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ON THE SYNTHESIS AND PROPERTIES OF BLACK MAGNETIC IRON OXIDE PIGMENTS

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Abstract. *The authors synthesized a series of magnetites with different magnetic permeability. The technical, optical, and anti-corrosion properties of the pigments were investigated. The authors established the dependance of the hardness of paint and coatings on the magnetic permeability of the pigment.*

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Introduction

Black iron oxide pigment, derived from iron oxide (Fe_3O_4), is a key component in various industries, such as the production of paints and coatings, polymers, and composites. Its unique physicochemical properties, including high hiding power, dispersibility, and resistance to environmental factors, make it indispensable in a wide range of applications.

The relevance of research on black iron oxide pigment is driven by its widespread use in the paint and coatings industry and the production of polymeric materials. In the context of the modern market, the requirements for product quality and environmental sustainability are becoming increasingly stringent. Therefore, the use of inorganic pigments, such as black iron oxide, is particularly significant. The pigment provides the required colour palette and contributes to the improvement of material performance characteristics, such as UV resistance, chemical stability, thermal stability, electrical conductivity, etc. [1–6].

Black iron oxide pigment is a highly functional material. Due to its physicochemical properties, is in high demand in the paint and coatings industry and the development of modern composites. The advantages of the pigment make it essential for the development of new technologies and materials with tailored properties, ensuring steady demand across various industrial sectors [7].

Experimental part

The U-2 instrument was used to determine the impact strength of coatings (GOST 4765-73); the TML pendulum instrument we used to measure the hardness of coatings (GOST 5233-2021); the SF-18 spectrophotometer - to determine the colour of the pigment (GOST R 52662-2006); the KFK-2 - to determine the particle size of the pigment; the Z-1500J impedance metre - to study the anti-corrosion properties of coatings; the Waga torsyjna WT250 torsion balance - to weigh the magnetic pigment.

Main body

The purpose of this work is to synthesise magnetites with different magnetic permeability and study their properties. Currently, black magnetic iron oxide pigments remain insufficiently studied.

To obtain black iron oxide pigment (BIOP) from yellow iron oxide pigment (GOST 12.1.007), reduction of iron from Fe^{3+} is required. Oleic acid (TU 2634-144-44493179-11) can be used as a reducing agent. The production of BIOP occurs at a temperature of 400 °C for 1 hour according to the reaction [3]:

$$216FeOOH + 2C_{17}H_{33}COOH + 51O_2 = 72Fe_3O_4 + 36CO_2 + 34H_2O.$$

During the research, we conducted syntheses of BIOP with different contents of the reducing agent in the system (Table 1).

Table 1. Synthesis formulation of black iron oxide pigment with varying content of the reducing agent (oleic acid).

Component, wt.%	BIOP 1	BIOP 2	BIOP 3	BIOP 4	BIOP 5	BIOP 6	BIOP 7
Oleic acid	37.82	36.62	35.37	34.08	32.73	31.32	29.86
Content of yellow iron oxide pigment, %	62.18	63.38	64.63	65.92	67.27	68.68	70.14
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

To analyse the magnetic properties of the pigment, we used the torsion weighing method. It provides the quantitative assessment of the force of magnetic interaction. The mass of the pigment under study was measured on high-sensitivity torsion balances in the absence of an external magnetic field. Subsequently, we placed a strong magnet under the balance to form an external magnetic field. The mass of the pigment was re-measured in the presence of the strong magnetic field. The difference between the obtained mass values, Δm (with and without the magnet), was calculated. This difference is due to the interaction of the material with the magnetic field, reflecting its paramagnetic, diamagnetic, or ferromagnetic properties.

$$\mu = \frac{m_1 - m_0}{m_1} \cdot 100,$$

where μ is relative magnetic permeability, %.

m_1 is mass of the pigment in the presence of a strong magnetic field, g;

m_0 is mass of the pigment in the absence of a magnetic field, g.

For the obtained BIOP samples, the authors conducted investigations of their technical properties. Table 2 presents the dependance of the pigment properties on the reducing agent content.

Table 2. Technical properties of pigments.

