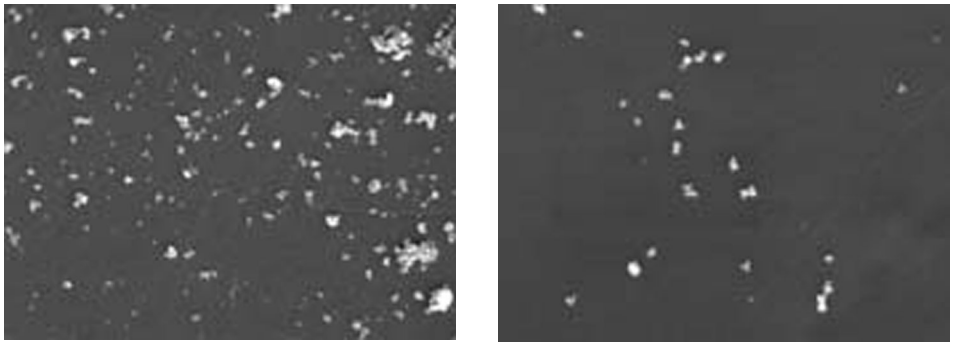
where W is whiteness (%) and R_{430} and R_{670} are coefficients of reflection at $\lambda = 430$ and $\lambda = 670$ nm.

The leather in crust was assessed for softness, grain smoothness, fullness and general appearance by experimental bleaching using a scale of 0–10 points (higher points indicate a superior property).

Qualitative and operational properties of obtained white leather were assessed according to indices of chemical analysis, physico-mechanical investigation of the finished leather and according to resiliency and plasticity of the leather [6,7]. Tensile strength, elongation and grain strength were investigated according to standard procedures.

3. RESULTS AND DISCUSSION

The medium size of the titanium dioxide particle is 0.2 μm. In water dispersion these particles have a tendency to form agglomerates due to surface attraction of adsorptive layers of the particles. The SEM photographs show this (Fig 1). The size of the agglomerates is much greater and may reach 1.5 μm and more. In such a state the activity of dispersed particles of the titanium dioxide is low and diffusion into derma structure is weak. Therefore the bleaching of the semi chrome finished item with such water dispersions has superficial character.



(a) (b)

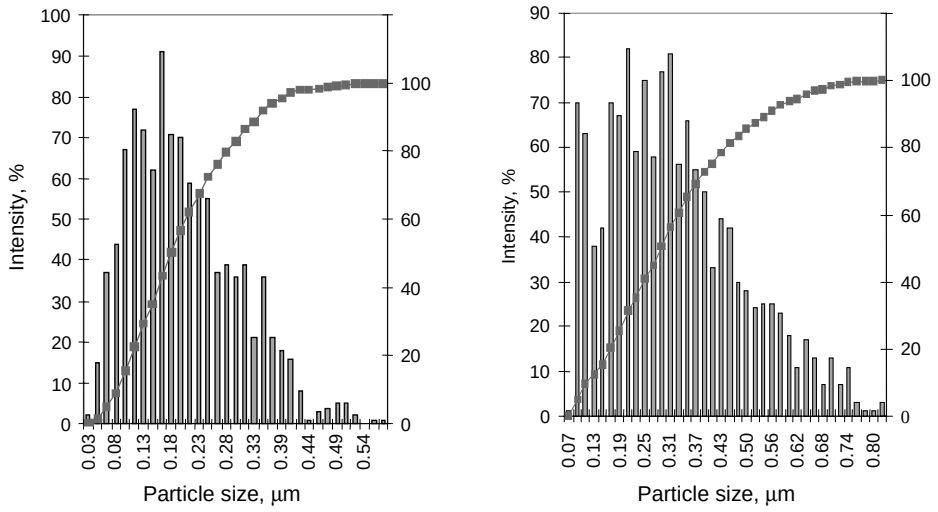
Fig. 1. SEM photographs of particles in the titanium dioxide dispersion (a) and in the modified dispersion of titanium dioxide (b); magnification is 10 000×.

The application of sodium polyphosphate allows to modify the water dispersion of titanium dioxide and to improve its technological properties. But at the same time, destruction of the agglomerates of titanium dioxide water dispersion takes place resulting in the dispersity of particles (Fig. 1b). Due to the more uniform particles distribution in the water dispersion, a rise of the stability and equilibrium occurs. It may be supposed that as a result of the modification of the titanium dioxide dispersion, the change of the state and nature of the layer of adsorptive particles occurs.

Hydrophilization of the surface of titanium dioxide particles takes place due to bringing in additional number of hydroxylic groups by sodium polyphosphate. Thus the activity of the water dispersion of titanium dioxide increases relative to the elements of the fibrous derma structure.

As a result of modification, most probably the adsorption of sodium polyphosphate takes place on the surface of titanium dioxide particles. Therefore after modification of the titanium dioxide dispersion, one can observe partial increase of the size of dispersion particles from the level of 0.03–0.54 μm to the level of 0.07–0.8 μm. Histograms are presented in Fig. 2.

Modification of the dispersions of titanium dioxide permits to increase the efficiency and quality of bleaching of semi chrome finished leather. Bleached, soft, pliable, well fat-liquored, without fatty grain surface, semi-finished items were obtained according to the described experimental procedure. Shrinkage temperature after retanning – bleaching and fat-liquoring does not decrease and remains on the level of 115°C both for control and experimental samples.



(a) (b)

Fig. 2. Histograms and cumulative curves of titanium dioxide particles distribution in water dispersion (a) and after modification (b).

The total degree of whiteness of bleached semi-finished item is higher (Table 2) and equals 44.4% (in control 37.5%). After coating the semi-finished item, the total whiteness of experimental white leather is higher and equals 87.0% (in control 77.8%).

