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CHAPTER 2

NANOPIGMENTS AND POLYMER-MINERAL DECORATION OF NATURAL LEATHERS

ABSTRACT

The work is devoted to the development of nanopigments based on modified montmorillonite for the formation of polymer-mineral decoration of natural leather.

The covering takes the main place among the processes of manufacturing natural leather and provides the leather with high operational and aesthetic properties. A promising direction of resource-saving and ecological leather production is the development of nanopigments on a mineral basis – modified montmorillonite, and their use for polymer-mineral finishing of leather.

An algorithm for obtaining nanopigments by successive modification of aqueous dispersions of montmorillonite with cationically active and anionically active compounds is proposed. Dispersion of montmorillonite particles with sodium carbonate and modification with hydroxochromic complexes provides a change in surface chemistry and is accompanied by structural transformations of the mineral. A high level of adsorption of anionic black and dark green dyes on the surface of particles of modified montmorillonite was established. The formation of chemical and physicochemical interactions between the dye and exchangeable cations of montmorillonite has been proven. The composition of nanopigments based on colored dispersions of montmorillonite, which are characterized by high hiding power and stability over time, has been developed.

The influence of nanopigments at a consumption of 1.5–2.0 % of montmorillonite on the physical and mechanical properties of polymer films was established, which was confirmed by a three-fold increase in the modulus of elasticity and strength limit, as well as a decrease by 11.5 % in elongation at break for polymer films. The increase in the physical and mechanical properties of polymer films is the result of physical adsorption and is associated with the formation of relatively strong coordination bonds of the polymer with the active functional centers of the montmorillonite surfaces. The mineral in the composition of nanopigments increases the physical and mechanical properties of covering films, plasticizes and structures the polymer composition, contributes to the production of leathers with high organoleptic characteristics of the front surface, namely, the volume of the network, graininess, pleasant fingerboard.

Using the method of simplex-lattice planning, the composition of covering compositions was optimized using nanopigments, rational ratios of the components of the covering composition were obtained, which ensure the formation of a polymer-mineral covering with the required level of operational properties, which is characterized by high adhesion to the leather, resistance to dry and wet friction, elasticity and strength.

The use of nanopigments in the composition of covering compositions allows to reduce the cost of covering paint for decoration, the thickness of the covering film and obtain a covering with high quality indicators in terms of the level of adhesion to dry and wet leather, resistance of the covering to repeated bending, dry and wet friction.

KEYWORDS

Leather, montmorillonite, modification, anionic dyes, nanopigment, polymer film former, polymer-mineral covering, decoration, covering compositions, quality, properties, composition optimization.

The modern assortment of leather materials, which are widely used for the manufacture of shoes, clothes, haberdashery, furniture, and interior upholstery of cars and airplanes, includes natural leather – face with covering decoration and pile. Depending on the quality of the front surface of the leather, it can be made with a natural front surface by covering it by applying a thin protective polymer film, sometimes transparent and colorless. However, the presence of defects on the front surface requires partial polishing of the front surface, the formation of a multi-layer colored covering and the production of leathers with an artificial front surface, the share of which is almost 60 % of the total output.

Finishing takes the main place among the processes of manufacturing natural leather and provides the leather with high aesthetic properties: uniform color over the entire area, good appearance, gloss or matte covering, a variety of imaginative combinations of several shades of colors. Also, the leather acquires the necessary operational properties: high adhesion of the covering to the leather, resistance to dry and wet friction, to stretching, to multiple bends, to the action of water, light, high and low temperatures, organic solvents used during chemical cleaning. Hygienic properties are also extremely important: vapor and air permeability of the leather and covering film.

The covering, which is applied to decorate the front surface of the leather in the form of a covering composition, has a composition: a polymer film former that forms a covering film; pigment concentrate or pigment that colors the covering film in the required color; wax emulsion, which gives the covering gloss and hydrophobicity; plasticizer to reduce the stiffness of the covering film or increase frost resistance; a dispersant or emulsifier that stabilizes the covering composition. The largest mass fraction in the covering composition belongs to the film-former (50–60 wt. parts) and pigment or pigment concentrate (10–15 wt. parts), which determines their crucial importance for the formation of a high-quality covering finish on the leather.

The range of polymer film-formers for covering leathers is quite wide and includes polyurethane, polyacrylate, nitrocellulose, and a mixture of film-formers of different nature is used to ensure sufficient operational properties of leathers.

To give the necessary color or shade to natural leather, pigment concentrates are used, which contain a pigment, a binder or thickener, a dispersant, a plasticizer, an antiseptic, and a solvent. Among the binders, the most common are casein, methylcellulose, or synthetic acrylic thickeners. In the case of manufacturing casein pigment concentrates, phenolic antiseptics are used to extend their shelf life.

Modern requirements for leather products due to changes in fashion trends and design solutions require constant and rapid updating of the range of leather, which is ensured by finishing the front surface in a wide color spectrum, forming a multi-colored covering with complex effects of embossing, cutting or imitating various textures.

Providing the required color or shade is the most difficult task for leather production, since the color range of existing pigment concentrates is quite limited, which is due to the complexity of their production and chemical basis. This situation is complicated by the fact that food protein – casein is mainly used as a binder to obtain pigment concentrate. Casein pigment concentrate has a number of disadvantages – low aggregative stability during storage, low covering ability, rots without an antiseptic, is characterized by a narrow range of colors.

A promising direction of resource-saving and ecological finishing of leather is obtaining nanopigments on a mineral basis – modified montmorillonite, and using them for finishing leather. The unlimited amount of the mineral in Ukraine, the ability of montmorillonite dispersions to be modified will make it possible to obtain environmentally friendly nanopigments of a wide color range, saturated color with improved technological properties (strength, elasticity, covering ability), and will also allow to exclude casein pigment concentrates and other auxiliary substances from the composition of covering compositions substances. The high dispersity of montmorillonite, the ability to thixotropy will lead to obtaining nanopigments stable over time, and the use of a mineral base in the covering composition will contribute to the structuring of the polymer and the improvement of the operational properties of the covering for leather.

Therefore, the development of nanopigments and parameters of polymer decoration of natural leather with their application is an urgent task.

The aim of this study is the development and application of nanopigments based on modified montmorillonite for polymeric leather decoration.

The object of the study is the modification of montmorillonite to obtain nanopigments and the parameters of their application for polymer finishing of leather.

The subject is the properties of nanopigments based on modified montmorillonite and the quality indicators of leather with a polymer finish.

To achieve this aim, the following objectives have been set:

– to investigate the effect of gradual modification of montmorillonite with compounds of anionic and cationic nature on the change in the structural properties of the mineral;

– to investigate the nature of the interaction of modified montmorillonite with anionic dyes, develop the composition and evaluate the properties of the nanopigment;

– to establish the influence of the mineral component on the formation of the structure of the polymer matrix for leather decoration;

– to establish the parameters of polymer structuring with nanopigment, physico-mechanical and chemical properties of covering compositions for finishing leather;

– to optimize the composition of the covering composition for decoration;

– to investigate the physical and mechanical properties and quality of leather covering.

2.1 INNOVATIVE MATERIALS AND TECHNOLOGIES FOR FINISHING NATURAL LEATHER

Leather production is an important component in the structure of the light industry of the countries of the world. In Ukraine, the light industry includes more than 10,000 enterprises, of which 1,500 specialize in the production of leather materials and leather shoes [1].

In the conditions of the war in Ukraine, caused by the aggression of the occupying country, the loss of a significant share of domestic and foreign markets is observed, the problem of stable activity of national product manufacturers, in particular leather and footwear production, is worsening. Today, one of the most important tasks of the state is the support of industrial production, domestic and foreign markets of light industry products [2].

The study of global prospects for the development of the leather industry and the production of multi-functional leather goods revealed a wide interrelationship between the projected dynamics of the development of raw materials and the technological support of leather production, taking into account the environmental and economic policies of the international environment.

According to the analysis of indicators of Ukraine's foreign trade activity for hides of various finishing methods [1], it was established that the main share of imports and exports of both the world and Ukraine is provided by hides with a natural surface (**Table 2.1**).

Table 2.1 The share of finished leather of various types of decoration in the world in 2022

Leather	**Cost, million USD**		**Share, %**	
	export	**import**	**export**	**import**
1	**2**	**3**	**4**	**5**
In general, all types of leathers	18091.6	18870.6	–	–
Hides from raw cattle				
additionally processed after tanning	8226.4	7872.2	45.47	41.72
with a natural front surface (whole)	3191.4	2760.7	17.64	14.63
with natural front surface (halves)	2126.4	2093.8	11.75	11.10

Continuation of Table 2.1

1	2	3	4	5
with a polished front surface	1609.5	1375.6	8.90	7.29
Other				
Goat, pig, reptile and antelope leathers, additionally processed after tanning	831.9	775.9	4.60	4.11
Sheep leathers treated after tanning	596.3	532.9	3.30	2.82
Suede, including combined suede	423.1	352.41	2.34	1.87

The share of world imports for leathers with a configuration in the form of whole leathers with a natural front surface is much smaller than the corresponding indicator for half leathers. Indicators of foreign trade activity of Ukraine point to the 7th place in the world import for hides with a natural front surface and halves, and only 20 for polished hides. The total volume of exports for hides with a natural front surface (whole and halves) significantly outweighs imports (**Table 2.2**).

Table 2.2 Ranking of importing countries in the world

Leather					
with a natural front surface (whole)		**with natural front surface (halves)**		**with polished front surface (not whole)**	
Importing country	**Cost, million USD**	**Importing country**	**Cost, million USD**	**Importing country**	**Cost, million USD**
World	2760.7	World	2093.8	World	1375.6
1. China	223.2	1. China	369.6	1. Vietnam	362.6
2. Italy	197.4	2. Vietnam	335.4	2. Indonesia	226.6
3. Mexico	174.3	3. Hong Kong, China	178.5	3. China	96.8
4. Vietnam	194.2	4. France	77.9	4. Thailand	84.7
5. Hong Kong, China	167.9	5. Italy	64.6	1. Italy	55.9
44. Ukraine	6.4	7. Ukraine	63.9	20. Ukraine	14.2

According to indicators of foreign trade activity, Ukraine ranked 17th in world exports in 2022 (**Table 2.3**) for leathers with a natural face surface, and for leathers with a natural face surface (whole) and polished leathers – only 47 and 48, respectively.

The share of export of polished hides is half as much as the total export volume of hides with a natural front surface (whole and half).

Table 2.3 Leading export countries in the world

Leather					
with a natural front surface (whole)		**with natural front surface (halves)**		**with polished front surface (not whole)**	
Exporting country	**Cost, million USD**	**Exporting country**	**Cost, million USD**	**Exporting country**	**Cost, million USD**
World	3191.4	World	2126.4	World	1609.5
1. Italy	1324.6	1. China	330.5	1. Thailand	401.9
2. Brazil	549.3	2. Italy	324.8	2. Italy	366.3
3. Austria	198.3	3. Republic of Korea	267.0	3. China	233.2
4. Germany	173.2	4. Hong Kong, China	190.2	4. Vietnam	131.9
5. Hong Kong, China	125.3	5. Brazil	121.9	5. India	77.2
47. Ukraine	1.0	17. Ukraine	30.2	48. Ukraine	0.6

This indicates the significant interest of the international community in leathers with a natural facial surface, which is due to their competitiveness and significant advantages in terms of functional and hygienic properties [1].

