

Natural Iron Oxide Pigments for the Construction Industry

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Abstract: Are the main provisions of coloristics based on the knowledge of the use of natural pigments for coloring of construction products. Describes regularities of formation of iron oxide pigments in the extraction and enrichment of high-grade iron ores of the Kursk Magnetic Anomaly. The classification of pigments under the terms of their origin. The results of the study iron oxide pigments and technology of paints and varnishes based on them. The influence of plasticizers, dispersants on the colloidal properties of the iron oxide pigments. Are the most effective surfactants and optimal dosages.

Key words: Iron oxide pigments • Color use • Iron ore • Hydraulic borehole mining • Enrichment • modification • Dispersing agents • Paints and varnishes

INTRODUCTION

In recent years, more attention is paid to architectural and aesthetic level of industrial and civil construction. Color has become one of the most important opportunities to improve the system "man - Material - environment", reflecting the moods and styles [1-3]. A significant role is given lacquer coating on mineral pigments.

Consumption of mineral pigments for the past 35-40 years, growing by 0.3-0.6%, accounting for 0.1-0.3 kg per person. [4] The total global production of iron oxide pigments and pigment extenders - 1000-1100 tons / year.

Leading in world oil are the United States, France, India, Ukraine, Spain, etc. In the Russian Federation produces 25-30 tonnes per year iron oxide pigments, representing about 5.5% of world production [5-7].

The main areas of consumption in the world market of iron oxide pigments (ocher, the mummy and the minium iron) - the production of paints and varnishes (45%) and construction materials (40%) [7].

At the current scale of production of paints in the Russian Federation share the use of artificial pigment is 65-70%. At the same time, high-quality natural mineral pigments for color and paint and technical indicators to successfully compete with artificial dyes.

Involvement in the production of natural pigments hampered by the financial costs of finding and developing

of fields. The use of mine waste significantly reduces the capital cost of building raw materials of mineral pigments. In connection with this important task is the development of raw materials iron oxide pigments from the waste mining production, particularly of sludge hydraulic borehole rich iron ore and creation on the basis of their paint products.

Methods. Assessment of natural iron oxide pigments carried out on the basis of the analysis of geological and industrial resources base forming pigments based on the study of waste (sludge) hydraulic borehole. Used systematic analysis of existing methods for the study of pigments in the depths, methods of enrichment and modification of natural pigments. The estimation of the adequacy justify the use of iron oxide pigments for paints.

The main part. The perfection of the quality of products is the construction industry, including by enhancing its architectural and aesthetic level and design. Developing according to the laws of coloristics, infrastructure design creates a special material factor created by man of industrial products, which determines their architectural value.

Over the last decade the trend of decoration of construction and finishing materials finally entered the building. Gray elements paving, walling and roofing materials give way to a variety of color scheme in the field of architecture and design of buildings, structures, areas and individual buildings.

Coloristics as part of the science of color, includes knowledge about the nature of color, its characteristics, coloring, color harmony and color culture. Color is a means of communication and is the force that stimulates the senses and moral human perception of any industrial product and determines the level of consumer demand. Not surprisingly, the use of the range of color shades of building products, greatly increases their attractiveness compared with gray and white hues, such as the facades of buildings.

Colors affect people at every level of existence: the physical, emotional and intellectual. The color harmony is widely used in the organization of production processes, creating domestic and social comfort. Color has become a major focus of psychotherapy in the 21st century and one of the most important design elements that reflect the mood and styles.

The use of mineral pigments produces materials of different color shades and adjust the most important properties of composite materials - deformation and strength, insulation, anti-corrosion, adhesion strength, to improve the properties of the coatings: their weather resistance, water resistance, heat resistance, fire resistance and antifriction resistance.

Pigments under the terms of their origin we are classified as natural (mineral paints concentration in the earth's crust), technological (in industrial wastes) and artificial, as a product of the industrial synthesis of inorganic and organic substances (Table 1) [8].

