

*Досліджено процес сорбції азобарвників на модифікованих колагенових волокнах і шкіряному напівфабрикаті хромового дублення залежно від концентрації сполук титану різного хімічного складу. Розроблена технологія фарбування шкіряного напівфабрикату, яка передбачає використання сульфатотитанілату амонію на заключній стадії наповнювання-фарбування-жиркування, забезпечує суттєве зменшення витрат екологічно шкідливих сполук хрому та одержання сертифікованого шкіряного матеріалу*

*Ключові слова: фарбування шкіряного напівфабрикату, азобарвник, сполука титану, колористичні показники, механічні властивості*

*Исследован процесс сорбции азокрасителей на модифицированных коллагеновых волокнах и кожевенном полуфабрикате хромового дубления в зависимости от концентрации соединений титана различного химического состава. Разработана технология крашения кожевенного полуфабриката, предусматривающая использование сульфатотитанилата аммония на заключительной стадии наполнения-крашения-жирования, обеспечивающая существенное уменьшение расхода экологически вредных соединений хрома и получение сертифицированного кожевенного материала*

*Ключевые слова: крашение кожевенного полуфабриката, азокраситель, соединения титана, колористические показатели, механические свойства*

# IMPROVING THE PROCESS OF DYEING A LEATHER SEMI-FINISHED PRODUCT BY TITANIUM COMPOUNDS

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## 1. Introduction

Increasing demands for greener chemical technologies and to products quality necessitate improvement and development of new technological processes. This is especially important for multi-stage and material-intensive physical and chemical processes that require the use of a wide range of chemical reagents. In this regard, special attention should be paid to the production of leather materials, which uses significant amounts of water [1, 2]. In this case, the processes of dyeing a leather semi-finished product require consideration of its condition and essentially depend on the chemical composition of dyes and auxiliary reagents. The latter provide for diffusion capacity of dyes, the coloration of a semi-finished product, homogeneity and color saturation of the surface. It enables to reduce thickness of the coating film and manufacture high-quality leather with aniline sorption [3]. It should be noted that to achieve a uniform and intense coloration, modern technologies, after a combined process of dyeing-greasing, may include additional coloring with the fixation of the dye by environmentally harmful compounds of chromium. In this regard, it is relevant to design new dyeing compositions and conditions of their use for the development of resource saving environmentally friendly technologies.

## 2. Literature review and problem statement

Natural leather materials are distinguished by structure, difference in density for particular topographic plots and the

peculiarity of previously conducted technological treatment. In this regard, for the effective process of dyeing, the essential conditions are, first of all, is the search for and development of appropriate dyeing compositions that include dyes of natural and synthetic origin. Paper [4] explored the process of dyeing leather with henna extract, the major component of which was 2-hydroxy-1,4-naphthoquinone with the use of mordents of various chemical composition, in particular, aluminum sulphates, iron and zinc. The process was conducted at the concentration of dye 2,5–25 % and pH of the working solution 4–7. Under optimal conditions: the 20 % concentration of dye, medium pH 4, temperature 60 °C, the leathers were characterized by high resistance to wear and sweat, however by satisfactory light stability.

High lightfastness of dyed leathers was achieved as a result of the conducted research into the dyes of plant origin [5]. It was found that preliminary use of mordant salts of aluminum (III), copper (II), tin (II) and natural dyes rhine, indus, pacific, caspian, henna, hemine made it possible to obtain quality leathers with a wide range of color shades. The authors explained results they received by the effective diffusion of dyes into the structure of leather and their interaction with mordant salts.

The process of dyeing skin tissue of skin coat sheepskin by the hypericum extract was examined [6, 7]. The formation of high quality colored material of yellow, green, yellow-brown colors is explained by the authors by the creation of complex compounds of dye with mordents.

To increase the efficiency of the process of dyeing leather, authors of paper [8] recommend modifying acidic

dyes with plasma, which makes it possible to increase the stability of coloration towards dry and wet attrition, reduce the concentration and duration of dyeing a leather semi-finished product. Volumetric-surface modification of chrome-tanned leather for leather uppers by the method of treatment with high-frequency low-temperature plasma of reduced pressure [9] allows for the intensification of technological process of dyeing leathers from horned animals' raw materials. Additional treatment of leather with plasma after drum dyeing [10] provides for an increase in the depth of dye diffusion into the volume of a semi-finished product and physical-chemical properties. It should be noted that this leads to a longer duration of treatment and to labor intensity of the technological process that negatively affects the cost of products.