Indicator	Pigment						
	BIOP 1	BIOP 2	BIOP 3	BIOP 4	BIOP 5	BIOP 6	BIOP 7
Oil absorption, g/100g	52	53	48	45	47	47	51
CPV, %	27	27	29	30	30	30	28
Coverage, g/m^2	7.6	7.7	7.6	7.7	7.7	7.9	8
Acid number, mgKOH/g	6.28	4.56	5.02	5.54	3.94	3.53	4.31
Particle size, μm	2.4	3.5	3.7	2.3	3.2	2.9	3.5
Relative magnetic permeability, %	3.85	3.51	3.7	13.82	3.27	3.09	3.57
Content of compound Fe^{3+}, %	79.52	82.66	73.95	76.00	74.46	83.77	87.35

Fig. 1 presents the results of pigment dispersity measurements obtained by sedimentation turbidimetry.

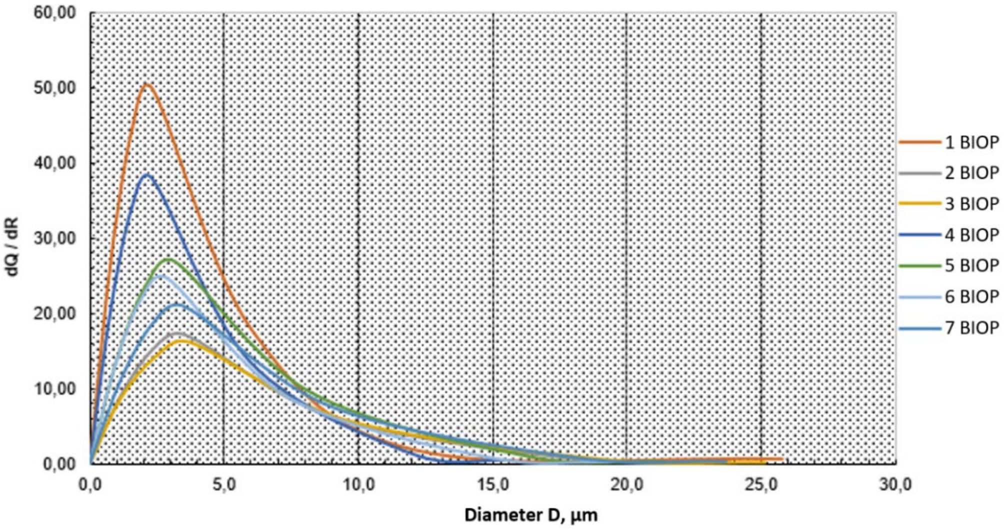

Fig. 1. Differential curve of pigment particle size distribution.

According to Table 2, the pigments have satisfactory oil absorption and the lowest value being characteristic of BIOP 4 at 45 g/100g. The hiding power of the pigments ranges from 7.6 to 8 g/m^2, indicating high values of the parameter. The best hiding power amongst the studied pigments is observed for sample BIOP 1. It is attributed to its narrower particle size distribution. All the pigments show a satisfactory content of Fe^{3+} converted to iron oxide. It correlates to the typical values for iron oxide pigments.

Indeed, an oleic acid content of 34% in the reaction mixture gives the pigment with the best magnetic properties. Its relative magnetic permeability is more than twice that of the other synthesised pigments. Moreover, BIOP 4 demonstrates the narrowest particle size distribution.

During the synthesis, despite the high process temperature (400 °C), traces of oleic acid may remain in the pigment composition. To evaluate this parameter, acid number tests were conducted on the obtained pigment samples. As a result, all BIOP samples have low acid numbers, indicating negligible residual oleic acid content. Furthermore, the acid number values of the samples correlate with the acid content in the reaction mixture according to the synthesis formulations (Table 1).

Studies of the optical properties of BIOPs obtained at different oleic acid concentrations in the reaction mixture during synthesis were conducted. The colour coordinates in the CIELab system [8, 9] and the lightfastness of the pigments in full shade and in a 1:5 tint with zinc white were investigated. Table 3 presents the results.

