NANOPIGMENTS FOR LEATHER FINISHING COATINGS

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The work is focused on obtaining nanopigments by adsorption of anionic dyes on positively charged montmorillonite. The effect of sequential modification of aqueous dispersions of montmorillonite with cationic and anionic compounds on the structural and charge characteristics of mineral dispersions was studied. The effect of chemical dispersion of agglomerates of aqueous montmorillonite dispersions after adding carbonate solutions was shown. The treatment of dispersions of original montmorillonite with sodium carbonate provides maximum dispersion of mineral aggregates by penetrating into the interstructural space of aluminosilicate packets, moving them apart and separating them. It was found that the modification of montmorillonite dispersed by sodium carbonate by adding basic chromium sulfate is accompanied by a change in the surface chemistry of the mineral and structural transformations. Structural changes are manifested by the formation of a developed structure of cationic montmorillonite. The cationic surface charge of montmorillonite and high specific surface of montmorillonite are important factors for ensuring effective adsorption of anionic dyes on the surface of the mineral. The efficiency of adsorption of anionic dyes on cationic montmorillonite is investigated. It was shown that the adsorption of dyes depended on the pH of the medium. The scheme of obtaining nanopigments, which were characterized by good covering power, saturated and intense colour was proposed.

Keywords: montmorillonite, pigment, leather finishing coating

INTRODUCTION

Traditional leather finishing involves applying a covering composition to the surface of leather. The finishing coating provides protection of leather from external atmospheric and mechanical impacts (Covington, 2009).

The type of leather coating depends on the content of pigments and can be (Covington, 2017; Zhuravsky *et al*., 1996; Kasyan, 2019): aniline – a transparent coating without the use of pigments; semi-aniline – characterized by a small content of pigments to provide, mainly, a shade of color; and pigmented – with a significant content of pigments for complete coverage of the surface of leather with a colored covering layer.

Pigments provide color and covering power to the finishing coating (Winter *et al*., 2017). Organic or inorganic pigments are used in the finishing coating of leathers. Covering compositions with organic pigments provide leather with shine, bright and intense color, but have low light fastness and heat resistance. Inorganic pigments create a high-quality coating with good light fastness and water resistance, but are characterized by a high tendency to sedimentation and are limited in color and brightness (Winter *et al*., 2017; Osgood, 1990).

The ability of the coating to form a uniform coating stable composition with required thickness depends on the properties of the pigment, the origin of their surface, and the size of the particles.

The use of nanopigments provide improved physical and mechanical indexes of the leather finishing coating (Bondaryeva and Mokrousova, 2020; Bondaryeva *et al*., 2021).

The aim of the work was to describe the scientific basis of patterns of anionic dyes adsorption on positively charged montmorillonite to obtain nanopigments for leather finishing coatings.

https://doi.org/10.24264/icams-2022.I.4

EXPERIMENTAL

Materials

Bentonite clay from the Cherkassky deposit (Ukraine), after thorough purification and washing was used as a basis for obtaining nanopigments. The main mineral was montmorillonite, the content was 85±3 %. The value of the exchange capacity was 72 mg-eq/100 g of clay. Humidity – 27 ± 3 %.

The sodium carbonate, basic chromium sulfate (Ш) and anionic dyes were used to modify dispersions of montmorillonite.

Methods

The nanopigments were obtained by sequential treatment of aqueous montmorillonite dispersions (100 g/l) with sodium carbonate, basic chromium sulfate and anionic dyes.

Firstly, 6,0% of sodium carbonate from weight of dry montmorillonite was used, and then the cationic form of montmorillonite was obtained by modifying the dispersion of Na^+-montmorillonite with chromium compound. For this purpose, the basic chromium sulfate was used – $Cr_2(SO_4)_n(OH)_{6-2n}$, chromium oxide (III) content was 25.6 %. A solution of basic chromium sulfate in the amount of 10.0% Cr_2O_3 (by weight of the montmorillonite) was added to the dispersion of Na^+-montmorillonite (MMT–Na^+). Mixing was continued until a homogeneous mass of gray colour was obtained. The pH value of the modified dispersion of cationic montmorillonite (MMT-Cr^{3+}) was 4.5-5.2.

The nanopigments were prepared by gradually mixing the cationic form of montmorillonite with the anionic dyes. Mixing was performed using a mechanical mixer (30–40 min, 40–45°C) to obtain time-stable dispersions in the form of nanopigments of saturated deep colour. The consumption of anionic dyes in a ratio of 1:1 according to the mineral component. The nanopigments were obtained as the colored modified dispersions of montmorillonite.

A laser-correlation spectrometer “ZetaSizer–3” (Malvern Instrument, USA) with a Multi Computing Correlator type 7032 CE was used to study the dispersion of mineral systems.