Receiving artificial pigments due to the high cost of materials synthesis and operation of chemical plants. The use of natural and man-made pigments benefit not only from the point of view of economic expediency, but also enables utilization of industrial waste.

Study devoted to the research of natural pigments EF Belenky, LI Ginzburg, IV Djachkov VI Loganiyov, AF Nechayev, TG Yurakovoy, AV Panfilov, PI Ermilova, EA Indeykin, H. Lepp, H. Kittle, etc. However, it should be noted that the study of iron oxide pigments based on the rich iron ore CMA has not yet been given sufficient attention.

Formation of the range of color shades of natural pigments occur as a result of infiltration processes of enrichment products of the weathering crust of the Earth with solutions containing various metal compounds, the main of which are iron oxides.

Based on the diversity in the presence of metal oxide pigments that determine their species, we have developed a classification of types of mineral pigments (Table 2), which builds on the first, the principle of unity of pigments under the terms of their education and forms of

representation in the bowels and in Secondly, they differ in chemical composition and colors.

From the traditional technologies defining methods of mining, mainly used underground and open systems development fields.

The introduction of a fundamentally new way to develop iron ore hydraulic borehole mining technology was the result of innovative research in the framework of the Federal Target Program "Research and development on priority directions of scientific-technological complex of Russia for 2007-2012".

The development of iron ore deposits way hydraulic borehole (SRS) includes the following processes: drilling-ore wells, installation of casing in them and pulpopodemnyh pipes, the destruction of ores by exposure to water jet streams of water under pressure to 100 atmospheres., Air-lift lifting ore pulp by pulpopodemnoy trumpet gidroskladirovanie of ore in pulpopriemniki (Figure 1) [9].

Waste Management in the hydraulic borehole is highly dispersed muddy slurry low-Fetotal that are difficult to dehydration, which considered as a basis of iron oxide pigments. Hereinafter referred to as sludge - pigments. The cost of these pigments (at little cost to modify them) much higher cost of commercial ore (respectively \$ 800 and \$ 100 per 1 ton).

The definition of the boundary separating marketable ore and slimes in pulpopriemnikah, carried out on the basis of our proposed method with the determination of the percentage of Fetot of selected samples of ore namyvali pulpopriemnika in the interpolation of the values obtained and the preparation of the plan isohypses Fetot% in the receiver (Figure 2) [10].

Research of granulometric composition rich ores found that their structure is clearly expressed in the allocation pattern iron and impurity components to the main particle size (Table 3).

From the foregoing it follows that the sludge is 0.78% of the ore mass have a particle size from 0.02 mm to <0.005 mm Fetotal <57.75% when the content of iron oxide (Fe₂O₃) from 39.53% to 82.57 %.

According to the research of the genesis and the chemical composition of the residual high-grade iron ore we have found the following:

- There is a pattern of decline in the share of iron oxide (Fe₂O₃) with a decrease in the percentage of Fe total (Figure 3);
- A reduction in the proportion of iron oxide (Fe₂O₃) with decreasing dispersion ore particle size from 0.02 mm (Table 3);

Table 1: Classification of pigments on the specifics the formation

No	Class of pigments	Conditions of formation
1	Nature	Geological processes of formation of pigments in the bowels
2	Technogenic	The processes of concentration of pigments in industrial waste
3	Synthetic	Industrial synthesis of of mineral and organic substances