The formation of the quality of natural leathers of various finishes is determined by the choice and characteristics of leather raw materials, the intended purpose of the finished leathers and is ensured at the stages of the technological process [3], which include:

– stage of preparatory processes: formation of a capillary-porous structure of the dermis with a clear separation of intertwined collagen fibers with different sizes of structural elements;

– stage of tanning processes: fixation and stabilization of the collagen structure of the dermis;

– finishing stage: complex formation of the volume of the dermis, hygienic, aesthetic and operational properties of the leather.

To obtain high-quality leathers, it is important to achieve an optimal state of the dermis structure at each stage of technological processing.

In the preparatory processes, sufficiently aggressive chemical compounds are used, including alkalis, acids, inorganic salts, as well as enzymes. The use of such compounds is due to the need to prepare the structure of the dermis for the main tanning process. For this purpose, interfiber water-soluble substances, keratin-containing proteins, breakdown products of collagen, elastin, and reticulin, etc., are removed [3].

For tanning processes, multifunctional compounds are used to achieve interaction with the functional groups of collagen and ensure structure fixation: inorganic substances (basic salts of chromium, aluminum, iron, titanium, etc. [3, 4]), organic compounds of the fatty series (formaldehyde, glutaraldehyde, higher unsaturated fats, etc. [5]) and organic aromatics (benzoquinone, polynuclear sulfoaromatic acids, vegetable tannins, etc. [6]. After tanning, leather acquires resistance to various external influences and resistance to storage.

Finishing is liquid and covering. Liquid decoration is carried out to provide the leather with the necessary physical, mechanical and hygienic properties, and covering, to a greater extent, is aimed at the formation of aesthetic properties and the appropriate appearance [6].

The main finishing stage of leather production is covering dyeing. It consists in applying a colored and sometimes colorless covering film to the leather to give the surface a good appearance and protect it from external influences [3, 6, 7].

The essence of covering decoration consists in the formation of films of covering paints on the surface of the leather, which are applied in the form of thin layers of solutions or dispersions. After the solvents evaporate from the paint during the drying process, a thin polymer film is formed attached to the leather, that is, a covering that gives the leather color, covers minor facial defects, makes the leather resistant to water and dirt, and gives it a shine or matte finish.

There are several types of leather finishing, which differ in nature, composition, sequence and method of covering formation. The main types of decoration are: aniline, semi-aniline, emulsion [8, 9].

Aniline decoration consists in creating a very thin colorless or colored covering film on the leather, through which the natural lace of the leather is clearly visible. In order to achieve high adhesion, film formers are used that penetrate well into the dermis.

Semi-vanillin decoration is more common, because it involves the processing of an unevenly colored semi-finished product with minor facial defects. Semi-vanillin finish leathers have a natural lace, uniform two-tone color and aniline finish effect.

Emulsion finishing is performed for leathers with a natural or polished front surface with successive application of non-pigmented and pigmented primers, middle and fixing layers of the covering. Non-pigmented soil, which firmly binds to the surface of the leather, ensures the adhesion of subsequent layers of the covering and eliminates defects – wrinkles and swelling. The pigmented soil ensures complete and uniform coloring of the entire leather area, evens out micro-unevennesses and sanding streaks. The middle layer of the covering is created by applying covering paint on the primed surface of the leather. Hard film formers are used for the middle layers of the covering, as they must ensure the resistance of the covering to various deformations and the use of leather products; to the action of elevated temperatures; give the leather a beautiful appearance. The fixing layer increases the resistance of the covering to wet and dry friction, the action of water, elevated temperatures and organic solvents. Fixation of coverings, especially emulsion ones, is caused mainly by their thermoplasticity.

The covering paint includes the following components: film formers; pigments; plasticizers (for inelastic film formers); solvents and thinners; emulsifiers; dispersants and other auxiliary substances [7].

The basis of the covering are film formers that form a polymer film. Polymer materials that are used for modern covering decoration of the leather are divided into:

– polymerization or emulsion – dispersions of copolymers of acrylic acid derivatives [10];

– nitrocellulose – solutions of nitroenamel in organic solvents and nitrowater emulsions;

– polyurethane – solutions of polyurethanes in organic solvents and their aqueous dispersions.

Polymerization film formers or polyacrylates are polymers based on esters of acrylic $CH_2=CH\text{-}COOR$ methacrylic $CH_2=C(CH_3)\text{-}COOR$ acids, where $R=CH_3$; C_2H_5 and C_4H_9. The properties of polyacrylates change significantly depending on the ether radical R, the presence of free carboxyl groups and free acrylic acid in the polymer [7].

Polyacrylates have a number of advantages: they bond well with pigments, are compatible with other film-forming agents, can form colorless, transparent, very elastic, water- and light-resistant films with high adhesion to the leather and resistance to aging. However, polyacrylic films are thermoplastic and have low heat and frost resistance. As the temperature rises, they soften and become sticky. The films are also unstable to the action of organic solvents. In order to obtain high-quality covering films, it is necessary to add polymers to polyacrylates that expand the temperature range of elasticity.

Nitrocellulose film formers [7] are used very rarely today, mainly as nitro-water emulsions for fixing the covering.

Polyurethanes are modern polymers containing the group -NH-COO-. The advantages of polyurethane coverings are high wear resistance, resistance to water and organic solvents, good gloss, appearance, high adhesion, good compatibility with other film formers.

Polyacrylates and polyurethanes are the most widely used today [11]. Polyurethane film formers provide high resistance to physical and mechanical loads, have sufficiently flexible chains and are easily modified. Given that polyurethanes are polar compounds, they show resistance to non-polar organic solvents, fat-containing materials. Polyacrylates are able to provide hardness, flexibility, resistance to organic solvents, gloss, etc. in the covering. They provide good water resistance to the covering, but do not provide high chemical and physical resistance.

Pigments or pigment concentrates are an important component of covering finishing compositions [12]. Pigments provide a specific color. Pigments are white or colored highly dispersed substances of organic or mineral origin, insoluble in water and film formers. A characteristic property of pigments is covering ability – the ability to cover the color of the painted surface, that is, to make it invisible [13]. Depending on the pigment content, the covering of hides is divided into three types [11]: aniline – a transparent covering without the use of pigments; semi-aniline – characterized by a small content of pigments to provide, mainly, a shade; and pigmented – with a significant content of pigments for complete covering of the facial leather surface with a colored layer [7].

Pigments in leather finishing provide the color and covering of the covering. Organic or inorganic pigments are used in the covering of hides. Organic pigments are characterized by a sufficiently large surface area, but during decoration they can complicate mechanical operations [12]. For the formation of the covering composition, it is necessary to dose a larger amount of binders, and the covering is characterized by low light resistance and heat resistance. At the same time, covering compositions with organic pigments differ in gloss and brightness of colors. Inorganic pigments create a high-quality covering with good light and water resistance, but are characterized by a high tendency to sedimentation and are limited in color and brightness [12].

To provide decorative effects, mixtures of pigments are usually used, which allows creating a wide color range of coverings. For this, pigments must be insoluble in water, organic solvents, plasticizers and wax emulsions to avoid migration with the subsequent change in color and lightfastness. The ability of the covering to form a uniform film that is stable over time, to form the required layer thickness depends on the properties of the pigment, the nature of their surface and the size of the particles.

Based on the size of the particles, all pigments are divided into transparent and covering. Transparent pigments include pigments whose particle size is smaller than the wavelength of light ($\lambda \leq 0.5\ \mu m$). In this case, most of the light that falls on the pigment layer is absorbed and only a small part is reflected. These pigments are used for aniline decoration. Covering pigments have optimal particle sizes of 0.8...1.5 microns [3].

To give the covering gloss or dullness, water resistance, leather-like texture and other properties, auxiliary substances are added: wax emulsions, casein, plasticizers, etc. Wax emulsions are designed to give the covering hydrophobic properties and prevent it from sticking to the hot plate when pressing the semi-finished product. Plasticizers are part of covering paints to lower their glass transition temperature. Dispersants wet the pigment during the preparation of pastes and ensure the stability of pigment particles in paints. Emulsifiers provide stability to the film-forming dispersion. Alkyl sulfates, alkyl aryl ethers, quaternary ammonium compounds are used as emulsifiers. Stabilizers are used for film-forming dispersions in order to prevent their premature coagulation.

This indicates the multicomponent nature of covering compositions and the complexity of their purposeful selection in order to form a high-quality finishing covering on the leather.

In general, the finishing of natural leathers provides the necessary resistance of leathers to mechanical loads, atmospheric phenomena and gives a good appearance. The correct choice of the film former, the selection of the pigment to give the color and stability of the covering paint, as well as the introduction of auxiliary plasticizing and stabilizing substances provides the optimal version of the covering composition, the main function of which is to achieve high adhesion of the covering to the surface of the leather, a uniform film, resistant to multiple folds and friction. Observance of all factors ensures effective finishing of leather and provision of the necessary quality indicators of natural leather.

Innovative approaches in the covering decoration of leather are mainly based on the creation of new film-forming agents and pigments, improvement of the composition of covering compositions, purposeful selection of film-forming agents, pigments and auxiliary substances, development of complex materials that would simplify the composition of the composition and ensure the formation of a covering with operational and aesthetic properties.

The creation of new film-forming materials is based on methods of chemical modification during the synthesis of polymers, in solutions, latexes, in the process of making mixtures, etc. When creating new or improving existing formulations for leather finishing, the fact that coverings based on polyacrylates and polyurethanes have good water resistance and resistance to wet friction, as well as vapor permeability is taken into account [14]. Aqueous dispersions of acrylurethane compositions are used due to the possibility of adjusting their colloidal chemical properties by changing concentrations and introducing auxiliary impurities. The combined use of acrylic dispersions and polyurethanes is promising in the production of elastic leathers. Synthesized polyurethane-acrylate film-forming compositions, depending on the molecular weight of the oligourethane component, can contribute to directed structural and chemical modification, which opens perspectives and opportunities for regulating the properties of materials based on them.

To improve covering compositions, their composition is optimized, components or the number of covering layers are changed, the film thickness is reduced, etc. In order to increase the effectiveness of covering painting, the use of structurally colored film formers based on acrylate derivatives is proposed [15]. But at the same time, questions arise regarding the low resistance of the resulting color to wet and dry friction, the tendency of the covering to age, the processes of dye migration to the surface of the covering, which requires additional fixing of the covering film. One of the ways to solve the above problems is to create colored polyurethanes. Colored polyurethanes are obtained by the interaction of polyol and organic diisocyanate in the presence of 0.1–5.0 % coloring agent – liquids or solids with a melting point of 48–226 °C [16].

Modern trends in covering painting are also aimed at the use of a rational method – compact decoration, the technology of which involves the use of the same composition for all layers of the covering composition [7]. For a compact decoration, the mixture of polymer dispersions should have universal properties: high curvature at a minimum film thickness, the ability to ensure its high adhesion to the leather while maintaining the elasticity of the covering in a wide temperature range.