The process of dyeing the suede of skin coat sheepskin tanned using the compounds of titanium and low-temperature plasma was explored [11]. The use of ammonium sulfate titanylte provides for the possibility to increase the absorption of acidic dyes when dyeing a semi-finished product and the saturation of the dyed surface in comparison with the samples of chrome-tanned leather. According to the obtained results, structure of a semi-finished product is significantly affected by the method of treatment with low-temperature plasma. Much to our regret, the authors did not examine the peculiarities of influence of low-temperature plasma and ammonium sulfate titanylte on the structure of a semi-finished product.

To intensify the process of dyeing a semi-finished product with anionic colorants at its filling with acrylic polymers of combining dyeing and greasing processes, it is recommended to use alkyl aryl sulphates in production technology for their stabilization [12]. In this case, the efficiency of colorants significantly increases.

Therefore, the efficiency of dyeing a leather semi-finished product is to a large extent determined by the properties and structure of the material that are achieved at the preceding stage of its treatment. In this case, when compared with the environmentally friendly natural colorants that require additional treatment of a semi-finished product by mordant reagents and do not yield lightfast coloring, the use of synthetic dyes that have a defined chemical composition and which allow the intensification of the process of dyeing looks promising. Thus, absolutely relevant is the search for technologically and environmentally effective dyes fixatives, which provide color saturation and uniformity of materials coloration.

### 3. The aim and tasks of the study

The aim of this work is to study the process of dyeing a leather semi-finished product, structured by compounds of chromium, with anionic colorants in the presence of titanium compounds.

To achieve this aim, the following tasks were set:

- to determine the peculiarities of interaction between titanium compounds and azo dyes;
- to explore the sorption of azo dyes by collagen fibers and their diffusion capacity;
- to determine optimal conditions for dyeing with modified azo dyes of a leather semi-finished product in the comprehensive process of filling-dyeing-greasing.

### 4. Materials and methods of research

In accordance with the set aim, in the work we used a semi-product of chrome-tanned leather (SCT) for the production of leathers of thickness 1.1–1.6 mm for upper and lining of shoes and haberdashery in line with TU U 00302391-03-98, obtained from horned cattle raw materials (HC) of the wet-salted conservation by technique [1]. Before the process of dyeing, a leather semi-finished product, structured by tannic compounds of chromium (III) was exposed to mechanical treatment on rolling machines to remove excess moisture and alignment of thickness throughout the area with subsequent restoration of hydrophilic condition of the dermis structure.

To examine the interaction between the components in the system colorant-titanium compounds-collagen, we used the gelatin T-7 in line with TU U 24.6-00418030-002:2007, pH 5.7 and the hide powder in line with TU 8670-020-05431555-95. Gelatin was applied as gel of 4 % concentration. A model preparation of a leather semi-finished product was the hide powder, obtained at the leather factory named after Radishchev (St. Petersburg, Russia) as a result of alkaline scattering of middle layer of skin of bull of 35–40 kg weight, which is in a structural sense is a set of polypeptide fibrils composed of macromolecules of collagen fibers (CF). To lock the carboxyl groups, CF was structured by the basic chromium sulphate (BCS)  $\text{Cr}_2(\text{SO}_4)_n(\text{OH})_{6-2n}$  in line with TU 2141-033-54138686-2003 by technique [13].

A study of the sorption of the dye ABD was conducted on CF, modified by a mixture of dispersions of polymers (MDP) of the composition: the emulsion MBM-3 (TU6-01-186-89) and the dispersion MX-30 (TU6-01-289-82) in the ratio of 1:1.

In the work we used anionic dyes [14, 15] (Fig. 1).