Table 3. Optical properties of pigments

Indicators	Pigment						
	BIOP 1	BIOP 2	BIOP 3	BIOP 4	BIOP 5	BIOP 6	BIOP 7
In full colour							
Colour coordinates before exposure	L*=27.09 a*=0.93 b*=3.70	L*=26.38 a*=1.27 b*=4.13	L*=27.63 a*=1.03 b*=3.3	L*=28.91 a*=1.21 b*=2.18	L*=26.36 a*=0.84 b*=2.77	L*=25.64 a*=1.04 b*=3.33	L*=28.85 a*=1.10 b*=3.34
Colour coordinates after exposure	L*=27.97 a*=0.80 b*=3.54	L*=27.52 a*= 1.31 b*=4.03	L*=29.36 a*=1.09 b*=3.51	L*=27.91 a*=0.98 b*=4.03	L*=26.20 a*=0.75 b*=3.59	L*=26.52 a*=0.94 b*=3.29	L*=30.31 a*=1.28 b*=3.59
Light resistance of pigment, ΔE	0.90	1.15	1.74	2.12	0.84	1.97	1.80
Lightness difference, ΔL	0.88	1.14	1.73	- 1.00	- 0.16	- 0.88	1.78
In tint							
Colour coordinates before exposure	L*=41.99 a*=0.96 b*=0.18	L*=43.43 a*=2.05 b*= -0.23	L*=43.22 a*=1.52 b*= -0.65	L*=41.41 a*=1.88 b*= 0.46	L*=46.63 a*= 0.92 b*= -1.36	L*=43.17 a*=1.28 b*=-0.73	L*=44.34 a*=1.81 b*= -0.01
Colour coordinates after exposure	L*=41.33 a*=1.16 b*= -0.61	L*=43.20 a*=2.02 b*= -0.44	L*=42.89 a*=1.45 b*= -0.72	L*=41.59 a*=1.97 b*= -0.29	L*=46.60 a*=0.95 b*= -1.41	L*=43.29 a*=1.29 b*= -1.04	L*=44.14 a*=1.81 b*= -0.32
Light resistance of pigment, ΔE	1.05	0.31	0.34	0.26	0.07	0.33	0.37
Lightness difference, ΔL	- 0.66	- 0.23	- 0.33	0.18	- 0.03	0.12	- 0.2

The colour coordinates of all pigment samples are similar in value. However, sample BIOP 7 exhibits a higher lightness value (L). Furthermore, there is a difference in the hues of the BIOP samples: as the reducing agent content increases during pigment synthesis, the redness increases and the yellowness decreases.

The lightfastness of the pigments was investigated by evaluating the total colour difference, ΔE (Table 3). Sample BIOP 5 demonstrated the best lightfastness in the tests. For the other samples, the colour change under UV irradiation ranged from 0.9 to 2.12 ΔE. This phenomenon is likely associated with redox processes within the pigment initiated by UV radiation. Moreover, in coatings prepared as a tint (with zinc oxide), the difference in shades is visible. A decrease in the lightness value was also noted upon UV exposure. It may be attributed to the high photoactivity of zinc oxide and its strong ability to absorb UV rays.

The obtained magnetic pigment samples were incorporated into an ED-20 epoxy resin. We used polyethylene polyamine (PEPA) as a hardener. Coatings with a pigment content of 7.14 wt.% were formed from the filled epoxy compositions, and their properties were studied.

The anticorrosion properties of the filled epoxy coatings were evaluated using electrochemical impedance spectroscopy (EIS) [10]. Table 2 presents the results of the impedance measurements for the epoxy coatings containing the BIOP pigments.

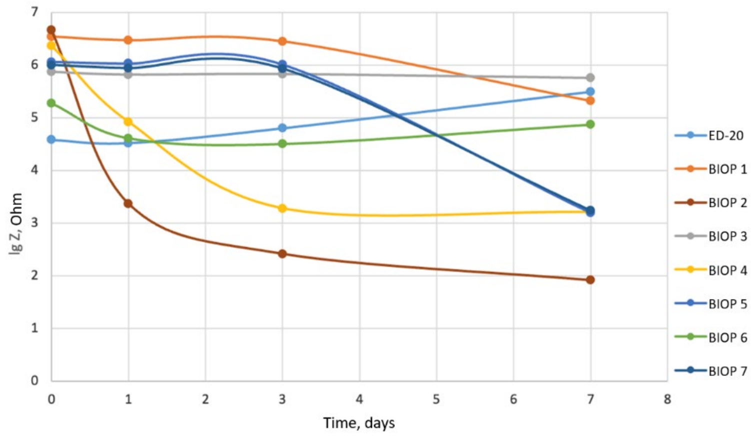

Fig. 2. The change in the impedance value of the coatings upon exposure to the electrolyte solution at a frequency of 56 Hz.