A number of innovative developments have established the possibility of creating pigments or nanocomposites for covering leathers on a mineral basis, namely, on the basis of montmorillonite [17, 18]. The ecological and economical use of the mineral opens up the possibility of obtaining pigments of different colors, saturated colors and polymer-mineral nanocomposites with improved technological properties (heat resistance, elasticity, good hiding power) [18, 19]. The high dispersity of montmorillonite, the ability to thixotropy contributes to the production of hybrid pigments and time-stable polymer covering compositions based on them.

It is known [18] that an organic-inorganic pigment based on the mineral hydrocalcite and azo dyes is recommended for creating polymer composites as a filler or for providing a deep, intense color. Such a pigment is characterized by high thermal stability, which causes an increase in the resistance to flammability of coverings. Also, the combination of pigment with film formers helps to increase the physical and mechanical characteristics of the covering.

An increase in the brightness and intensity of color, resistance to atmospheric phenomena, high aggregative stability is characteristic of painted pigments based on clay. The authors note the characteristic phenomenon of pigment intercalation in the polymer covering and uniform distribution of nanoclay particles in the polymer medium [18].

The use of nanocomposites based on montmorillonite changes the rheological behavior of polymer systems. The dominant elasticity and high physical stability of the "polymer-nanocomposite" system becomes characteristic. The obtained nanocomposite polymer emulsions show a good film-forming ability and increase the elasticity of the covering during the decoration of the front surface of natural leathers for clothing. The authors note that using montmorillonite solves the problem of obtaining stable nanocomposite polymer dispersions of organically modified montmorillonite with latexes. The obtained nanocomposite latex is aggregatively stable and contributes to the formation of a thin covering due to the nano-sized characteristics of the mineral particles [19]. Nanocomposite latexes are electrostatically stable and provide increased temperature resistance to the covering.

It has been shown that pigments can be obtained by deposition on inorganic substrates (metal oxides or salts, clay) of acidic and direct fixatives [20]. The latter are cationic products obtained by condensation of primary amines (or mixtures of amines and phenols) with formaldehyde. The obtained pigments are resistant to the action of water, organic solvents and light, but are unstable to the action of alkali solutions. To increase the specified stability, substances obtained by alkylation of condensation products of primary, secondary or tertiary amines with formaldehyde are used as fixatives.

The synthesis of organobentonite pigments is known [21] by modifying natural bentonite minerals with cationic polyelectrolytes (salts of aminoformaldehyde resins, their N-methyl substituted) followed by deposition of water-soluble anionic (direct) dyes on the formed aminoorganominerals. The use of organobentonite pigments makes it possible to reduce the cost of the technology of obtaining pigments of saturated shades with high technological properties: high heat resistance and covering ability, lack of bronzing in acrylic coverings, etc. The high dispersion of organobentonite pigments and the ability to thixotropy make it possible to obtain aqueous pigment pastes that do not delaminate in the absence of a binding component.

Organobentonite pigment concentrate can also be obtained [21] by adsorption modification of aqueous silicate dispersion with aminated collagen hydrolyzate, followed by deposition of water-soluble organic dyes on the formed organobentonite. Montmorillonite modified with an aminated hydrolyzate has a higher affinity for dyes than its non-aminated counterpart. The dye itself is sorbed on the surface of the organomineral, while low molecular weight impurities remain in the filtrate. The high resistance of the coloring of the obtained pigments to the action of alkalis and alcohols is due to the penetration of the anion of the dye into the interlayer space of the organomineral. The resulting pigment concentrate does not contain a binding component, mixes well with the components of the covering composition, has high aggregative stability and covering ability. Physico-chemical properties of the covering film formed on the leather based on organobentonite concentrate meet regulatory requirements [22]. Finished leather has a pleasant neck, with the effect of additional filling of the face layer with a mineral that is part of the pigment concentrate.

In general, according to the analysis of scientific developments [7, 17–22] regarding the effectiveness of the use of montmorillonite in the covering of leather, it was found that by modifying montmorillonite with multifunctional substances, pigments can be obtained, which are characterized by nano-sized particles, brightness and color saturation, and a wide range of colors. As part of the polymer covering, montmorillonite will provide aggregative and electrostatic stability of the polymer system, it is able to improve the physical and mechanical properties of the resulting covering, and increase its heat resistance.

All of the above indicates the promising use of montmorillonite for the creation of nanopigments and improvement of the polymer-mineral decoration of leather.

2.2 NANO PIGMENTS-BASED ON MODIFIED MONTMORILLONITE

Montmorillonite (MMT) is the main mineral of bentonite clays. MMT belongs to the group of layered water silicates and is characterized by high dispersion and hydrophilicity, ability to sorption, ion exchange, etc. Given these properties, MMT is widely used in the light, chemical, pharmaceutical, textile, paper industries, oil and gas production, geological exploration, etc. [23].

According to the structure, MMT consists of two tetrahedral meshes and one octahedral mesh located between them (**Fig. 2.1**). All the vertices of the tetrahedra face the center of the structural layer and form a single layer with the hydroxyls of the octahedral mesh, in which oxygen atoms are located at the vertices shared by the tetrahedral and octahedral meshes, and hydroxyls are located at the vertices of the octahedra that are not connected to the tetrahedra – hydroxyls OH.

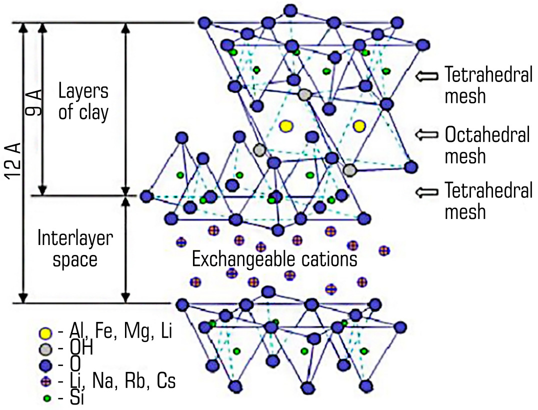


Fig. 2.1 Features of the montmorillonite structure

In the structure of montmorillonite packets, the oxygen surface of one layer contacts and interacts with the similar oxygen surface of the adjacent layer due to van der Waals forces, which indicates a weak connection between the layers. In this regard, molecules of water or other polar liquids can freely penetrate into the interstructural space and expand it. The basic basal distance between the layers in the montmorillonite lattice is a variable value and, depending on the number of water molecules or exchangeable cations, can vary from 0.96 nm in the dry state to 14.0 nm and more in the state of strong water saturation [24]. Given that MMT particles are highly aggregated in aqueous dispersions, and their surface is bifunctional, for purposeful application of the mineral, it is necessary to eliminate the electrical inhomogeneity of the surface and maximally disperse aggregates of particles in the dispersions, which will allow further modification of the MMT surface and give it the necessary properties.

The specified features of the MMT structure explain the possible variety of physico-chemical, colloidal-chemical, rheological and other properties of the mineral, which is manifested in the cation exchange capacity, specific surface area and particle size (**Table 2.4**).

Table 2.4 Basic physical and chemical characteristics of the research objects

Mineral	**Average particle size, (μm) [3, 6]**	**Exchange capacity, E, (mg-eq/100 g)**	**Specific surface area, S, (m^2/g) during adsorption**		**The value of the layer charge item/[Si_4O_{10}]**
			water	**methylene blue**	
Cherkasy montmorillonite	0.05–0.3	72	311	520	0.35

Bentonite clay – $Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O \cdot nH_2O$ (Dashukivske deposit, Cherkasy region, Ukraine) was used to obtain nanopigments. The main mineral of bentonite clay is montmorillonite, its content is 85±3 %. The value of the exchange capacity is 72 mg-eq/100 g of clay. Humidity – 27±3 %.

To obtain the most dispersed dispersions of montmorillonite, after cleaning and washing, the bentonite clay was transferred to the Na-form by introducing into the water dispersion of the mineral a concentration of 100 g/l of sodium carbonate with a consumption of 6 % or 10 % of sodium pyrophosphate based on the mass of the mineral.

To predict the change in the properties of montmorillonite as a result of modification, it is taken into account that there is a special van der Waals bond between neighboring structural elements, which is easily broken when polar molecules enter the interpacket space, causing a significant "swelling" of the lattice up to the complete rupture of individual packets. As a result, montmorillonite particles in water can disperse spontaneously, their number per volume unit increases significantly, and the number of direct contacts for further interactions also increases. In general, strong spatial coagulation structures are formed at a low concentration of the dispersed phase.

A manifestation of such transformations is a change in the number and size of the mineral particles in the volume, which is important for the creation of potential nanopigments for leather decoration. Under this condition, the size of the pigment particles should not be greater than the thickness of the covering formed on the front surface of the leather.

The analysis of studies on the distribution of montmorillonite dispersion particles by intensity, number, and volume after treatment with sodium carbonate and pyrophosphate is presented in **Fig. 2.2**. Aqueous dispersion of montmorillonite with a solid phase concentration in water of 100 g/l (**Fig. 2.2, a**) is characterized by a monomodal distribution of mineral aggregates in size, intensity, and volume. In the dispersion of native montmorillonite, there are mainly aggregates with sizes of 1678 nm, 2265.8 nm, and 3059.5 nm. The volume of the dispersed medium is 40 % filled with aggregates with a size of 2265.8 nm, and the number of particles in this volume is 60 % of the total number in the dispersion. As a result of adding to aqueous dispersions of montmorillonite sodium carbonate in the amount of 6.0 % (**Fig. 2.2, b**) or 10.0 % (**Fig. 2.2, c**) of sodium pyrophosphate based on the mass of the dry mineral, significant changes in the distribution of montmorillonite particles were established.

After processing montmorillonite with sodium carbonate, the largest number of mineral particles with sizes of 34.6–93.2 nm was found, which indicates the dispersion of montmorillonite aggregates into individual smaller particles. It was also found that the number of mineral particles with sizes in the range of 153.0–1826.9 nm increases in the volume, which indicates the polymodal nature of the dispersion of montmorillonite after treatment with sodium carbonate.

After treatment of the aqueous dispersion of montmorillonite with sodium pyrophosphate (**Fig. 2.2, c**), a higher level of dispersion of montmorillonite into particles with a size of 16.8–28.3 nm was found, however, a significant part of the volume is filled by larger particles with a size of 2375.7–2082.6 nm.

The revealed effect is possible due to the nature of four-charge phosphate anions. It is likely that nanosized particles in aqueous dispersions are prone to coagulation and clumping. Considering the idea of creating nanopigments based on montmorillonite, it is reasonable to obtain dispersions without coagulation or peptization effects.

A comparative analysis of the effect of sodium salts on the level of dispersion indicates the expediency of carrying out the first stage of modification of montmorillonite with sodium carbonate and obtaining a sodium-modified dispersion (MMT–Na^+). At the same time, this dispersion contains nano-sized particles with a significant number of contacts for further purposeful modification with hydrochromic complexes and obtaining a cationic form of montmorillonite, as a basis for creating colored dispersions of montmorillonite and, subsequently, nanopigments.

The basis of obtaining nanopigments is the idea of adsorption of anionic dyes on the surface of particles of modified cationic montmorillonite. To ensure a high level of adsorption of dyes on the surface of the mineral, it is important to achieve the maximum value of the positive charge of the latter, that is, to carry out cationization of the surface of montmorillonite particles or "recharging". As stated in the paper [25], the maximum effect of recharging the surface of the mineral can be achieved by superequivalent adsorption of multi-charged metal hydrox complexes (Al^{3+}, Fe^{3+}, Cr^{3+}, Zr^{4+}, Ti^{4+}) [26].