The results in Table 3 show that the increase of the whiteness degree allows to decrease the amount of the coating dyestuff (almost twice). This is very efficient from the economic point of view. Thus the film thickness in experiments was 160.0 mg/dm^2 (in control 280.0 mg/dm^2). The adhesion of the coating in experiments was higher than that in the control and constituted 365.0 and 260.0 N/cm respectively. It is, perhaps, because in the control version a great amount of titanium dioxide was adsorbed on the leather grain surface and, as a result, antiadhesive film was formed and adhesion decreased.

The results of physico-mechanical measurements and chemical analysis were used for the evaluation of qualitative and operational properties of the obtained white leather. As shown in Table 4, in experimental leathers the amount of mineral matter increases by 2.1% in comparison with the control ones. This may

Table 2. Indices of the whiteness level

Method of treatment	Whiteness after bleaching, %			Whiteness after coating, %		
	Blue spectrum	Red spectrum	Total	Blue spectrum	Red spectrum	Total
Experimental	48.5	52.6	44.4	83.0	79.0	87.0
Control	43.9	50.3	37.5	74.5	71.3	77.8

Table 3. Properties of the covering film

Method of treatment	Adhesion of the coating film in dry condition, N/cm	Thickness of the coating film, mg/dm^2
Experimental	365.0	160.0
Control	260.0	280.0

Table 4. Indices of physico-mechanical tests and chemical analysis

Indices		Experimental	Control
Mineral matter, %*		8.6	6.5
Chromium oxide Cr_2O_3, %*		3.6	3.3
Dermal substance, %*		75.2	77.4
Substances extracted by organic solvents, %*		6.8	4.5
Rigidity, 10^{-2} N		25.0	34.0
Grain strength, 10 MPa		1.62	1.52
Tensile strength, MPa		1.90	1.74
Elongation, %:	at stress 10 MPa	34.0	32.0
	at cracks	47.5	42.0
	at break	53.5	48.0

* Based on the weight of dry cake.

indirectly indicate that modified dispersion of titanium dioxide is better fixed in leather. After washing, squeezing and setting, washing out titanium dioxide particles does not take place.

Bleaching by modified dispersion of titanium dioxide increases the effect of fat-liquoring of the semi-finished item. The amount of substances, extracted by organic solvents, is in experimental items higher and constitutes 6.8% (in control 4.5%). This testifies that modified titanium dioxide particles do not sorb fatty substances and as a result fat-liquoring occurs more efficiently. The better the effect of fat-liquoring the greater the plastification of leather structural elements. This facilitates the decrease of leather rigidity to 25.0×10^{-2} N, whereas the rigidity of the control leather is 34.0×10^{-2} N. Consequently, experimental leathers are more soft (have less rigidity), more elastic and have more yield of the leather area (Table 5).

Indices of grain layer strength, tensile stress and breaking elongation in experimental leathers are higher than those in the control leather (Table 4). Consequently, experimental leathers posses better operational indices than those of control.

It should be noted that the employment of modified titanium dioxide dispersions allows to obtain white leather with highly formed structure (Table 5). The yield of white leather area in experimental items is higher by 2.8%. The experimental white leather has better formation of leather volume and it was proved by increasing volume yield and decreasing specific weight of experimental leathers.

Control and experimental crust leather were evaluated for various organoleptic properties by hand evaluation. Higher numbers indicate better property (Fig. 3). Experimental leathers exhibit better softness, fullness and grain smoothness as compared with control leathers. In general, the appearance of the experimental leather is better than that of the control one.

Table 5. Indices of derma structure formation

Indices	Experimental	Control
Yield of white leather area, % from area of control leather	102.8	100.0
Volume yield, cm^3/100 g dermal substance	245.9	235.4
Apparent specific gravity, g/cm^3	0.618	0.634

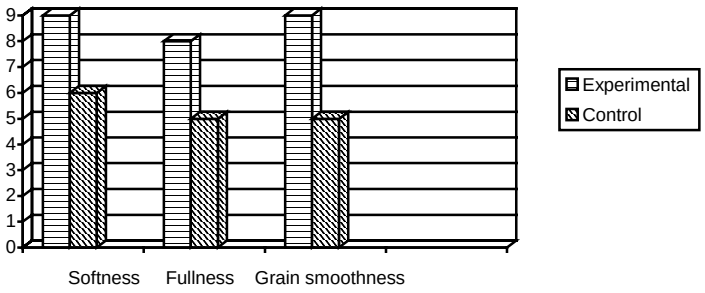


Fig. 3. Organoleptic properties of crust leather obtained from control and experimental processes, arbitrary units.

4. CONCLUSIONS

Bleaching semi-finished leather with modified dispersion of titanium dioxide allows without considerable changes of the technological cycle to increase qualitative and operational properties of white leather. By introducing auxiliary additives into bleaching process it is possible:

- to increase significantly yield in leather area;
- to increase whiteness of the leather surface;
- to improve fat-liquoring;
- to decrease the amount of the coating dyestuff on the leather surface;
- to improve adhesion of the cover to leather surface;
- to decrease rigidity of leather;
- to improve physicomechanical and elasto-plastic properties of finished leathers.

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Pleegitamine modifitseeritud titaaniühenditega valge parknaha valmistamisel

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On uuritud kroomiga töödeldud poolfabrikaatide pleegitamist Na-polüfosfaadiga modifitseeritud TiO_2 vesidispersioonidega, tõstmaks toimeosakeste dispergeeritust ja aktiivsust. On leitud, et modifitseerimine aitab tõsta pleegitatud naha kvaliteeti ning kasutusomadusi, muuta naha pinda valgemaks ja vähendada jäikust.