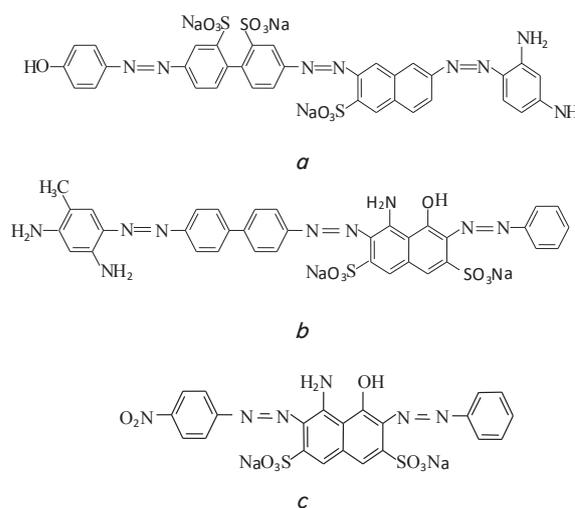


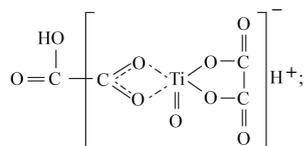
Fig. 1. Anionic azo dyes: *a* – brown 345, *b* – black K, *c* – acidic blue-black

Anionic acidic blue dye (ABD) belongs to the dis-, while brown 345 (K345) and black K (BK) – to the tris-azocompounds with molecular weights 614, 867 and 795, respectively. They have different uniformity of location and concentration of sulphate- and other functional groups and the length of hydrophobic section, which pre-determines their technological properties. The examined azo dyes are characterized by stability of coloration at pH of their solutions at 2–7.

We used titanium compounds as the dye fixatives:

– ammonium sulfate titanylte  $(\text{NH}_4)_2\text{SO}_4 \times \text{TiO}_4 \times \text{H}_2\text{O}$  (AST) in line with TU 95.290-79 g contained 19.6 % by weight of titanium oxide (IV) at a Schorlemer basicity of 44.8 %;

– titanyl oxalic acid (TOA) of the 1,05 mol/dm<sup>3</sup> concentration, synthesized by technique [16] according to structural formula:



– potassium salt of titanyl oxalic acid (PTOA).

Ammonium sulfate titanylte was used in the form of a solution with the concentration of 0.66 mol/dm<sup>3</sup>, pH=0.75. The concentrations of working solutions of TOA and PTOA are 0.2 mol/dm<sup>3</sup>, pH are 0.85 and 2.1, respectively. Combining titanium compounds with dyes was carried out at temperature 20 °C and in the proportions by weight of TOA (PTOA)/dye 0.5 – 2.0/1.0.

Sorption of dyes on CF was carried out in a hermetically closed glass container at temperature 18–22 °C and by stirring with the mixer rotation speed of 43–47 min<sup>-1</sup> with subsequent washing at 58–62 °C for 60 and 80 min, respectively. The dye consumption was 8 % by weight of CF; that of TOA and PTOA – 75 % by weight of the dye; water for CF – 16/1.0. The content of dye, not bound by hide powder, was determined by its difference after sorption and washing with distilled water of the colored CF with consumption of 32/1.0 at temperature 63–67 °C on the device “Water Bath Shaker” 357 (Poland) at the mixing frequency of 150 min<sup>-1</sup>. The degree of chemisorption of the dye by the structure of CF was defined by its absence in the washing water.

The sorption of dyes on CF, mg/g, was examined by the colorimetric method by optical density  $D$  at the photoelectric colorimeter KFK-2M at 670 nm and thickness of the layer of solution of 5 mm. With this purpose we used calibration dependences of optical density on the concentration of dye in the range of 0.05–2.5 g/dm<sup>3</sup>. The change in pH of the working solution at coloring was determined by the potentiometric method using the universal ionometer EB-74 (Ukraine).

Physico-chemical properties of the dyed leather material were determined by techniques [13]. In particular, the load and elongation at the gap of material  $\sigma_b, \sigma_g$  and  $\epsilon_b, \epsilon_g$  – at the tensile machine RM-50M at the rate of deformation of the sample of 90 mm/min, its elasticity by rigidity  $R$  at the device for determining rigidity and elasticity of leather PZhU-12M (Russia). Colorimetric indicators of a semi-finished product were measured at the device for determining resistance of coloration against dry and wet attrition PT-4 (Russia) by the gray scale standard. Hydrothermal stability of CF was determined by the temperature of early shrinkage of the fibers when heated in water ( $T_{hs}$ ).