Cr (III) compounds are traditionally used in leather practice as tanning agents. They have the maximum tendency to complex formation with the formation of reactive polynuclear positively charged hydroxocomplexes, therefore they are able to ensure the production of stable cationic forms of montmorillonite in a certain pH range of 3.9–6.9.

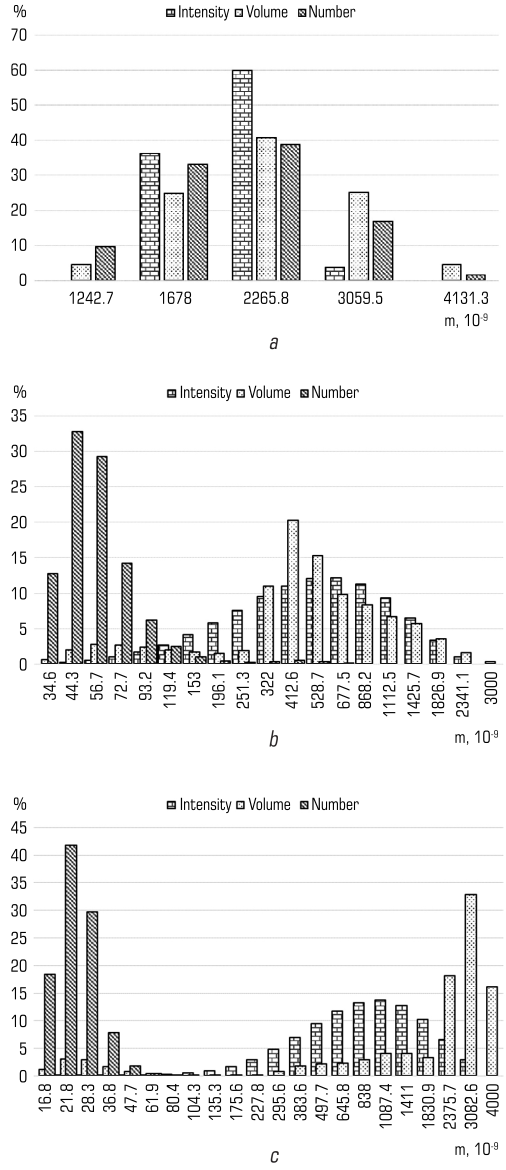


Fig. 2.2 Distribution of montmorillonite particles in an aqueous dispersion: *a* – native, *b* – modified with sodium carbonate, *c* – sodium pyrophosphate

To obtain the cationic form of montmorillonite, the expediency of using basic chromium (III) sulfate with a consumption of 10–12 % of the mineral mass has been proven [27]. Basic chromium sulfate was used for research – $Cr_2(SO_4)_n(OH)_{6-2n}$ (Kazakhstan), chromium (III) oxide content 25.6 %, basicity 33 %. To modify montmorillonite, a solution of basic chromium sulfate in the amount of 10.0–12.0 % of the mass of the mineral in terms of Cr_2O_3 was added to the Na-form dispersion. Mixing continued for 120 minutes until a homogeneous mass of gray color was obtained. The pH of the modified cationic montmorillonite dispersion was 4.3–4.5. Chromium-modified montmorillonite dispersion (MMT–Cr^{3+}) was obtained as a result of successive treatment of aqueous dispersion of montmorillonite with sodium carbonate and basic chromium (III) sulfate.

Modification of montmorillonite with basic chromium (III) sulfate is accompanied by changes in the mineral's surface chemistry and structure. According to the obtained diffractograms (**Fig. 2.3**), changes in the structure of the mineral were established after the replacement of native Ca^{2+} and Mg^{2+} ions of native montmorillonite with Na^+ and Cr^{3+} cations after successive treatment with sodium carbonate and chromium (III) compounds.

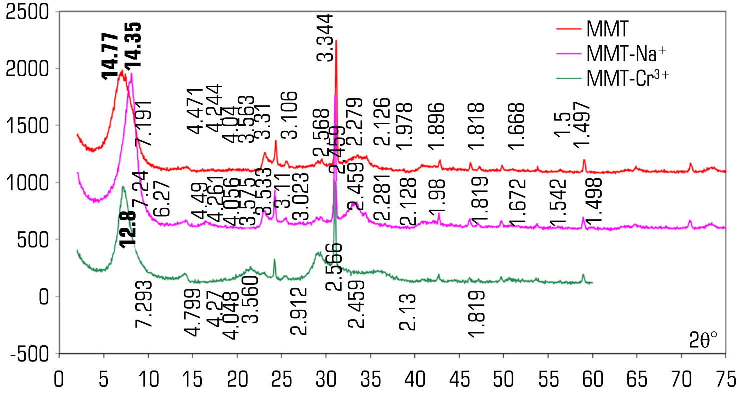


Fig. 2.3 Diffractograms of native and modified forms of montmorillonite

Taking into account that the value of the interplanar distance is determined as the difference between the value of d_{001} and the thickness of the elementary package of montmorillonite of 9.6 Å, it is established (**Table 2.5**) that the level of the indicator is 14.8 Å for native montmorillonite.

The replacement of exchangeable cations Ca^{2+} and Mg^{2+} of native montmorillonite with Na^+ cations in modified montmorillonite leads to a shift of the basal reflex to larger 2θ°-angles (**Fig. 2.3**) and a decrease in d_{001} to 12.8 Å (**Table 2.5**). The transformation of MMT–Na^+ into the form of MMT–Cr^{3+} is accompanied by a shift of the basal reflex toward smaller 2θ°-angles and a subsequent increase in the value of d_{001} to 14.4 Å. At the same time, the change in the diffraction pattern is caused by the different placement of chromium (III) complexes in the interlayer space of montmorillonite. This indicates structural changes in the mineral and is further confirmed by an increase in the specific surface area of montmorillonite (**Table 2.5**) from 60 to 280 m^2/g. The growth of chemical affinity and expansion of the interpacket space is a prerequisite for effective modification of the montmorillonite surface with anionic dyes.

Table 2.5 Indicators of structural changes of montmorillonite

Indicator	**A form of montmorillonite**		
	native	**MMT–Na$^+$**	**MMT–Cr^{3+}**
Value of basal interplanar distance d_{001} for native MMT, Å	14,8	12,8	14,4
Adsorption (specific) surface area of montmorillonite, m^2/g	60	160	280

A study of the surface chemistry of the modified MMT–Cr^{3+} revealed that in the pH range of 4.3–6.2 the surface of the mineral particles acquires the maximum positive charge (**Fig. 2.4**). Increasing the pH level above 7.0 contributes to the return of the anionic surface charge of the mineral particles, which is associated with the destruction of the chromium (III) complex [28].

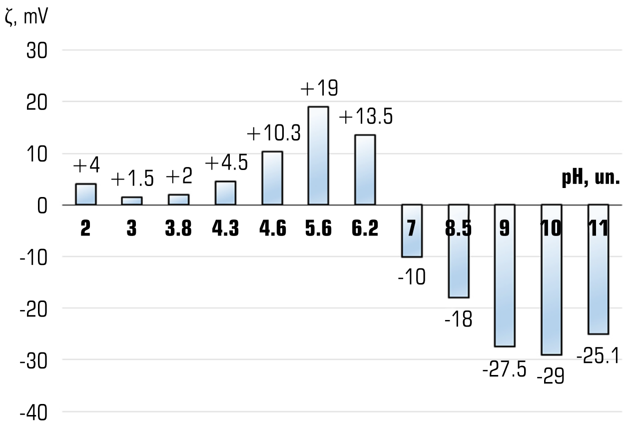


Fig. 2.4 Effect of pH on the ζ-potential of montmorillonite MMT-Cr^{3+}

Taking into account the fact that the composition of the nanopigment includes mineral and organic components, it is necessary to ensure the maximum fixation of the organic dye on the

MMT–Cr^{3+} surface. The presence of an unbound dye in the nanopigment will require the use of additional binding components in the preparation of the covering paint for finishing the leather, or will have a negative effect due to the migration of the dye to the surface of the covering film with its subsequent contamination. At the same time, an important condition is the achievement of high covering power of pigments without delamination as part of the covering composition for finishing the leather.

The key aspect of ensuring effective and complete adsorption of the anionic dye [29] on the surface of the MMT–Cr^{3+} dispersion is:

– the presence of a sufficiently long chain of conjugated bonds in the polarized dye molecule;

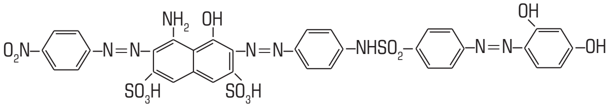
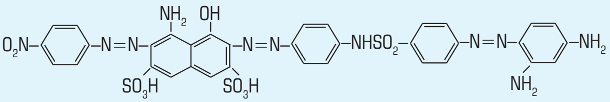
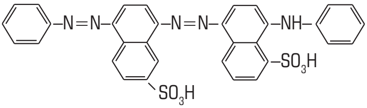
– linear and coplanar structure of the dye;

– the presence of substituents in the structure for a positive conjugation effect in dye molecules;

– the presence of active groups in dyes capable of forming a coordination bond with chromium compounds introduced into the montmorillonite dispersion for the purpose of cationization.

For adsorption on the cationic surface of montmorillonite, the most typical anionic dyes for leather production were used: anionic dark green; anionic black; anionic blue (**Table 2.6**). Anionic dyes or azo dyes are mono-, di-, or triazo compounds of a cyclic structure with active hydroxyl, amine, nitro, and sulfo groups. The dye molecule contains one or more azo groups -N=N- that bind two or more aromatic radicals.

Table 2.6 Physicochemical characteristics of dyes

Dye / molecular weight	Structural formula
Anionic dark green, Mr 863	
Anionic black, Mr 859	
Anionic blue Mr 637	

Quantitative assessment of the adsorption of anionic black, anionic blue, and anionic dark green dyes to MMT–Cr^{3+} [30, 31] is represented by isotherms of dye adsorption on the surface of modified montmorillonite (**Fig. 2.5**).

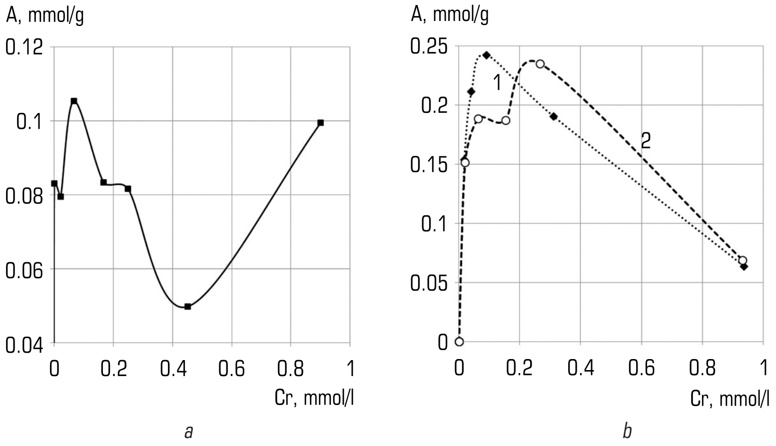


Fig. 2.5 Adsorption isotherm on MMT–Cr^{3+} dyes: *a* – anionic black, *b* – anionic dark green (curve 1) and anionic blue (curve 2)

It should be noted that the nature of adsorption for all dyes corresponds to the Langmuir curve. At the beginning, the curves are characterized by rapid growth, the dye molecules are adsorbed on the surface of the montmorillonite particles due to the electrostatic interaction of the chromium cation with the dye anion. Next, the peak of the curve is reached, the surface of the mineral is saturated with dye molecules and the surface charge of montmorillonite is neutralized. The interaction with montmorillonite is completed by polymolecular dye adsorption due to Vander-Waals forces [30, 31].