Table 2: The classification of types of mineral pigments

No	Type of pigments	Geological formation			Characteristics of chloroform		Oxide content,%	Denotation
		stages of residual high-grade ore	Presence in the Earth's crust	Strength properties	Type of minerals	Color shade		
1	2	3	4	5	6	7	8	9
1	Iron oxide and manganese-iron oxide	Oxidative (subaerial) and recovery (subaqueous) in the Tournaisian-Visean age of lateritic weathering	Dense and powdery earthy the formation	Friable and stable	Iron oxides and manganese oxides	Yellow, red, brown, black	30-60 (sometimes up to 85)	Minium iron, ocher, the mummy
2	Clayey		Colored clay and clayey rocks	Friable	Hydrates of iron oxide, iron oxide and manganese oxides, organic substances	Yellow, red, pink, purple, gray, black	5-12 (sometimes up to 20-30)	Ocher, jarosites, siena
3	Carbonate		Limestone, dolomite powder, chalk. Large concentrations of calcite grains with the presence of residues of micro-organisms	Friable and stable	Calcium oxide Iron oxide	White, yellow Brown, blue and green	25-50 0,1-30	Chalk carbonate yellow, ocher carbonate, copper deposit, lapis lazuli blue
4	Carbonaceous		Weathered brown coals mixed with clay particles	Friable	Organic substances Iron oxide	Brown Black	41-72 20-27	Cassel earth Natural soot
5	Siliceous		Minerals and rocks are enriched with silicic acid	Stable	Iron oxide, chrome oxide and others	Yellow, red, pink, blue, green	Up to 10	lapis lazuli
6	Sulfate		Minerals and rocks are riched with sulphates	Friable	Sulfate	Yellow, pink, blue	Up to 15	Jarosite
7	Phosphoric acid		Formations of bog and peat bog	Friable	Acidic iron, organic substances	Brown, red	Up to 5	Vivianite

Table 3: Granulometric and chemical compositions of produced a high-grade iron ore and sludge

		The average content, %							
Size of class, mm		Yield class%	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	TiO ₂	CaO	MgO	MnO
Sludge	-0,02								
	+0,005	0,36	82,57	8,14	3,29	0,11	1,29	0,26	0,038
	-0,005	0,42	39,53	23,45	17,8	0,11	3,04	0,99	0,043
The original ore	100,00	97,59	0,83	0,47	0,05	0,16	0,16	0,015	68,25



Fig. 1: Receipt of the ore slurry to the receiver

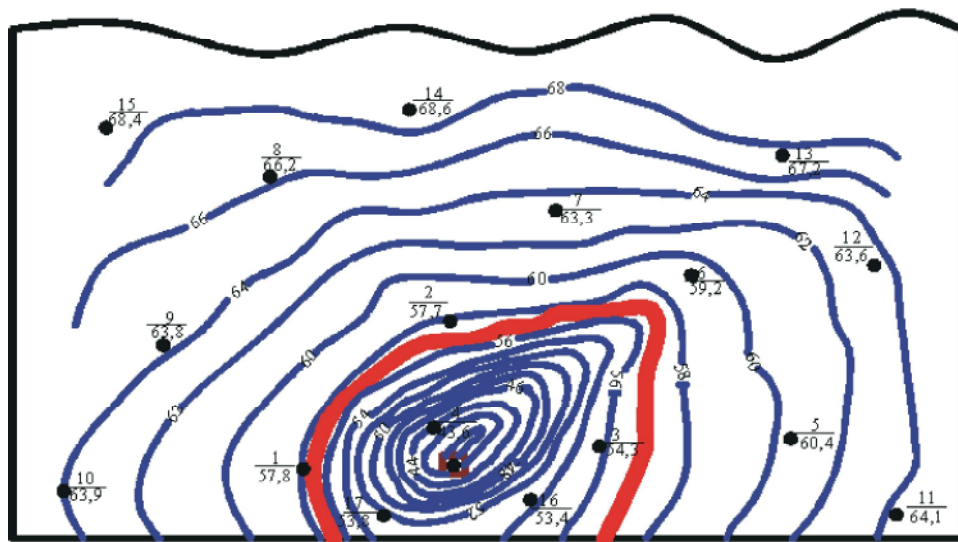


Fig. 2: Plan isohypses Fetot content of the dam near the well the receiving vessel, %: $\frac{9}{638}$ – Sample number / Fetot

- content, %;
- stoplog well;
- ~ 66 ~ – isohypses % Fetot cross section in 2%;
- ~ – border of "commodity-ore" and sludge in Fetot < 57%.