Thus we used a complex of research methods to determine effectiveness of using titanium compounds in the technology of dyeing elastic leather material.

### 5. Interaction of titanium compounds with anionic colorants and their sorption on the hide powder

A study of the interaction of anionic colorants with titanium compounds (IV) was carried out by examining the kinetics

of change in pH of the working solutions and optical density at their combination. As demonstrated by the received results (Fig. 2, *a*), for all variants of interaction between the dyes and titanium compounds, at increasing the content of titanium modifier, there is a decrease in pH of the system. After reaching pH 2.9–3.9, the intensity of this effect decreases.

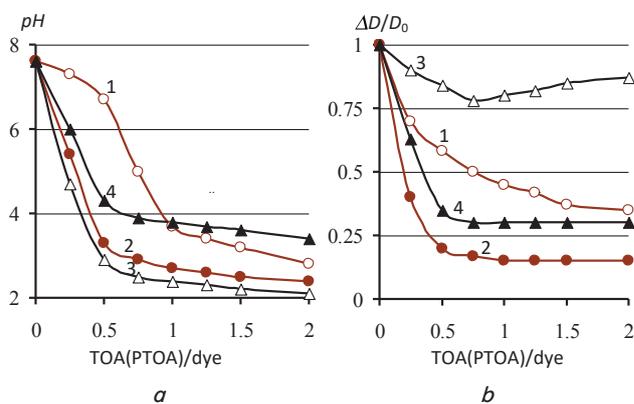


Fig. 2. Dependence of pH of the solutions of dyes K345 (1, 2) and BD (3, 4) and their relative optical density  $\Delta D/D_0$  on the ratio dye/TOA (1, 3) and the ratio dye/PTOA (2, 4): *a* – pH index; *b* – optical density

It should be noted that when we combine 0.2 M of the solutions of TOA and PTOA with pH 0.85 and 2.1, respectively, with the dye, pH decreases to a lesser extent in the case of the dye K345 when interacting with TOA, especially at pH 4.0. At the same time, pH of the solution of the dye BD is more sensitive to the TOA action. An intermediate position is taken by the curve of dependence of pH of the dye K345 on the PTOA content in the system. When further increasing the content of chromium compounds in the system, the nature of change in pH may indicate less effective interaction between the dye BD and PTOA.

The interaction between azo dye and titanium compounds is revealed by the results of observation of optical density at the change in composition of their solutions after combining the components (Fig. 2, *b*). With an increase in titanium compounds in the solution of dye to the ratio 0.5–0.75, there is a reduction in specific optical density of the working solution. In this case, this effect is expressed to a larger degree for the system PTOA/azo dye K345. After a sharp change in optical density, the intensity of this effect is significantly reduced except for the solution TOA/BD. Inflection point on the curves of dependences of optical density on the composition of the system titanium compounds-dye and adequacy of the dependences may indicate the interaction between their components, defined by their chemical structure.

Chemical activity of the anionic dyes and their products of interaction with titanium compounds also occurs when interacting with a hydrophilic adsorbent of protein nature – structured collagen fibers with the groups of basic character that are available for interaction. Results of the sorption of anionic dyes on CF are demonstrated in Fig. 3. In accordance with the Fick's law [17], the kinetic dependences received demonstrate their conformity with the curves of kinetics of the type III sorption and the absence of induction period in the course of sorption of anionic dyes on CF. As demonstrated by the obtained data (Fig. 3, *a*), the dye K345 is absorbed more effectively on the surface of particles of CF

compared with the BD, and practically does not depend on the temperature of the process.