Comparison of adsorption isotherms of different dyes (**Fig. 2.5**) indicates the maximum adsorption of anionic dark green (**Fig. 2.5, b, curve 1**). Despite the fact that the adsorption of all dyes increases, the smallest adsorption maximum is observed for an anionic black dye (**Fig. 2.5, a**). This is explained by earlier micelle formation in anionic black solutions. It is steric complications that explain the fact of a lower level of adsorption of dyes from micellar solutions than from molecular solutions. But increasing the concentration of anionic black above 0.4 mmol/g causes rapid polymolecular adsorption, which is positive when obtaining a pigment [30, 31].

An increase in the concentration of anionic blue and anionic dark green dyes (**Fig. 2.5, b**) causes a further decrease in the dye adsorption level, which may be due to the predominant micelle formation.

It should be noted that for all the selected anionic dyes, it was established to obtain colored modified montmorillonite dispersions (MMT–AD) of saturated, intense color, especially in the case of using the anionic black dye.

In order to identify the optimal conditions for obtaining colored modified montmorillonite dispersions as nanopigments, the influence of pH of the environment on the efficiency of sorption of anionic dyes by the surface of modified montmorillonite was investigated [30, 31]. The presented data (**Fig. 2.6**) show that the maximum adsorption occurs in the range of pH 5–6.5, which is consistent with the data in **Fig. 2.6**.

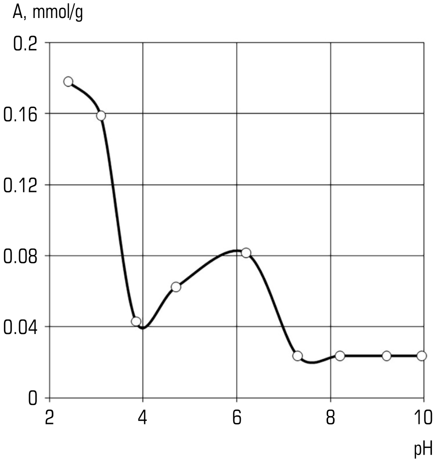


Fig. 2.6 Influence of medium pH on the level of adsorption of anionic black on MMT–Cr^{3+}

The high level of anionic black adsorption in the range of pH 2.0–4.0 is due to inhibition of the dissociation of acidic functional SO_3H– groups on the surface of MMT–Cr^{3+}, a sharp decrease in solubility and precipitation of the dye. The decrease in adsorption and its plateau when pH≥7 shifts to a more alkaline zone is associated with the transformation of the composition of chromium (III) complexes and the recharging of the montmorillonite surface from cationic to anionic, which indicates a change in the sign of the surface charge from positive to negative. On the positive side, it should be noted that the adsorption of anionic black on the surface of the cationic form of montmorillonite is stable within pH 3–10, while no desorption of the dye was detected.

Spectroscopic studies of MMT–Cr^{3+} revealed the following characteristic absorption bands, taking into account the fact that the studied silicate molecules contain hydroxyl groups, silicon oxide groups, and a chromium complex (**Fig. 2.7, 2.8**) [32].

The interpretation of the bands characteristic of silicates was carried out by isolating the characteristic bands associated with the vibrations of the Si-O group, which lies in the region of 1034 cm^{-1} and 798–779 cm^{-1}. In the spectra of the azo dye and MMT–Cr^{3+} there are bands of functional groups capable of forming hydrogen and van der Waals bonds between the dye and exchangeable cations of montmorillonite.

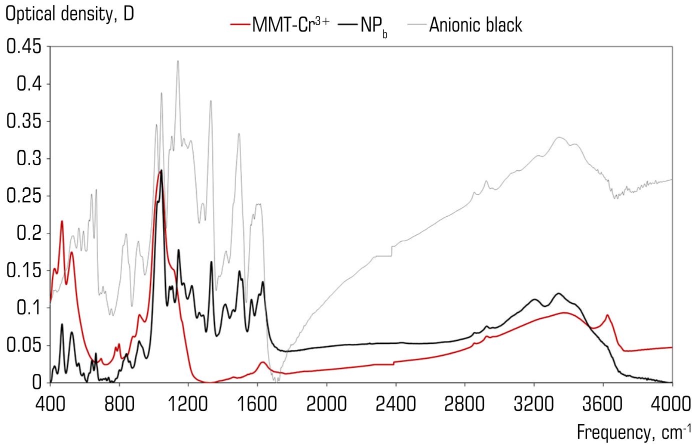


Fig. 2.7 Absorption spectra of MMT–Cr^{3+} montmorillonite, black nanopigment and anionic black dye

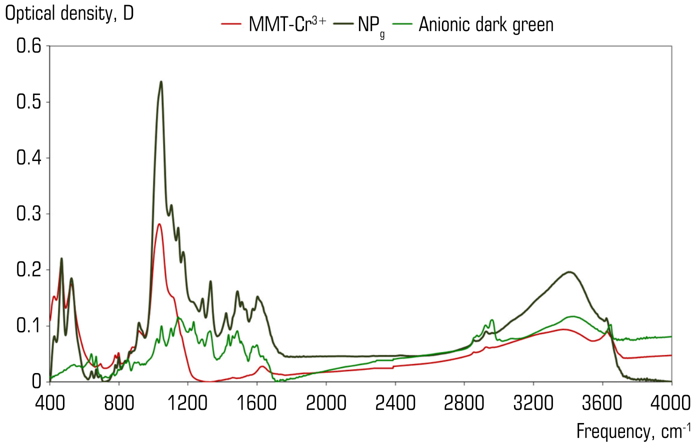


Fig. 2.8 Absorption spectra of MMT–Cr^{3+} montmorillonite, dark green nanopigment and anionic dark green dye

As can be seen from **Fig. 2.8**, a number of differences are observed in the spectra of the green nanopigment (NPg) compared to MMT–Cr^{3+}. Bands identical to the azo dye appear at 3621 cm^{-1}, 3401 cm^{-1} corresponding to bound hydroxyl groups, and a broad band at 3600–3100 cm^{-1} characteristic of hydroxyl groups of water of crystallization. There is also a shift of the 1629 cm^{-1} band to the lower frequency zone for the refinery, which characterizes the deformation oscillations of the H-O-H group, found in the spectrum of montmorillonite.

The appearance of a band in the region of 1510 cm^{-1}, and an increase and shift of the vibration bands at 1231 cm^{-1} and 1021 cm^{-1} to the low-frequency region by 60 and 100 cm^{-1}, respectively, as well as an increase in the intensity of the pigment concentrate bands at 1143 cm^{-1} and 1104 cm^{-1}, which are characteristic for the oscillation of the $-O-NO_2$, $-O-NH_2$, SO_3H groups, probably indicate van der Waals bonds between the indicated functional groups of the dye and the oxygen atom of montmorillonite.

To evaluate the interaction of azo dye and MMT–Cr^{3+}, a comparative analysis of the optical densities of the absorption bands of MMT–Cr^{3+} and NP (**Table 2.7**) was performed using the internal standard method. The band 2925 cm^{-1} was chosen as standard bands for frequencies 4000–2500 cm^{-1}, and 916 cm^{-1} for frequencies 1900–400 cm^{-1}, which are characteristic of valence and deformation vibrations of CH groups. Such changes in optical densities, as well as broadening and shifting of the corresponding bands on the NP spectra, indicate the formation of new bonds with the participation of functional groups of dyes and MMT–Cr^{3+}.

As can be seen from the **Table 2.7**, on the spectra of the black nanopigment (NPb) with an anionic black dye, mainly in the region of 1629–600 cm^{-1}, changes in the optical densities of the characteristic bands of the $-SO_3H$, $-ONO_2$, $-ONH_2$ groups are observed.

The amino group, one of the most reactive, is manifested at frequencies of 3339 cm^{-1} and 3202 cm^{-1} by valence vibrations of NH groups. The hydroxyl group is manifested by valence vibrations at 3435 cm^{-1} and 3339 cm^{-1} and deformation vibrations at 1629 cm^{-1}.

The mechanism of obtaining colored dispersions of montmorillonite as the NP basis for leather decoration by successive modification of montmorillonite with sodium carbonate, basic chromium sulfate, and anin dyes is presented in the diagram (**Fig. 2.9**).

According to the proposed scheme, native montmorillonite is treated with sodium salts to disperse the aggregates and expand the distance between the aluminosilicate layers, which is confirmed by X-ray structural analysis and the values of the basal interplanar distance of MMT. Further treatment of MMT–Na^{+} with chromium hydroxocomplexes leads to the formation of MMT–Cr^{3+} with a turbostratic highly developed structure, which is accompanied by wedging of the marginal areas of the aluminosilicate layers of MMT and an increase in the adsorption surface of montmorillonite to the level of 280 m^2/g.

At the same time, the montmorillonite layers have a cationic surface charge at the level of +4.5–13.5 mV in the range of pH 4.3–6.2. The maximum value of +19.0 mV the level of the cationic charge of the MMT–Cr^{3+} surface reaches at pH 5.4. Subsequently, effective adsorption grafting of anionic dyes occurs on the surface of highly developed MMT–AD as the basis of nanopigments.