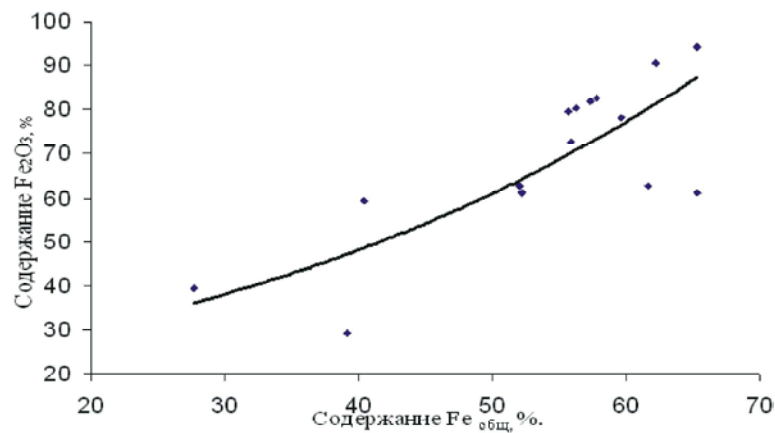


Fig. 3: Dependence presence of iron oxide based on total weight of the iron ore

Table 4: Iron oxide pigments of sludge

Name of pigment	Size of sludge, mm	Mineral	Quantity of Fe ₂ O ₃ , %	Color	Application area
Minium iron	0,02– 0,005	Hydrohematite	> 70	Brownish red	Grade A - for the manufacture of coatings, enamels, coatings for steel roofs, grade B - adhesive collers
Ocher	< 0,005	Goethite	< 30	Yellow, yellow-brown	For exterior and interior painting

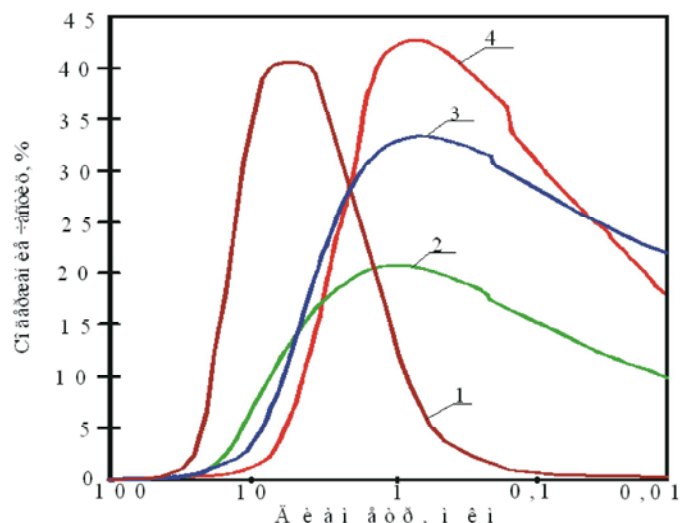


Fig. 4: Differential distribution of the particles in sedimentation analysis: 1 - initial pigment sludge, 2 - modified SBM-3 (0.3%) 3 - modified with stearic acid (1%); 4 - модифицированный C-3 (0,3%)

- At least reduce the proportion of particles having a size less than 0.02 mm is increased more than 20 times the amount of silicon oxide and aluminum to 12 times of calcium oxide, 2 times magnesium and manganese oxides, which, together with the iron oxide determine the color gamut of shades pigments (Table 3);
- Sludge having different range of colors can be regarded as the iron oxide pigment (Table 4).

Thus, according to the research of material composition and pigment slurries produced based on them, it was found that the content of Fe₂O₃, they correspond to high-quality natural iron oxide pigments.

Quality paint and varnish materials determined by the physico-chemical and physico-mechanical properties of the pigments used and depends on the dispersion of pigment powders.

To establish effective paint and varnish materials we carried out the modification iron oxide pigments, which consists in the introduction of modifiers to the suspension iron oxide pigments in the milling process. Studies on evaluation dispersion, sorption hygroscopicity pigments and obtaining ultrafine pigment slurry [11].