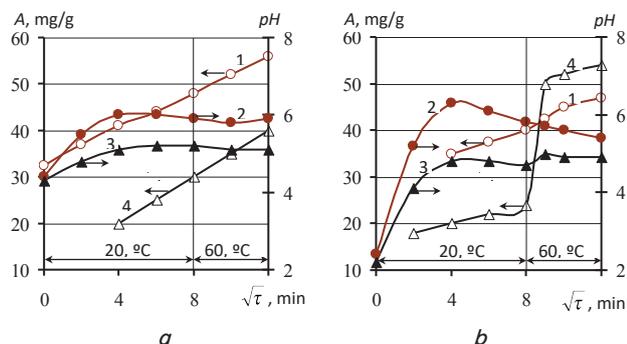


Fig. 3. Kinetics of sorption (1, 4) of the dyes K345 (1, 2) and BD (3, 4) on CF and change in pH of their solutions (2, 3) in the interaction of the components: *a* – without TOA; *b* – in the presence of TOA

In the course of the sorption of dyes on CF, the system's pH at the start of the process of sorption increases to a larger extent for the dye K345 for 30 min. with its consequent practical stabilization. The absence of induction period and temperature dependence of sorption of the examined dyes on CF may indicate an insignificant role of the diffusion mechanism of the process and the availability of functional groups of its surface particles for the interaction with molecules of the dye.

The results of the sorption of anionic dyes in the system colorant–titanium compounds–CF (Fig. 3, *b*) indicate that the modified dye is sorbed less effectively compared with the original dye at 20 °C. When the temperature increases to 60 °C, there is a sharp increase in the sorption of the dye BD that exceeds the sorption of the dye K345. It should be noted that pH of the solutions of both dyes during 30 minutes of interaction significantly increases and reaches 5–6 at the subsequent stabilization.

Thus, titanium compounds significantly affect the sorption of anionic dyes on the hide powder, especially so while increasing temperature of the process up to 60 °C.

### 6. Technology of dyeing a leather semi-finished product using ammonium sulfate titanylate

Given an active interaction of azo dyes with titanium compounds and collagen fibers, the important role of pH and temperature of the medium, further on for the development of technology of dyeing a leather semi-finished product of chrome tanning, we used the industrial product ammonium sulfate titanylate and the azo dye ABD, which differs from the dye BD by a lower molecular weight and less concentration of azo- and amino groups.

To determine the optimum ratio of AST/dye in the process of dyeing a semi-finished product, we conducted research into the influence of this ratio to the depth of diffusion into gel of gelatin. As the results we obtained demonstrate (Fig. 4), the depth of diffusion increases with the increasing concentration of the dye and the ratio of AST/dye. Moreover, if, at the concentration of the dye 16 g/dm<sup>3</sup>, maximum value is reached in the range of ratios 1:10–1:2.5, then with increasing concentration of the dye, a maximum is achieved at the ratio of 1:5.

For the simulation of technological process of dyeing a leather semi-finished product, we carried out research into

the sorption of the azo dye ABD on CF at its modification with a mixture of dispersions of polymers depending on the stage of introduction of AST into the sorption system (Table 1).

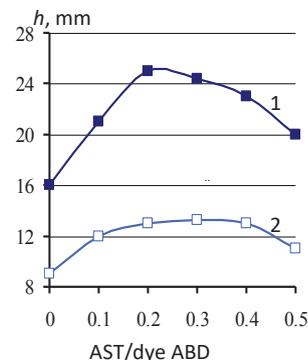


Fig. 4. Dependence of diffusion depth of dye into the gel of gelatin on the ratio of AST/ABD and concentration of the dye, g/dm<sup>3</sup>: 1 – 16, 2 – 80

Table 1

Sorption of the dye ABD on collagen fibers at the ratio of AST/dye 1:5 and concentration of structured protein in the system at 6 %

Variant	Stage of AST introduction	Sorption of dye, %	Chemisorbed dye, %	pH	T <sub>hst</sub> , °C
1	Without AST	81,0	36,0	5,1	78,0
2	Modification of MDP – before	97,0	52,0	3,8	81,0
3	– after	99,0	79,0	3,6	83,0

As demonstrated by the obtained results (Table 1), the sorption of dye significantly increases in the presence of AST. In this case, chemisorption of an azo dye particularly intensively increases when adding AST after the modification of collagen with MDP. If, while adding AST before the modification of collagen, the chemisorption of dye by collagen fibers increases by 44 %, then after its modification – by 120 %, which indicates a fixative role of AST in the process of sorption the dye into the structure of collagen. This is confirmed by the increase in temperature of hydrothermal stability of CF by 5 °C compared with the variant of treatment without using AST. In this case, pH of the system is reduced by 1.5 units. Thus, the effectiveness of sorption interaction between a dye and collagen significantly increases after its modification with MDP.