Table 2.7 Change in optical densities in the spectra of modified montmorillonite

Band, cm^{-1}	Group	Optical density, D/Ds		
		$MMT–Cr^{3+}$	NPg	NPb
3732–3621	NH, OH	1.43	1.18	0.65
3401–3339	NH_2, NH val., OH val.,OH bound	1.5	1.58	1.45
3202	NH_2, NH val	–	1.45	–
2855	C-H vak., OH crystal	–	0.88	0.88
1629	H-O-H def.	0.31	2.5	–
1608–1602	C=C arom., NO_2 as.,C-N=N-C	–	2.14	2.04
1575–1564	C=C arom., NH_2 def.	–	2.14	1.69
1510	NH_2 def.	–	–	2.5
1494–1486	C=C arom	–	2.68	2.5
1460	C=C arom, C=N	–	1.75	–
1420–1413	C=C arom, C=N	–	1.96	1.79
1330	NO_2 val., sym.	–	2.86	2.86
1284–1261	OH, R-SO_3H, -SO_2- val.	–	1.61	1.61
1218	O-NH_2	–	2.32	–
1171	-SO_2-N, C-NO_2, O-NH_2	–	2.32	2.32
1143	-SO_2-N, C-NO_2, O-NH_2	–	3.21	3.21
1104	O-SO_2	–	2.32	2.32
1045–1034	OH, -SO_3-H val., Si-O	3.2	5	5
916	OH, C-N=N-C	1	1	1
840–862	O-NH_2	–	0.71	0.5
797	CH arom., $(Si\text{-}O)_4$	0.55	–	0.3
780	CH arom., $(Si\text{-}O)_4$	0.53	–	0.11
737	CH arom., $(Si\text{-}O)_4$	–	0.13	–
694	CH arom., $(Si\text{-}O)_4$	0.36	0.09	0.09
663–668	$(Si\text{-}O)_4$, Cr^{+3}	–	1.24	0.4
642	O-NH_2, O-NO_2 def, monosub. benzene ring	–	0.23	0.5
593–564	O-NH_2, O-NO_2 def, м monosub. benzene ring	–	0.46	–
524	$(Si\text{-}O)_4$, Cr^{+3}	1.94	1.21	1.12
468	$(Si\text{-}O)_4$, Cr^{+3}	2.39	1.41	1.41
425	$(Si\text{-}O)_4$, Cr^{+3}	1.11	0.04	0.35

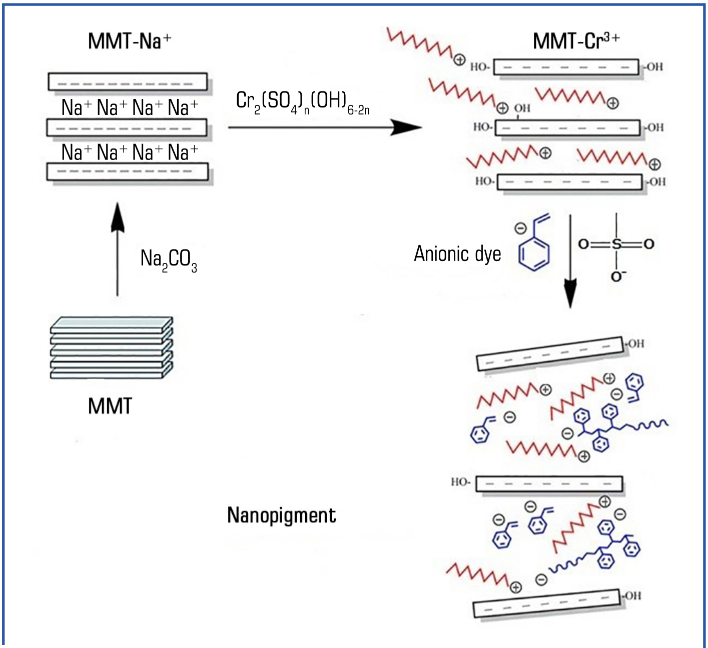


Fig. 2.9 Mechanism of interaction of modifiers with montmorillonite

The obtained results of structural and electro-surface changes of montmorillonite indicate the expediency of mineral modifications by sequential treatment with multifunctional substances to obtain nanopigments for leather decoration.

The diagram of the stages of obtaining a nanopigment is presented in **Fig. 2.10**. Nanopigments were prepared by gradually mixing the modified cationic form of montmorillonite with a dye. Mixing was carried out using a mechanical stirrer at a certain temperature to obtain time-stable dispersions in the form of nanopigments of a saturated deep color. The pH of the obtained nanopigments is 5.8–6.0.

According to the chemical composition, the nanopigment contains montmorillonite, sodium salt, basic chromium sulfate, anionic dye and water in the following ratio of components, by weight. %:

– montmorillonite – 10;
– sodium salt – 0.6;
– basic chromium sulfate in terms of Cr_2O_3 – 1.0–1.2;
– anionic dye – 10.

For comparison with typical pigment concentrates used in the practice of finishing natural leather, the chemical composition and variants of the obtained nanopigments are presented (**Table 2.8**).

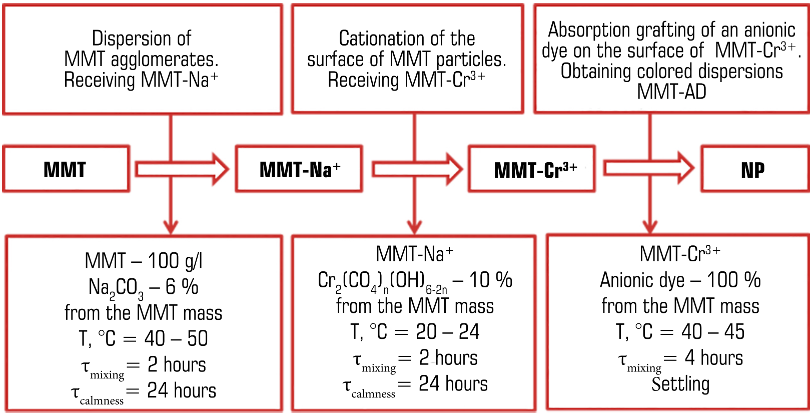


Fig. 2.10 The scheme of obtaining nanopigments

Table 2.8 Chemical composition of nanopigments for leather decoration

Components, mass %	NP	
	NPb	**NPg**
Montmorillonite	10	10
Sodium carbonate	0.6	0.6
Basic chromium sulfate *	1.0	1.0
Black anionic dye	10	–
Dark green anionic dye	–	10
Water	78.4	78.4

*Note: *in terms of* Cr_2O_3

Table 2.9 shows the properties of nanopigments. According to the results of the evaluation of the NP quality indicators, it was established that the nanopigments are characterized by high curvature and stability over time, their delamination is not observed for 24 hours or more.

In general, nanopigments are characterized by high covering, stability over time, which will allow to reduce the thickness of the covering film during leather finishing and obtain a covering with high quality indicators in terms of adhesion to dry and wet leather, resistance of the covering to multiple bends, dry and wet friction while reducing the cost of nanopigments and reducing the cost of covering paint for decoration. At the same time, an expansion of the range of NPs for leather finishing is ensured.

Table 2.9 Properties of nanopigments for leather decoration

Quality indicators	NP		
	NPb	**NPg**	**Analogue**
Color of pigment concentrate	Black	Dark green	Black
Dry residue of pigment concentrate, %	22.9	20.1	16.5
Curvature of pigment concentrate, g/m^2	9.1	9.5	11.0
Sedimentation of pigment concentrate, %	95.6	95.5	87.7
Color uniformity, points	5	5	5

*Note: *studies were carried out on samples without fixation*

2.3 APPLICATION OF NANO PIGMENTS FOR POLYMER-MINERAL LEATHER DECORATIONS

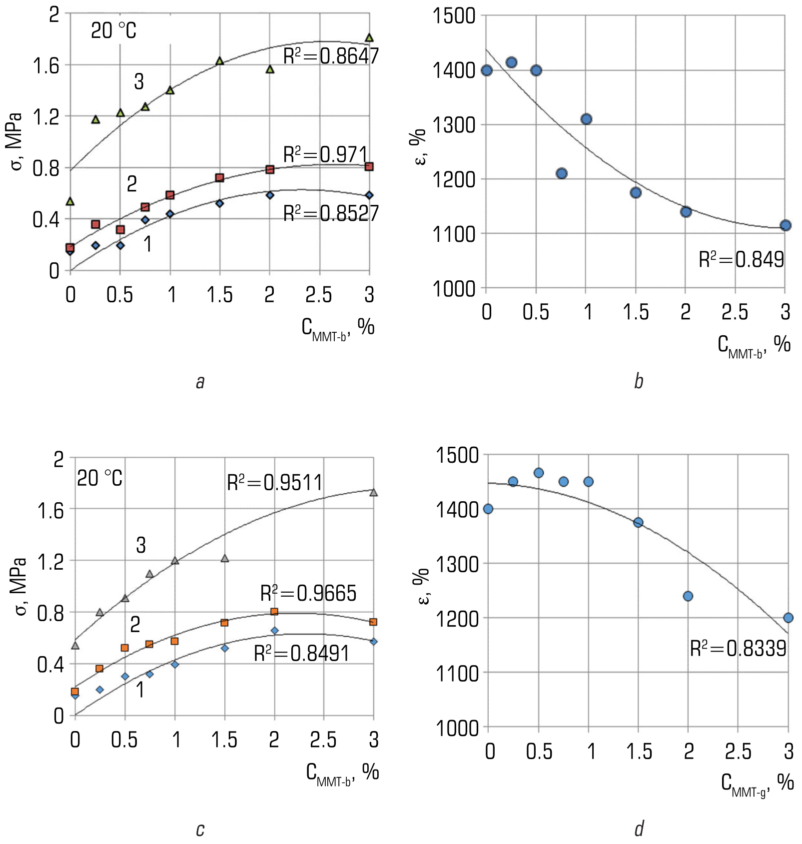
The polymer is used in covering compositions as a film former to create a uniform protective covering on the surface of the leather of a certain color or shade. However, in the process of using leathers, for example, as parts of the uppers of shoes, furniture, clothes, etc., significant physical and mechanical loads, repeated bending and bending, abrasion in dry and wet conditions, stretching, etc. occur. Because of this, the required level of operational properties of the covering on the leather depends on the physico-mechanical and physico-chemical parameters of the covering films [33]. In this regard, one of the ways to improve the quality of the covering on the leather is the use of nanopigments, which would allow correcting and purposefully forming a complex of physical and mechanical indicators of the polymer covering of the leather.

To study the effect of the developed nanopigments on the structure and properties of the polymer film former, nanopigments of black (NPb) and dark green (NPg) colors were used.

As a film former, an acrylic polymer was used – copolymer acrylic emulsion MBM–3 (aqueous dispersion of methacrylate copolymer), butyl acrylate and methacrylic acid in the amount of 3.0 % by weight of monomers [12]. The molecular structure of the copolymer determines sufficient elasticity and strength of the polymer in the temperature range necessary for covering on the leather. The emulsion is characterized by a high molecular weight, which determines the film-forming ability necessary for the covering. Dry residue MBM–3 – 38.5 %, pH – 4.35.

The introduction of nanopigments into the composition of the polymer matrix can purposefully adjust the quality of the finishing covering on the leather. It can be predicted that the mineral particles of nanopigments, having a high sorption surface and exchange capacity, will be able to adsorb on their surface and interact with the active groups not only of the dye used to modify the mineral dispersion, but also with polymer acrylic emulsions [34, 35].

The study of the effect of nanopigments on the physical and mechanical properties of polymer acrylic matrices (**Fig. 2.11**) indicates structural and elastic changes in the parameters of polymer films under conditions of varying degrees of loading and elongation. The introduction of montmorillonite into the polymer matrix (concentration of montmorillonite C-MMTb and C-MMTg, respectively, according to the color of the pigment) in the form of NPs helps to increase the strength (s) of polymer films. The maximum level of strength of the films is achieved at consumption of 1.5–2.0 % of montmorillonite from the dry polymer residue (**Fig. 2.11, a, c**). The introduction of NPb and NPg increases the modulus of elasticity of the films by 3.5 times, as evidenced by the strength indicators of the films at 100 % elongation (**Fig. 2.11, a, c, curve 1**).



⬡ **Fig. 2.11** Changes in the physical and mechanical properties of polymer films as a result of the addition of black (*a*, *b*) and green (*c*, *d*) nanopigments at elongation 100 % – 1, 300 % – 2, and break – 3

For the indicated consumption, the level of strength at the break (**Fig. 2.11, a, c, curve 3**) in the case of the use of NPb dispersion increases to the level of 1.6 MPa, and in the case of the use of NPb – to 1.7 MPa. Compared to the strength indicators of the native polymer film (0.54 MPa), as a result of the modification of the polymer with NPb and NPg dispersions, it is possible to achieve its strengthening by almost 3 times. A significant increase in the break strength indicators (**Fig. 2.11, a, c, curve 3**) of polymer films is associated with conformational strengthening of the polymer structure due to the formation of strong compact crosslinks with the participation of active functional groups of the polymer and azo dyes in the composition of colored montmorillonite dispersions. Also, the introduction of nanoparticles [31] of montmorillonite in the composition of NPb and NPg with a characteristic highly developed sorption surface of mineral particles contributes to the physical adsorption of the polymer and the corresponding stabilization of its structure.