Dispersibility of pigment solids assessed by sedimentation analysis and by laser granulometry using MicroSizer Position 201. One of the conditions of the

method of sedimentation analysis is the ability of each particle to settle freely and independently of its neighbors.

The differential distribution of the pigment particles of the initial sludge and modified by various dispersants (Fig. 4).

According to the sedimentation analysis, we can conclude that the positive effect of additives on the grindability. The most probable size of the pigment particles without additives - 7-10 microns. With the introduction of modifiers this peak is shifted to 1-0.1 m.

Thus, it was found that the efficiency of the dispersion is increased by adding the dispersing medium, surfactant dispersants promote better wetting and disaggregated particles. In addition, special additives prevent flocculation of the pigments and also improve the decorative physical and mechanical properties of coatings.

The dependence between the density of the disordered structure in the coagulating sedimentation degree of precipitation and aggregation of particles is to reduce the density of the coagulation structure with an increasing number of primary particles. Equilibrium liquid interlayer between the particles to increase in height due to decreasing sludge extruding liquid under the action of gravity of the upper layers of particles.

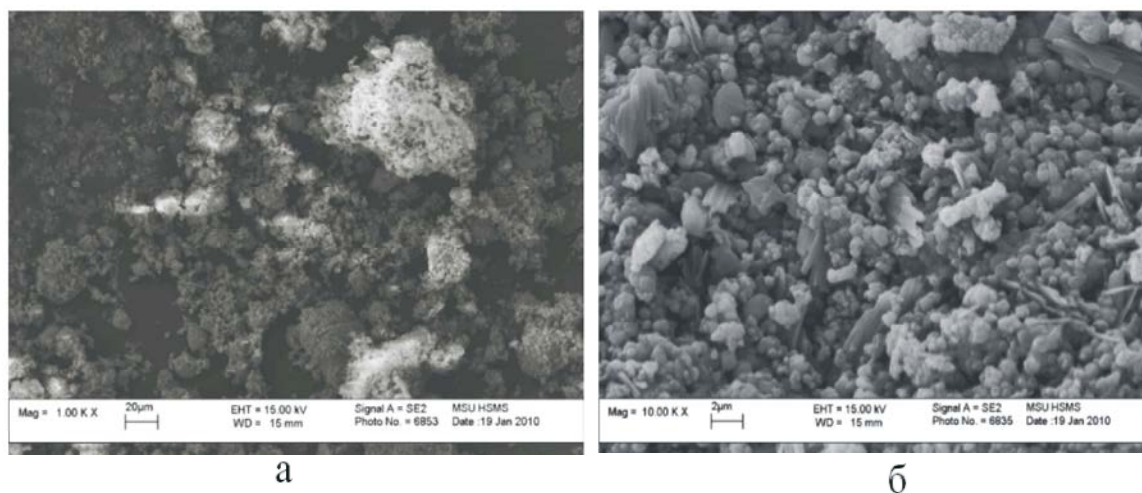


Fig. 5: The microstructure of the modified pigment sludge

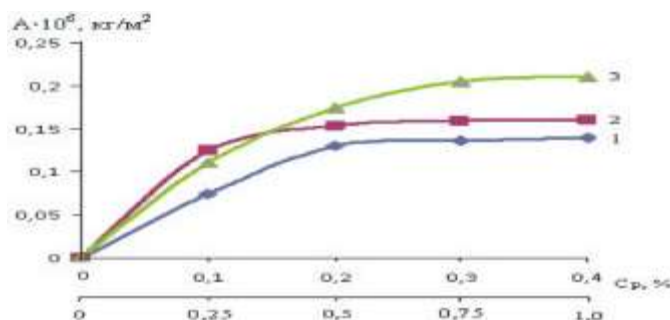


Fig. 6: Adsorption isotherms of modifiers iron oxide 1, 2 and 3 - pigment modified P-3 respectively; SBM-3 and stearic acid (abscissa second sample with stearic acid)

When introduced into the process of disintegration of dispersants decreases the value of the surface interaction of the particles of the fine fraction, which allows us to observe a uniform distribution of particulate matter throughout the survey area (Fig. 5a, b). However or no significant aggregates of pigment substance.