The adsorption of dyes from aqueous solutions on the cationic form of montmorillonite was determined by measuring the light transmittance of dye solutions of different concentrations.

The electrokinetic potential was determined by microelectrophoresis.

RESULTS AND DISCUSSION

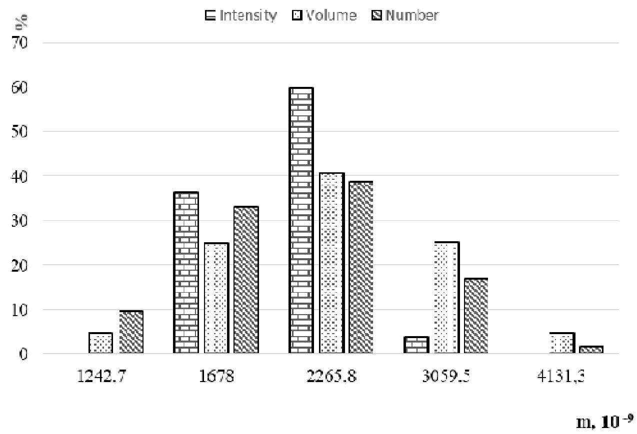
In montmorillonite modification, molecules of polar liquids (for example, sodium carbonate) can freely penetrate into the interpackets space of montmorillonite, push them apart and increase the distance between packets. As a result, montmorillonite particles disperse spontaneously in water, their number per unit volume increases significantly, and the number of direct contacts for further interactions increases.

It is shown that treatment of dispersions of native montmorillonite with sodium carbonate provides maximum dispersion of mineral aggregates by penetrating into the interstructural space of aluminosilicate packets, moving them apart and separating them.

https://doi.org/10.24264/icams-2022.I.4

Aqueous dispersion of original montmorillonite with a concentration of 100 g/l (Fig. 1a) is characterized by a monomodal distribution of mineral aggregates in terms of 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. In the aqueous dispersion of montmorillonite, there are aggregates of 1242.7 nm (the smallest size) and 4131.3 nm (the largest size).

a)



b)

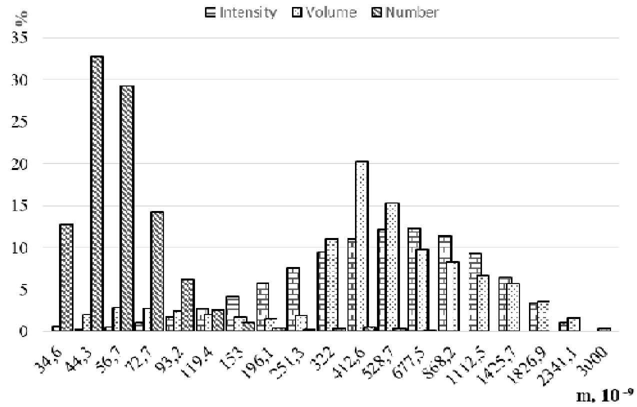


Figure 1. Distribution of montmorillonite particles in aqueous dispersion

After processing montmorillonite (Fig. 1b) with sodium carbonate, the largest number of mineral particles with sizes of 34.6-93.2 nm was found. This indicates the dispersion of montmorillonite aggregates. It was also found that the amount of mineral particles with sizes of 153.0-1826.9 nm increases in the volume, which indicates the polymodal nature of the montmorillonite dispersion after treatment with sodium carbonate.

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That is, the dispersion of $MMT–Na^{+}$ contains nano-sized particles with a significant number of contacts for further effective modification with chromium compounds and obtaining the cationic form of montmorillonite.

It was found that 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 and a decrease in d_{001} to 12.8 Å (Table 1). 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 (Table 1). The change in the diffraction pattern is due to the different orientation of chromium complexes in the interlayer space of montmorillonite.

Table 1. The structural changes of montmorillonite

Indicator	Montmorillonite		
	native	$MMT–Na^{+}$	$MMT–Cr^{3+}$
The basal spacing (d_{001}) values MMT, Å	14.8	12.8	14.4
The specific surface area, m^2/g	60	160	280

The specified effect was confirmed by the results of an increase in the specific surface of montmorillonite (Table 1) from 60 to 280 m^2/g.

It was also shown that the surface of the mineral particles acquires the maximum positive charge in the pH range of 4.6-6.2 (Fig. 2).