A further increase in the consumption of montmorillonite in the polymer matrix above 2.5 % slightly reduces the level of strength of the polymer films. Due to the introduction of a significant number of adsorption centers of montmorillonite, more structuring of the polymer occurs, which leads to a decrease in its film-forming ability due to a significant content of mineral particles.

The introduction of a mineral in the polymer matrix as part of NPb and NPg contributes to the correction of the relative elongation of the films (e) (**Fig. 2.11, b, d**). The structuring of the polymer matrix by montmorillonite with a consumption of 2.0–3.0 % manifests itself in a decrease in the relative elongation index to the level of 1100–1200 %. In the case of application of NPg dispersion in the range of 0.25–1.5 % of the polymer mass, a slight (by 3.0–3.5 %) increase in elasticity and corresponding elongation of polymer films is observed. A further increase in the consumption of NPg dispersion to the level of 2.0 % leads to a decrease in the relative elongation of polymer films by 11.5 % (**Fig. 2.11, d**). In the case of using NPb, a gradual decrease in relative elongation is characteristic already at consumption above 0.5 % of the polymer mass (**Fig. 2.11, b**). The maximum reduction of the relative elongation to the level of 1180–1200 % is typical for NPb consumption in the range of 1.5–3.0 % of the dry polymer residue.

Such changes in the physical and mechanical properties of polymer films are positive in the formation of a covering on the surface of the leather with high resistance to operational loads, abrasion and repeated bending. Because the difference in elongation and significant ductility of polymer films can have a negative effect on the quality of leather decoration due to the characteristic differences in the physical and mechanical loads of the polymer matrix and the collagen structure [31–33].

Due to the highly developed sorption surface, nanoparticles of modified montmorillonite adsorb the polymer, stabilize its structure and increase the colloidal stability of the polymer-mineral composition (**Fig. 2.12**). Such polymer compositions are effective for forming the finishing covering of elastic leathers for various purposes [34–36].

It was also established that montmorillonite as part of a nanopigment can improve the physical and mechanical properties of the polymer covering and increase its heat resistance [35].

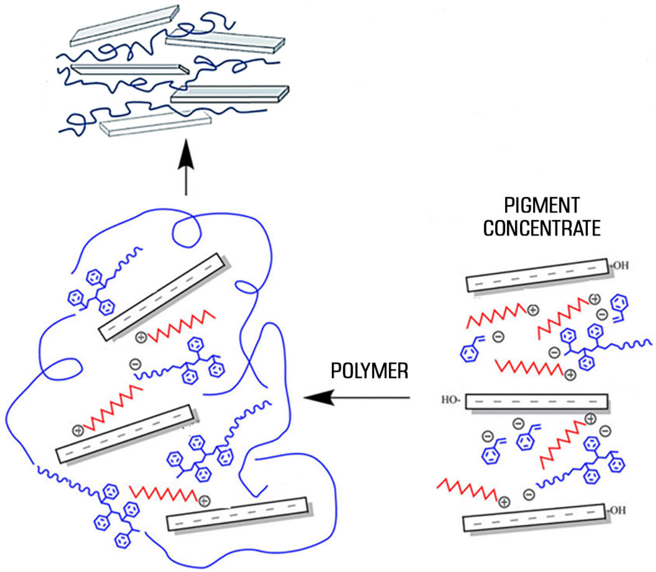


Fig. 2.12 Mechanism of polymer matrix structuring by nanopigment

In general, MMT consumption at the level of 1.5–2.0 % (based on the mass of montmorillonite from the mass of dry polymer residue) is appropriate for creating a high-quality polymer-mineral covering on the leather, resistant to operational loads.

Further research made it possible to optimize the composition of the covering composition based on film-formers and nanopigment to improve the quality indicators of the leather finishing covering [37]. To optimize the composition, the method of simplex-lattice planning was used [38].

Covering compositions were prepared for the research, including NPch and NPz nanopigments and film formers. A film former with a high modulus of elasticity (soft polymer) and a film former with a low modulus of elasticity (hard polymer) were used as film formers. Polyacrylate SMITCRYL 2100 (Smit & Zoon) was chosen as a soft polymer – highly elastic, flexible, with high covering capacity, the covering of which is characterized by resistance to water and cracks at low temperatures, as a hard polyurethane PUR 3365 FF (Codyeco, Smit & Zoon) – high strength, resistant to physical and mechanical loads, friction and wear.

When studying the properties of the mixture, which depend only on the ratio of components, the factor space is a correct simplex [38, 39]. For such systems, the ratio is performed when the sum of the relative concentrations of all components of the mixture is equal to 1. The relative concentration of each component varies from 0 to 1, that is, within 0–100 %.

It is known [3, 7, 37] that a significant content of pigment in the covering causes an increase in its hardness, but insufficient content negatively affects the covering ability of the covering. Therefore, the following intervals for changing the concentration of components in the studied composition [13, 38] were chosen: pigment (x1) – 0–30 %, hard film former (PUR 3365 FF) (x2) – 0–100 %, soft film former (SMITCRYL 2100) (x3) – 0–100 %. The parameters of the covering films were selected as response functions: Y1 – modulus of elasticity at 100 % elongation, MPa; Y2 – tensile strength, MPa; Y3 – relative elongation at break, %; Y4 – covering adhesion to the leather, N/m; Y5 – covering resistance to wet friction, rotation.

If there are restrictions on changes in the concentrations of some components (for example, pigment) in the mixture, the local area on the diagram represents an irregular simplex. In this case, renormalization is carried out and the compositions at the vertices of the local simplex are taken as pseudo-components (z_1, z_2, z_3) so that the condition (2.1) is fulfilled:

$$\sum_{i=1}^{q} x_i = 1, \tag{2.1}$$

where $x_i \geq 0$ – component concentration; q – the number of components.

Planning the experiment and obtaining its mathematical model were performed in the coordinate system of pseudo-components. To conduct the experiment, the transition from pseudo-components z_1 to initial components x_1 was performed. The plan of the experiment and the values of the response functions are given in the **Table 2.10**.

Table 2.10 Characteristics of the experimental plan

Experiment No.	Plan						Y_1	Y_2	Y_3,	Y_4	Y_5
	z_1	z_2	z_3	x_1	x_2	x_3	MPa	MPa	%	N/m	Revolutions
1	1	0	0	30	0	70	9.6	9.7	110	160	40
2	0	1	0	0	100	0	2.1	12.6	990	320	120
3	0	0	1	0	0	100	0.43	4.8	1285	160	230
4	0.7236	0.2764	0	21.71	27.64	50.65	4.9	5.9	250	180	20
5	0.2764	0.7236	0	8.29	72.36	19.35	2.8	6.3	625	240	50
6	0.7236	0	0.2764	21.71	0	78.29	4.1	10	610	200	20
7	0.2764	0	0.7236	8.292	0	91.71	1.34	5.1	750	320	40
8	0	0.7236	0.2764	0	72.36	27.64	1.63	7.1	825	225	80
9	0	0.2764	0.7236	0	27.64	72.36	0.8	4.35	1070	230	130
10	0.3333	0.3333	0.3334	10.00	33.33	56.67	2.03	6.35	690	195	40
11	0.22	0.56	0.22	6.6	56	37.4	2.0	6.6	915	290	40
12	0.44	0.12	0.44	13.2	12	74.8	2.4	8.4	700	290	20

A polynomial of the third order (3.2) was used as a model for a three-component system:

$$\begin{aligned} y &= \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \gamma_{12} x_1 x_2 \left(x_1 - x_2\right) + \\ &+ \gamma_{13} x_1 x_3 \left(x_1 - x_3\right) + \gamma_{23} x_2 x_3 \left(x_2 - x_3\right) + \beta_{123} x_1 x_2 x_3, \end{aligned} \qquad (3.2)$$

where x_i is the concentration of components; β_i, β_{ij}, γ_{ij}, β_{jk} – the corresponding polynomial coefficients, and $1 \leq (i,j,k) \leq 3$; $i \neq j \neq k$.

The resulting models of the output variables have the following form:

Model 1. $Y_1 = 9.6z_1 + 2.1z_2 + 0.43z_3 - 9.9998z_1z_2 - 11.475z_1z_3 - 0.25z_2z_3 - 7.0102z_1z_2(z_1 - z_2) - {} - 7.4955z_1z_3(z_1 - z_3) + 0.46498z_2z_3(z_2 - z_3) + 10.814z_1z_2z_3$.

Model 2. $Y_2 = 9.7z_1 + 12.6z_2 + 4.8z_3 - 25.25z_1z_2 + 1.5z_1z_3 - 14.875z_2z_3 + 5.0138z_1z_2(z_1 - z_2) + {} + 15.142z_1z_3(z_1 - z_3) - 4.1265z_2z_3(z_2 - z_3) + 43.425z_1z_2z_3$.

Model 3. $Y_3 = 100z_1 + 990z_2 + 1285z_3 - 537.49z_1z_2 - 62.499z_1z_3 - 949.99z_2z_3 + {} + 128.62z_1z_2(z_1 - z_2) + 2179.8z_1z_3(z_1 - z_3) - 632.12z_2z_3(z_2 - z_3) + 1905.1z_1z_2z_3$.

Model 4. $Y_4 = 160z_1 + 320z_2 + 160z_3 - 150z_1z_2 + 499.99z_1z_3 - 62{,}499z_2z_3 + 64{,}579z_1z_2(z_1 - z_2) - {} - 670.83z_1z_3(z_1 - z_3) - 427.95z_2z_3(z_2 - z_3) - 1357.5z_1z_2z_3$.

Model 5. $Y_5 = 40z_1 + 120z_2 + 230z_3 - 225z_1z_2 - 524.99z_1z_3 - 349.99z_2z_3 + 32.289z_1z_2(z_1 - z_2) + {} + 363.19z_1z_3(z_1 - z_3) - 4.5169z_2z_3(z_2 - z_3) + 869.95z_1z_2z_3$.

The adequacy of the obtained equations was checked using the Student's t-test, using 2 control points (experiment number 11–12) of the experimental plan (**Table 2.10**). With the number of experiments $N = 12$, the number of parallel experiments $n = 5$ and the level of significance $p = 0.05$, the tabular value of the Student's criterion $tt = 2.17$. For all control points, the t-ratio is less than the tabular one, that is, models (1–5) are adequate [37–39].

For the practical use of the results of the analysis of regression models, the transition from pseudo-coordinates to natural variables was performed using formulas for transferring coordinates from one system to another [37]. Using the calculated formulas of the connection between the coordinates z_i and x_i:

$$x_1 = 0.3z_1;\ x_2 = z_2;\ x_3 = 1 - 0.3z_1 - z_2 = 1 - x_1 - x_2;$$

the optimal ratios of the components of the covering composition in the initial (natural) coordinates and the optimal values of each output variable are determined.