Due to the introduction in the process of disintegration of dispersants and their effects riving at the same time grinding the pigment slurry has a higher specific surface area ($S_{sp} = 10\,980\text{ m}^2/\text{kg}$), which is clearly seen in the photomicrograph (Figure 5b). In this case, the particles uniformly milled, but not aggregated.

The absence of a pronounced positive effect on aggregate indicators such as pigments, as oil absorption, coverage, etc.

It is known that the best results (dispersion, slurry homogeneity) achieved when "wet" processing of raw materials. In this case sludge already are "semi-finished" and the challenge studies facilitated by the chemical dispersant in the mixture is in dry form.

Knowledge of the mechanism of destruction of natural particles contained in the waste SRS in the presence of chemical dispersants, allowed us to achieve the following objectives:

- To reduce the viscosity of the pigment slurry;
- Obtain a suspension of ultrafine (nano) pigments - fillers that are not inferior obtained by chemical means;
- To reduce the energy consumption for drying as a result of reducing the moisture content of suspensions.

The use of modifiers is the most profound destruction of the primary particles of pigment slurry SGD. On the effectiveness of the use of additives proranzhirovanny as follows: SBM-3 → Melment → C-3 → stearic acid.

The mechanism of action of chemical dispersants is that the particles adsorbed on the surface of the slurry

Table 5: Physico-chemical properties of iron oxide pigments

No	Characteristic	Value of the characteristic	
		Natural pigments from SRS waste	Minium iron according to GOST 8135-74
1	Appearance	Red-brown color substance	Red-brown powder
2	Mass fraction of iron in terms of Fe ₂ O ₃ , %	73–84	70
3	The content of nanodispersed components, %	10–15	–
4	pH of water extract	9,1	6,5–7,5
5	Oil absorption, g/100g	19,5	до 25
6	The residue after wet sieving with a sieve with mesh # 0063, %	0,1	0,1–0,3
7	Temperature resistance 0C	500	400
8	Spreading rate g/m ²	54,6	not standardized
9	Content of water soluble salts, %	0,2–0,25	0,2
10	Density, kg/m ³	4,47	3,5

Table 6: Anticorrosive enamel paint for vehicle components anticorrosive (red-brown color)

No	Name of the substance	Substance content, %
1	Varnish MS-25 (dry)	28,5
2	Iron oxide pigment	11,0
3	Acrylic dispersion	5,0
4	Solvent	50,5
5	Corrosion inhibitor	0,5
6	Functional additives	4,5
Total:	100	

Table 7: Polyurethane primer enamel (color yellow)

No	Name of the substance	Substance content, %
1	Polyurethane ester (50% solution with solvent)	70,0
2	Iron oxide pigment	18,0
3	Talc	4,0
4	Hydrophobic chalk	5,0
5	Functional additives	3,0
Total:	100	

Table 8: Alkyd primer GF-021 (red-brown color)

No	Name of the substance	Substance content, %
1	Alkyd varnish and linseed oil	45
2	Iron oxide pigment	10
3	Dispersant	1,0
4	Microtalc	10
5	Microcalcite	29,5
6	Zinc phosphate	2,2
7	Desiccant calcium	2
8	Anti- membranian additive	0,2
Total:	100	

suspension, they contribute to a weakening of the contacts between the particles and destroy hydrated adsorption layer on the surface of the iron-containing particles, which not only leads to the release of a certain amount of water, but also to further destruction particles.

Adsorption studies of modifier dispersants for iron oxide pigments from aqueous solution was performed and stearic acid - of an organic solvent (Fig. 6).

Found that the adsorption of chemical dispersants on the surface of waste SRS causes a change of surface characteristics (hydrophilicity, organophilic, ability to adsorb water vapor and organic matter) and modifies the nature of the interaction with the macromolecules in the polymer compositions. This opens possibilities for creating new composite pigment and materials including paints and construction with improved properties.