A study of the process of coloring with the dye ABD of a leather semi-finished product using AST was carried out according to the technology for coloring and greasing processes at the PAT “Vozko” (Ukraine). With this purpose, in a moving device at constant rotation, the semi-finished product was neutralized by formate and sodium bicarbonate, washed, filled with acrylic polymers and dyed at the consumption of the dye ABD at 4 % by weight of the semi-finished product, the ratio of water/semi-finished product – 0.5 and temperature of 18–22 °C. After that, the ratio of water/semi-finished product was increased to 1.5 and, at 60 °C, the emulsion of greasing material was added. Then in 40 min. the solution of AST was dozed as 0.4–1.6 % by weight of the semi-finished product and the system was stirred for 30 min. more. The obtained samples of the semi-finished product after washing at

18–20 °C were dried and exposed to mechanical treatment in a stretching-vibration machine.

According to the control technology, a semi-finished product after the filling-dyeing-greasing process was to be exposed to the final dyeing with the consumption of dye at 1 % and dry chrome tanner at 4 % by the weight of the semi-finished product, the ratio of water/semi-finished product 1.5 and temperature of 38–42 °C. Total duration of treatment is 60 min.

Results of the conducted studies of the process of dyeing a semi-finished product of chrome tanning using the dye ABD and the fixative AST, obtained under conditions of laboratory and research workshop at the PAT "Vozko" (Ukraine), are displayed in Table 2. High saturation of coloration of both obverse surface and flesh side of the hide of the semi-finished product is achieved at the consumption of 0.6 % of AST by weight of the semi-finished product. In this case, the values of coloring saturation of the semi-finished product's surface exceeded control samples by 2.1–2.9 %. Compared with the control variant of the technology, we achieved saving of 1 % of azo dye and 5-fold decrease in the mass of AST as a dye fixative instead of chromium compounds at its interaction with collagen.

Table 2

Coloring saturation of the surface of a leather semi-finished product, stabilized by ammonium sulfate titanylate

Semi-finished product side	Consumption of AST, % by weight of pressed-out semi-finished product				Control technology at the PAT "Vozko"
	0,4	0,6	1,0	1,6	
papillary	96,5 –	97,2 97,7	96,9 96,3	96,2 –	96,0 94,8
flesh side of the hide	96,1 –	97,8 97,2	96,8 96,9	95,8 –	95,5 95,1

Note: numerator and denominator display the data of laboratory and industrial tests, respectively

To determine optimal conditions for performing a comprehensive process of filling-dyeing-greasing process of a chrome-tanned semi-finished product, we conducted appropriate research under conditions of experimental workshop at the PAT "Chinbar" (Ukraine). It should be noted that the experiments were carried out taking into account previous studies with the use of AST at the stage of fixation of the anionic dye after greasing a semi-finished product by the technology of PAT "Vozko" (Ukraine) by reducing the consumption of azo dye and excluding the compounds of chromium as a dye fixative according to the control technology. As demonstrated by the results given in Table 3, the effectiveness of dyeing a semi-finished product by its coloristic characteristics increases with an increase in the content of AST in the working solution and reaches maximum value at the ratio of AST/dye 1:5–1:2.5. At the same time, the resulting material displays a tendency towards certain enhancement of mechanical indicators.

Thus, by the set of physic-chemical properties, the resulting dyed leather semi-finished product in line with the examined technology with the use of AST meets the requirements of DSTU 3115-95 on elastic leather materials for garments.

Therefore, the designed technology of comprehensive dyeing-greasing-filling of a chrome tanned leather semi-finished product in the manufacture of elastic leather materials

implies the use of ammonium sulfate titanylate for fixing acidic and direct azo dyes in the structure of a semi-finished product. In this case, ecologically harmful chromium compounds are excluded and the consumption of dye significantly decreases compared to the industrial technology. The quality of leather material, obtained by the developed technology, meets the Ukrainian standard on elastic leather raw materials from horned cattle.