The problem of optimization of processes characterized by several feedbacks, as a rule, is reduced to optimization according to one criterion with constraints in the form of equations and inequalities. Depending on the response surface and the nature of the constraints, a number of methods are used for optimization. One of the most successful ways to solve the optimization problem with a large number of responses is to use the so-called Harington criterion or the generalized desirability function D as a generalized optimization criterion, as well as the fair trade-off method. To construct a generalized desirability function D, the measured feedback values were converted into a dimensionless scale of desirability d using the method of quantitative assessments with an interval of desirability values from zero to one. The value $d=0$ (or $D=0$) corresponds to an absolutely unacceptable value of this response; 0.63–0.79 = good; 0.80–0.99 = very good value; and $d=1$ (or $D=1$) = the best response value, and its further improvement is either impossible or unreasonable [38].

As can be seen from **Fig. 2.13**, the generalized desirability function D has a maximum value of $D=0.60$–0.65 in the specified region of the simplex, which characterizes this region of the simplex as the region of optimal values of the initial variables, and allows optimization of the composition of the covering composition with high reliability.

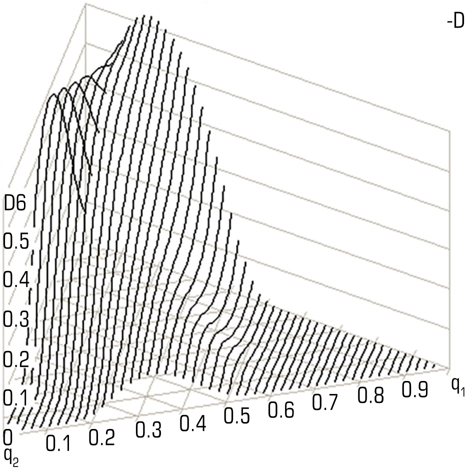
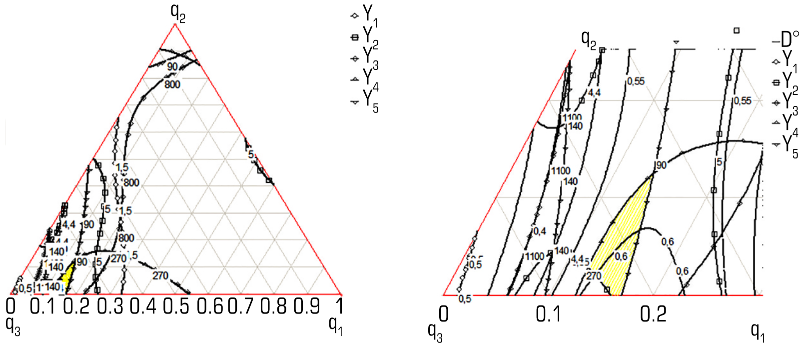


Fig. 2.13 Generalized desirability function

If a certain process is described by several regression equations and the results of several output variables are important, then in this case a compromise problem should be solved – to determine the extreme value of one output variable under the conditions of restrictions imposed on others and on the border of the research areas (fair compromise method). Optimum parameters, which are achieved when such conditions are met, are called conditional or relative, and the area of process parameters, within which the output variables that satisfy all the specified requirements are obtained, are called the rational or compromise area [38, 39]. The peculiarity of the optimization method is that by changing the limits of the initial variables, it is possible to adjust the ratio of the components of the covering composition in order to obtain the initial variables, taking into account the technological requirements for the formation of the covering on the leathers of a certain assortment.

Determination of the optimal (rational) composition of the covering composition was carried out by means of multi-criteria optimization using a graphical method based on the curves of equal values of the covering indicators Y_1–Y_5 on the plane of the regular simplex (**Fig. 2.14**).



a

b

Fig. 2.14 The range of optimal values of the initial variables: Y_1 – modulus of elasticity at 100 % elongation, MPa; Y_2 – tensile strength, MPa; Y_3 – relative elongation at break, %; Y_4 – adhesion of the covering to the leather N/m; Y_5 – covering resistance to wet friction, rotation

Taking into account the special requirements for covering leathers for the upper of shoes, namely strength, adhesion to the leather and resistance to wet friction, the following restrictions of minimum and maximum values were imposed on the output variables: Y_1=0.5–1.5 MPa; Y_2=4.4–5.0 MPa; Y_3=800–1100 %; Y_4=270–300 N/m; Y_5=90–140 revolutions.

As a result of the optimization, optimal ratios of the components of the covering composition were obtained, which provide the covering film with the necessary quality indicators [37].

The optimal composition of the covering composition (%):

– nanopigment – 4.5–5.0;
– urethane film former PUR 3365 FF – 3.0–5.0;
– acrylic film former SMITCRYL 2100 – 90.0–92.5.

The use of this covering composition ensures the formation of a covering on the leather with the following quality indicators: Y_1=0.96–1.06 MPa; Y_2=4.4–4.5 MPa; Y_3=900–915 %; Y_4=280–290 N/m; Y_5=100–110 revolutions.

To confirm the results of the optimization of the composition of the covering paint, a covering paint of the optimal composition was prepared and the front surface of the leathers was decorated. The results of studies of the quality of the leather finishing covering are given in **Table 2.11**.

● **Table 2.11** Indicators of the quality of leather covering

№	**Covering quality indicators**	**Value**	
		calculated	**experimental**
1	Modulus of elasticity σ100, MPa	0.98	1.1
2	Tensile strength limit σp, MPa	4.48	4.65
3	Relative elongation at break, ε %	915	905
4	Adhesion of the covering to the leather, N/m: – dry; – wet	285 –	300 185
5	Covering resistance to: – wet friction, spins; – multiple bends, thousands of bends	100 –	110 <100000
6	Air permeability, $cm^3/cm^2 \times h$	–	42.3
7	Evenness of color, points	–	5
8	Color fastness to wet rubbing, score	–	5

The obtained experimental data (**Table 2.11**) correlate with the calculated data of mathematical modeling, which confirms the reliability of the optimization results and indicates the high quality of the developed covering on the leather. A slight difference between the experimental and calculated indicators of the quality of the covering may be related to the conditions of the formation of the covering film.

Later, taking into account the results of the optimization of the covering paint composition [37], leathers were decorated with covering compositions of black and dark green colors based on nanopigments and the quality indicators of the obtained leathers were evaluated (**Table 2.12**).

A characteristic feature of the covering according to the developed formulations is high hiding power. With a minimum consumption of covering paint at the level of 33.7–33.8 g/m^2, it is possible to achieve a complete uniform coloring of the leather surface. At the same time, the minimum thickness of the covering film and high color uniformity at the level of maximum points are obtained. It should be pointed out a sufficiently high level of air permeability for leathers after polymer-mineral finishing, which indicates increased hygienic properties. Since the presence of a mineral component in the polymer composition and obtaining an exfoliative type of composite allows to avoid the creation of a monolithic polymer covering layer on the surface of the leather.

Dark green coverings are characterized by adhesion to dry leather at the level of 360 N/m, to wet leather at 190 N/m and high resistance to wet friction at the level of 385–390 revolutions, which depends on the nature of the interaction of montmorillonite particles with an anionic dye and on the level structuring and plasticizing covering paint based on film formers. The formation of a black covering on the leather is characterized by high values of adhesion to dry and wet leather at the level of 380 N/m and 205 N/m, the indicators for the dark green covering are slightly lower, but not significantly – 360 N/m and 190 N/m for the corresponding type of adhesion that, in general, meets the requirements of the standards.

Table 2.12 Indicators of quality of covering and finished leathers

№	**Covering quality indicators**	**Covering colour**		
		Black	**Dark green**	**DSTU 2726-94 [22]**
1	Adhesion of the covering to the leather, N/m: – dry; – wet	380 205	360 190	100/200 50/100
2	Covering resistance to: – wet friction, rotation; – multiple bending, points	390 5	385 5	60 >3
3	Air permeability, $cm^3/cm^2 \times h$	42.3	41.5	–
4	Evenness of color, points	5	5	–
5	Color fastness to wet rubbing, score	5	5	–
6	Covering ability of the covering, g/m^2	33.7	33.8	–
7	Thickness of the covering film, g/m^2	13.5	15.1	–

The analysis of the obtained indicators indicates the formation of a thin-layer, uniformly colored covering with a high level of air permeability and operational stability, which indicates the feasibility of using the proposed nanopigments as part of a polymer-mineral covering for the formation of a finishing film on the front surface of leathers. This covering allows to enhance the effect of "naturalness" of the leather surface, volume, graininess and fullness of the network. At the same time, the high level of adhesion to the leather surface, the elasticity and strength of the film based on the polymer-mineral composition creates a high-quality covering and ensures its resistance to repeated bending and wet loads.

In general, it can be concluded that the use of nanopigments based on modified montmorillonite makes it possible to obtain a high-quality leather covering with good performance indicators at a reduced cost of covering paint for decoration, allows to purposefully regulate the technological processes of leather production related to providing the necessary color range, level and depth of color and its resistance to external influences.

CONCLUSIONS

1. The work is devoted to the development of nanopigments based on montmorillonite for polymer-mineral decoration of natural leather.

2. According to the analysis of the dynamics of Ukraine's foreign trade activity, key trends in the development of the leather industry in the production of leather with a natural face surface have been identified as the most competitive and in demand on the world market.

3. The role of leather decoration through the rational selection of film-forming materials and pigments of different nature in the formation of high performance indicators of leather is shown. It has been proven that modern approaches in covering leather are based on the principles of using compact finishing, which involves an improved composition of covering compositions, a reduction in covering thickness, a rational selection of film-formers and pigments with high covering ability and compatibility.

4. The influence of sequential modification of aqueous dispersions of montmorillonite with cationic and anionic compounds was established, and the change in structural and charge characteristics of mineral dispersions after dispersion and cationization of the surface of mineral particles for intensive attraction of molecules of the dispersion medium of anionic dyes was proved. The maximum level of adsorption of anionic black and dark green dyes on the cationic surface of montmorillonite occurs in the range of pH 5–6.5 and is characterized by stability in the range of pH 3–10, which is explained by the presence on the surface of modified montmorillonite of chromium cations with strong complexing ability and susceptibility to chemical and physico-chemical interactions between oxygen atoms of the mineral and nitro-, amino- and sulfo groups of dyes due to the formation of hydrogen and van der Waals bonds.

5. The mechanism of obtaining colored dispersions of montmorillonite was substantiated and the composition of nanopigments with high hiding power and stability over time was developed.

6. It is shown that the use of colored dispersions of montmorillonite and nanopigments based on them increases the physical and mechanical properties of polymer films, plasticizes and structures the polymer-mineral composition, contributes to the production of leathers with high organoleptic characteristics of the front surface, namely, the volume of the network, graininess, nice vulture.

7. The composition of the covering composition was optimized by the method of simplex-lattice planning, which includes (%): pigment – 4.5…5.0; film former with high and low modulus of elasticity (polyurethane) – 3.0…5.0; film former with a high modulus of elasticity (acrylic) – 90.0…92.5. It is shown that the combination of film-formers and nanopigments based on modified montmorillonite ensures the formation of a thin-layer covering with the required level of operational properties, characterized by high adhesion of the covering to the leather, resistance to repeated bending, dry and wet friction, elasticity and strength.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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