Iron oxide pigments obtained studied in filled polymeric systems, including polymeric coatings in comparison with iron minium (Table 5). The experimentally determined that the contents of nanosized pigment component is 10-15%.

The table shows that the pigment from the waste SRS has high heat resistance, optimum oil absorption, good coverage, it can be used not only in conventional paint formulations, but in primers and paints for special purposes.

The resulting pigments in many ways superior to conventionally used by Russian and foreign counterparts, which allowed us to create a high-quality coating materials based on them [12].

The analysis of experimental data were developed primers and paint formulations based on polymers (Tables 6, 7, 8), which have improved performance characteristics painter.

These formulations have been tested in a climate chamber Feutron 3001/3002-01.

Economic efficiency of the production and use of the pigment due to the use of available technogenic raw materials and a reduction in the cost of building raw materials. The annual economic effect of the utilization of sludge at SRS Bolshetroitskom Mine Ltd. "Belgorod mining company" will be 9,490,000 rubles. using 7.8 thousand tons of pigments in the year (2011).

CONCLUSION

For the development of high-quality pigments from waste (sludge) hydraulic borehole mining of iron ore and paint products based on them:

- The conditions and the regularity of formation of sludge hydraulic mining of high grade iron ore as a man-made raw materials iron oxide pigments;
- Modification of iron oxide pigments for producing ultrafine powders;
- The compositions and the properties of multi-purpose paints derived from iron oxide pigments.

Findings: Theoretically justified the use of sludge (waste) hydraulic borehole rich iron ore, the accumulation of which is the result of the gravitational differentiation of ore in pulpoperiennike with the formation of commercial ore and mud, as the natural iron oxide pigments. The classification of types of natural pigments, based on the geological formation of genetic conditions, the material composition and color shades. The regularities of the formation of pigments in hydraulic borehole sludge, raw materials are iron oxide pigments. According to the content of iron oxide (Fe_2O_3) in the sludge The following types of pigments: iron ochre, ochre.

The nature of the dependence of properties of modified pigments of the time of grinding, the type of surfactant phase and quantitative composition of ultrafine dispersion component in phase. The dependence between the density of the disordered structure in the coagulating sedimentation degree of aggregation and precipitation of particles, which is the density decreases coagulation structure with an increasing number of primary particles. Builders are ranked by efficiency in the following sequence: GMS -3 → Melment → C- 3 → stearic acid.

The effect of stearic acid on the formation of a more developed surface of the grains of pigments and change their shape, which is due to a deeper interaction of molecules of stearic acid with ultrafine particles of iron oxide. Polymineral composition and character of the pigment system characterized by the presence of grains of different habit (isometric, plate, needle), which allows you to create highly filled polystructural dispersion matrix for increasing the hardness, opacity, color intensity and shine of colorful films based on them.

Found that the optimal amount of modifier dispersant corresponds to the capacity of the adsorption layer is determined from experimental adsorption isotherms.

Adsorption iron oxide pigments modification leads to improved rheological properties of polymer dispersions and water (increase of strength, reduction of the effective viscosity, improve dispersibility), which in turn causes the change in opacity, oil absorption and other technical characteristics of the paint and coatings.

We propose a method for improving the quality of iron oxide pigments, which consists in grinding the hydraulic borehole cuttings and chemical additives. It was established experimentally that introduction of dispersants, plasticizers in aqueous suspension iron oxide pigments in the pulverizing step allows to obtain a particle size 1-0,01 microns.

The compositions of paint formulations based on iron oxide pigments from SRS sludge. Established process parameters for obtaining high-quality iron oxide pigments and paints multi-purpose thereof.

The economic impact of production on the basis of iron oxide pigments of paint products with improved technical performance characteristics achieved by reducing the cost of building raw materials iron oxide pigments from the waste hydraulic borehole mining of iron ore.

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