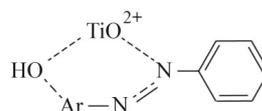
Table 3

Coloristic and mechanical properties of the dyed leather semi-finished product

Consumption of AST, % by weight of the dye	Ratio AST/ABD, mol/mol	Coloration stability, points, to			$\sigma_p$ , MPa	$\epsilon_p$ , %	R, sN
		wear		light			
		dry	wet				
0	0	3	2	3	18,9	59,0	24,0
5	1:10	4	3	3	19,1	59,0	24,0
10	1:5	5	4–5	4	19,3	58,0	25,0
20	1:2,5	5	5	5	19,7	57,0	26,0
25	1:2,0	5	5	5	20,0	55,0	28,0

## 7. Peculiarities of interaction in the system of azo dye-titanium compounds-dermis collagen

An analysis of results of the interaction between azo dyes and titanium compounds may indicate the formation of molecular and hetero molecular associates of dye-TOA (PTOA) involving the ionized auxochrome groups of the basic and acidic nature of the dye. A stronger interaction between the azo dye K345 and TOA and PTOA may be caused by the participation of phenolic hydroxyl groups of this dye and the ionized azo group in the range of pH 3.9–2.2 in the formation of chelate compounds with ions  $TiO^{2+}$  similarly to  $Ti^{4+}$  [18] according to scheme:



Less active interaction between the azo dye BD and PTOA is largely due to the presence in its molecule of hydrophobic radical and of less active HO-group of naphthenic ring. In this case, minimum values of optical density of the system titanium compound/azo dye predetermines, at their ratio 0,5/1,0, a decrease in electron density of the conjugated bonds of azo groups of molecules of the dye.

Results of the sorption of azo dyes on the structured collagen fibers by chromium compounds (III) indicate the formation of bonds between the ionized sulphate groups of azo dyes and amino- and imino-groups of protein fibers. In this case, carboxylic groups of CF are coordinated in the complex compounds of chromium (III).

In the process of sorption of dyes of CF, significant role is played by the process of aggregating their molecules. Less active interaction of azo dyes in the presence of TOA might be due to the greater degree of aggregation of molecules of the azo dye BD and, accordingly, its less participation in the sorption interaction between its molecules and CF. With an increase in the temperature of medium up to 60 °C, the degree of aggregation of the azo dye BD sharply decreases

compared with the azo dye K345 and its sorption significantly increases. As a result of this, a product of the interaction between a dye and TOA in the structured CF is sorbed more intensively.

A study of diffusion process of the acidic azo dye ABD modified with ammonium sulfate titanate into the gel of gelatin that models the structure of dermis collagen of a semi-finished product indicates the possibility to regulate the process of dyeing. Kinetics of the process of gelatin coloration with a dye of lower molecular weight is due to the existence in the system of two processes associated with the interaction of AST/azo dye and reduction in chemical activity of auxochrome groups of the dye that helps its diffusion into the gel of gelatin. After the deactivation of these groups, the interaction between gelatin and AST increases, leading to its additional structuring as a result of which the diffusion of the modified azo dye slows down. This effect is more pronounced when using a dye solution of higher concentration.

The use of the model system of dermis collagen in the form of collagen fibers in the sorption of the modified azo dye ABD made it possible to reveal their participation in the interaction with CF. An increased sorption of the dye by CF after its modification with AST and their treatment by acrylic polymers may indicate active collagen participation in the dye sorption, especially in the presence of AST. A role of the interaction of modified dye during its sorption by CF in the presence of dispersions of acrylic polymers manifests itself especially vividly by the magnitudes of chemisorption, which reaches maximum value in the case of treatment of CF with polymer dispersion. An increase in the chemical activity of the modified dye to collagen can be explained by the formation of complex compounds [19] with active collagen groups at pH 3.6–3.8. This is evidenced by an increase in hydrothermal stability of the dyed dermis collagen. An increase in the concentration of groups, active to the dye, in the system of dermis collagen-acrylic polymers-modified dye predetermines further increase in chemisorption of the azo dye ABD. The use of such a dye in the technological process of dyeing a leather semi-finished product provides for high saturation of the tone of coloring of its surface, as well as resistance to wear and light.