According to Figure 2, the coatings filled with BIOP have higher protective properties at the initial time point compared to the unfilled ED-20 varnish coating. However, for coatings filled with BIOP 4 and BIOP 2, a decrease in anticorrosion properties is observed after just 1 day of exposure to the sodium chloride solution. After three days of exposure, the impedance value remains virtually unchanged. Coatings filled with BIOP 1, BIOP 3, BIOP 5, BIOP 6, and BIOP 7 maintain their initial level of corrosion protection for up to three days of exposure. However, coatings with BIOP 5 and BIOP decrease the protective properties after three days of exposure to the electrolyte solution. Coatings filled with BIOP 1, BIOP 3, and BIOP 6 retain their protective properties throughout the entire observation period.

Fig. 3 presents the results of the study on the influence of magnetic permeability on coating hardness.

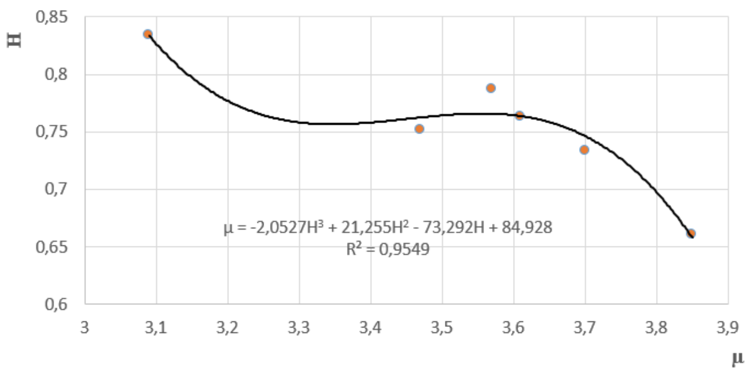

Fig. 3. The dependance of coating hardness on relative magnetic permeability.

According to Figure 3, the relationship between coating hardness and pigment magnetic permeability can be accurately described by the following equation:

$$\mu = -2.0527H^3 + 21.255H^2 - 73.292H + 84.928.$$

An increase in the hardness of the epoxy coatings is observed with an increase in the relative magnetic permeability of the BIOP pigments. Higher magnetic permeability likely leads to the magnetic agglomeration of particles. Under optimal conditions, anisodiametric magnetite particles aline along the force lines of the magnetic field (including that of the Earth). It enhances their reinforcing capability.

To study the compatibility of the obtained BIOP samples with non-polar media (solvents and film formers), microscopic studies were conducted. In a non-polar xylene medium (Figure 4), particles of pigments obtained with a reducing agent content in the reaction mixture of up to 32% are distributed uniformly; the agglomerate size in the bulk does not exceed 20 μm; the number of large agglomerates is low. Increasing of the reducing agent content used in pigment synthesis up to 35% gives the incompatibility of the resulting pigments with xylene: all particles are gathered into large agglomerates. A further increase in the oxidiser content has a positive effect on the compatibility of the obtained pigments with non-polar media: particles of BIOP 1 and BIOP 2 pigments form uniform agglomerates sized 15-50 μm; large agglomerates are absent.