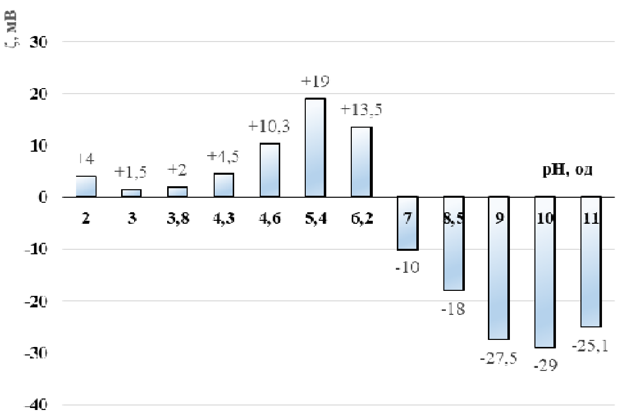

Figure 2. Effect of pH on the level of ζ-potential of modified $MMT–Cr^{3+}$

The cationic surface charge of montmorillonite and high exchange capacity are important factors for ensuring effective adsorption of anionic dyes on the surface of the mineral.

Adsorption of anionic dyes on the surface of modified montmorillonite is based on energy unsaturation, which after cationization of montmorillonite with Cr^{3+} compounds causes intense attraction of molecules of the dispersion medium and the formation of a monomolecular layer with the help of hydrogen bonds.

https://doi.org/10.24264/icams-2022.I.4

A high level of adsorption of anionic blue and anionic dark green dyes was shown. Adsorption isotherms of these dyes on the surface of modified montmorillonite are presented in Fig. 3.

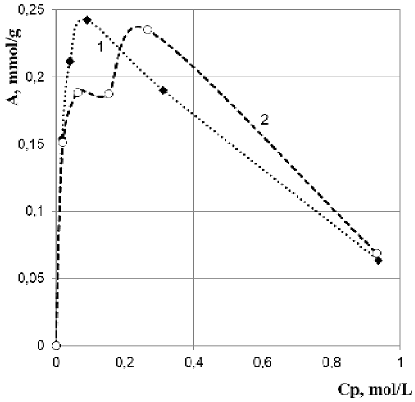

Figure 3. The adsorption isotherms of anionic dyes of montmorillonite after dye treatment: anionic dark green (1), anionic blue (2)

Colored modified montmorillonite dispersions of blue and dark green colors were characterized by color saturation and intensity. Color stability was also established in the range of pH 5.0–6.5, which indicates the possibility of using colored dispersions of montmorillonite as nanopigments for finishing coating leather.

The mechanism of obtaining nanopigments for leather decoration by sequential modification of montmorillonite with sodium carbonate, basic chromium sulfate, and anionic dyes is presented in the scheme (Fig. 4).

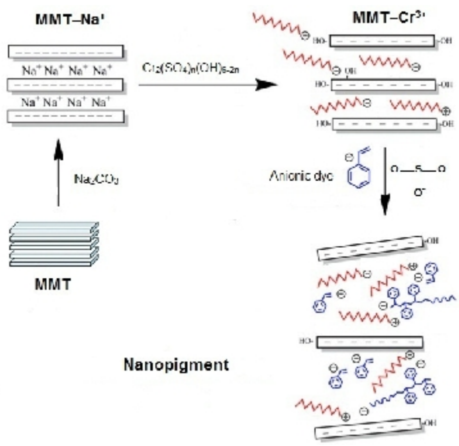

Figure 4. The mechanism of obtaining nanopigments

Nanopigments of dark green and dark blue were obtained according to the presented scheme. The properties of the nanopigments obtained are presented in Table 2.

https://doi.org/10.24264/icams-2022.I.4

Table 2. The properties of nanopigments

Indicator	Nanopigment / color	
	Dark green	Blue
The dry residue, %	21.1	23.7
Sedimentation, %	0	0
Covering power, g/m^2	14.0	16.0
Resistance to stratification, days	more than 240	

In general, the results of studies of structural and electrosurface changes of montmorillonite indicate the expediency of mineral modifications by sequential processing with multifunctional substances to obtain nanopigments for covering compositions and leather finishing.

CONCLUSIONS

The effect of sequential modification of aqueous dispersions of montmorillonite with cationic and anionic compounds on the structural and charge characteristics of mineral dispersions was studied. The effect of chemical dispersion of agglomerates of aqueous montmorillonite dispersions after adding carbonate solutions and obtaining a polymodal distribution of montmorillonite dispersion particles was shown. It was found that the modification of montmorillonite dispersed by sodium carbonate by adding basic chromium sulfate is accompanied by a change in the surface chemistry of the mineral and structural transformations. Structural changes are manifested by the formation of a developed micro- and mesoporous structure of cationic montmorillonite. The intensive attraction of molecules of the dispersion medium of anionic dyes on the surface of the cationic form of montmorillonite was studied. It has been proven that anionic dark green and anionic blue dyes were capable to adsorb on the cationic surface of montmorillonite at a ratio 1:1. The maximum level of adsorption of anionic dark green and blue dyes on the cationic surface of montmorillonite occurs in the range of pH 5–6.5. The nanopigments were characterized by deep intense colour; they were stable over time and had good covering power.

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