Thus, for the volumetric interaction between a collagen material, structured by compounds of chromium (III), and azo dyes using, as a fixative agent, titanium compounds in the sorption interaction of components, it is necessary to perform the process of dyeing after filling a semi-finished product. In this case, ammonium sulfate titanate is expedient to introduce to the system after the treatment of a leather semi-finished product and increase in the temperature of medium up to 60 °C.

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## 8. Discussion of results of research into the process of dyeing a leather semi-finished product

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As a result of a comprehensive study of the interaction between azo dyes with different chemical composition and titanium compounds in the process of their sorption by collagen fibers, we established a dependence of this process on the chemical composition. In this case, the sorption capacity of azo dyes increases during their interaction with titanium compounds. A study of the interaction between ammonium sulfate titanate and an azo dye during its diffusion into the model system of dermis collagen, the gel of gelatin, revealed

a special role of titanium compounds, which manifests itself in its additional structuring. It should be noted that chemisorption of an azo dye when interacting with AST is intensified after treating the collagen fibers with a mixture of acrylic polymers, which formed the basis for a more efficient conducting of the process of dyeing a leather semi-finished product after its filling. It provided for the possibility to use AST as a fixative for azo dyes at the final stage of a comprehensive process of filling-dyeing-greasing a leather semi-finished product.

Under optimal conditions of the technological process, when using azo dye of acid type, one achieves a volumetric dyeing of dermis with high saturation of the coloration of the upper surface, resistance to wear and light upon the interaction with ammonium sulfate titanate. Compared with the control technology, which implies a final dyeing with the use of chromium compounds, the developed technology excludes this harmful reagent and azo dye. This technology makes it possible to achieve a uniform coloring of the surface of a semi-finished product. In turn, this enables us to form leather with a thin polymer coating of aniline finish that highlights natural pattern of the front surface, characteristic of a certain type of leather raw materials.

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## 9. Conclusions

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1. We explored physical and chemical properties of the working solutions of azo dyes modified by titanium compounds of different chemical composition. A more energetic interaction was established between the brown azo dye 345, the molecules of which contain phenolic group, and titanium compounds with possible formation of chelate compounds.

2. A study of kinetics of the sorption of azo dyes by collagen fibers, structured by the compounds of chromium, revealed a significant dependence of sorption of the dye, the molecules of which contain less auxochrome  $-SO_3Na$ -groups, on temperature in the presence of titanate oxalic acid. In this case, absolute values of the sorption of a dye at temperature of 20 °C are two times lower compared to the brown dye 345. With increasing concentration of the dye with a lower molecular weight, acidic blue-black, modified by ammonium sulfate titanate, its diffusion capacity into the gel of gelatin is reduced by two times with an increase in concentration to 80 g/dm<sup>3</sup>. An increase in the concentration of dye in the system is symbiotic to an increase in the activity of its interaction with collagen, accompanied by reduced diffusion capacity into the gel of gelatin. It was found that filling a semi-finished product of chrome tanning with acrylic polymers contributes to the increase in chemisorption of azo dye when using ammonium sulfate titanate by 1.5 times.

3. The effect of the composition of dyeing solution on the coloristic properties of a filled semi-finished product was demonstrated when fixating the dye on its surface by ammonium sulfate titanate. We determined optimal ratio of ammonium sulfate titanate and a dye, which ensures the formation of leather material with a higher saturation of coloration of the surface of a semi-finished product by 2.1–2.9 %, maximum resistance to wear and light fastness in comparison with the control technology. The designed technology of comprehensive filling-dyeing-greasing makes it possible to reduce the consumption of azo dye, exclude at the final stage of dyeing additional consumption of a dye and environmentally harmful compounds of chromium by the

use of ammonium sulfate titanilate as a fixative of dye with a 5-fold saving of reagent. Elastic leather material formed by the developed technology complies with the interstate stan-

dard on leather for the upper part of shoes "GOST 939-88" and meets requirements of the ISO 9001:2008 international standard of quality management systems.

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