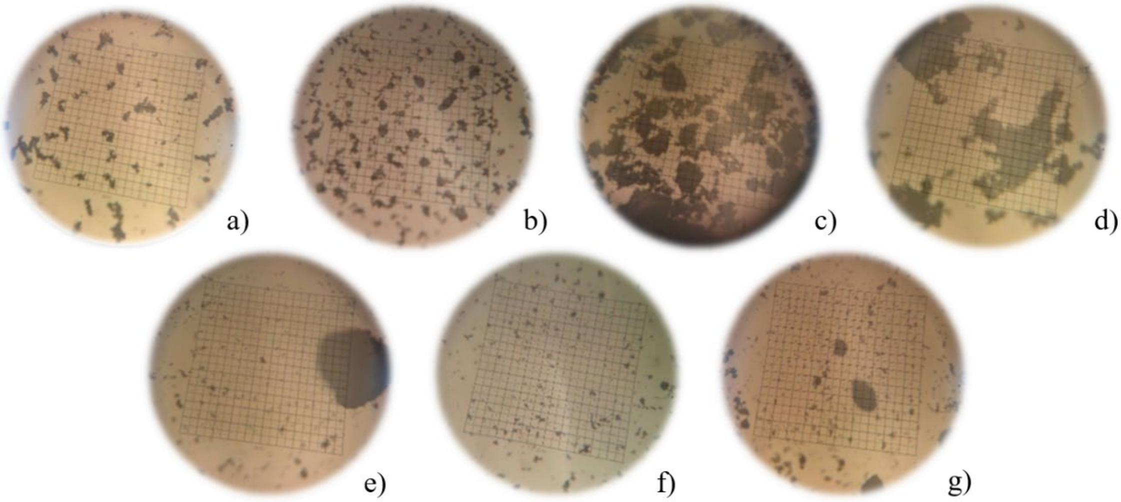

Fig. 4. Microphotographs of pigment suspensions in xylene: a) BIOP 1, b) BIOP 2, c) BIOP 3, d) BIOP 4, e) BIOP 5, f) BIOP 6, g) BIOP 7. The grid cell size is 30 by 30 μm.

An increase in the polarity of the dispersion medium (ED-20 epoxy oligomer) results in a more uniform distribution of the pigment particles (Fig. 5).

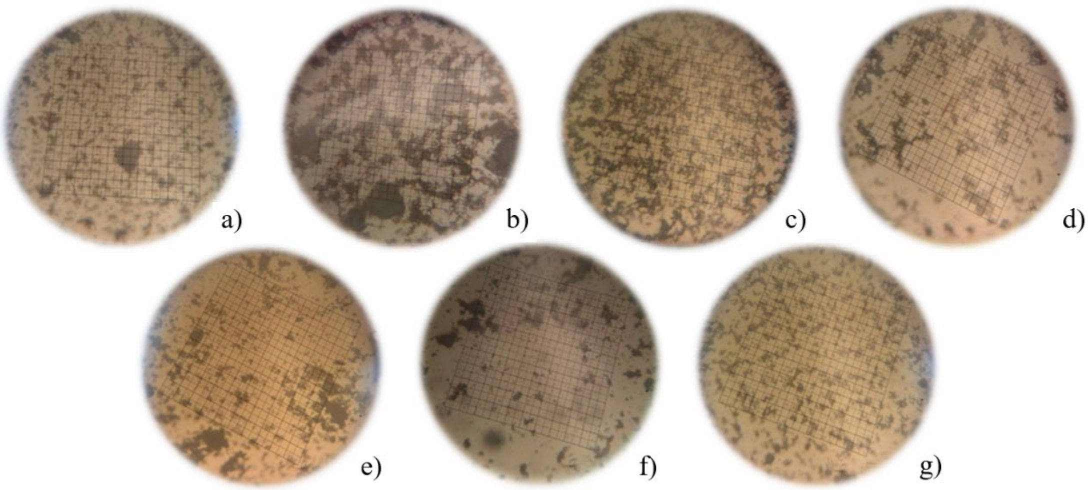

Fig. 5. Micrographs of the ED-20-based coatings containing: a) BIOP 1, b) BIOP 2, c) BIOP 3, d) BIOP 4, e) BIOP 5, f) BIOP 6, g) BIOP 7. The grid cell size is 30 by 30 μm.

According to the micrographs of the filled systems, the epoxy composition filled with BIOP 1 and BIOP 3 exhibits the most uniform distribution of pigment particles within the matrix. It explains the superior anticorrosion properties of the coatings formed from these systems. For the other compositions, the presence of pigment particle agglomerates is observed, particularly in systems containing BIOP 2 and BIOP 4.

Thus, the research results are as follows:

1) A series of black magnetic iron oxide pigments was synthesized. The possibility of controlling color characteristics by varying the amount of reducing agent was demonstrated.

2) The technical properties of the synthesized pigments are not inferior to those of conventional iron oxide pigments.

3) The influence of the magnetic permeability of the black iron oxide pigment on the hardness of the coating formed on the basis of the epoxy oligomer was established.

4) The material is not wetted by polar liquids. It underscores the importance of the correct selection of surfactants and the necessity for further investigation of this issue.

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