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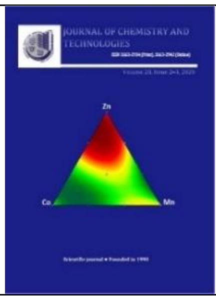

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RESEARCH OF TECHNOLOGICAL PROPERTIES OF PIGMENTS IN THE SYSTEM Fe-Al-Mg-O

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Abstract

Two groups of pigments were obtained by co-precipitation in the Fe-Al-Mg-O system. With the help of experimental studies, the influence of chromophore cations and heat treatment on the color tone, color purity, anti-corrosion properties of pigments in the Fe-Al-Mg-O system was established, which allows further targeted synthesis of pigments of beige, red and yellow colors. It is shown that the main technological properties of pigments are determined by the anionic and cationic composition. Color characteristics are determined by the cation occupying the tetrahedral position in the crystal lattice. For all considered systems, the increase in covalence after heat treatment leads to a shift in color to the long-wavelength region of the spectrum and to an increase in color intensity. The anticorrosive properties of pigments are largely determined by the hydrolysis of the formed compounds. The protective effect is mainly determined by the slowing down of the anodic process. In this case, anions containing aluminum atoms accelerate corrosion processes.

Keywords: pigments; color; color formation; spinel; extract pH; potential

ДОСЛІДЖЕННЯ ТЕХНОЛОГІЧНИХ ВЛАСТИВОСТЕЙ ПІГМЕНТІВ В СИСТЕМІ Fe-Al-Mg-O

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Анотація

Методом співосадження отримані дві групи пігментів в системі Fe-Al-Mg-O. За допомогою експериментальних досліджень встановлено вплив катіонів хромофорів і термообробки на тон та чистоту кольору, антикорозійні властивості пігментів у системі Fe-Al-Mg-O, що дозволяє в подальшому виконувати цілеспрямований синтез пігментів бежевої, червоної і жовтої колірної гами. Показано, що основні технологічні властивості пігментів визначаються аніонним і катіонним складом. Кольорові характеристики визначаються катіоном, який знаходиться в тетраедричному положенні в кристалічній решітці. Для всіх розглянутих систем зростання ковалентності зв'язків після термообробки веде до зсуву кольору в довгохвильову область спектра і до збільшення інтенсивності забарвлення. Антикорозійні властивості пігментів більшою мірою визначаються гідролізом утворених сполук. Захисний ефект в основному визначається уповільненням анодного процесу. Встановлено, що аніони, які містять атоми Алюмінію, прискорюють корозійні процеси.

Ключові слова: пігменти; колір; кольороутворення; шпінель; рН витяжки; потенціал.

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ИССЛЕДОВАНИЕ ТЕХНОЛОГИЧЕСКИХ СВОЙСТВ ПИГМЕНТОВ В СИСТЕМЕ Fe-Al-Mg-O

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Аннотация

Методом соосаждения получены две группы пигментов в системе Fe-Al-Mg-O. С помощью экспериментальных исследований установлено влияние катионов хромофоров и термообработки на цветовой тон, чистоту цвета, антикоррозионные свойства пигментов в системе Fe-Al-Mg-O, что позволяет в дальнейшем выполнять целенаправленный синтез пигментов бежевой, красной и желтой цветовой гаммы. Показано, что основные технологические свойства пигментов определяются анионным и катионным составом. Цветовые характеристики определяются катионом, занимающим тетраэдрическое положение в кристаллической решетке. Для всех рассматриваемых систем возрастание ковалентности после термообработки ведет к сдвигу цвета в длинноволновую область спектра и к увеличению интенсивности окраски. Антикоррозионные свойства пигментов в большей степени определяются гидролизом образованных соединений. Защитный эффект в основном определяется замедлением анодного процесса. При этом анионы, содержащие атомы алюминия, ускоряют коррозионные процессы.

Ключевые слова: пигменты; цвет; цветообразование; шпинель; pH вытяжки; потенциал.

Introduction

Currently, the field of use of materials with a spinel structure is expanding. These are pigments, magnetic carriers, sensors, catalysts, materials for supercapacitors [1–7.].

In the chemical technology of spinel pigments, various methods of producing spinels are currently used. The main one is ceramic technology. The method makes it possible to obtain the final product of a given composition, but it has some drawbacks, therefore, the method of co-precipitation [8; 9] with the use of alkalis and salts is of increasing interest to researchers.

The co-precipitation technology has a number of advantages over the traditional ones and makes it possible to significantly reduce the cost of obtaining refractory materials. Such a process, based on the use of the internal chemical energy of the system, allows synthesis to be carried out at significantly lower temperatures, shorter synthesis times, and low energy costs. The simplicity of the equipment, the possibility of synthesizing large quantities of the product of the required phase and granulometric composition, and the ecological purity of the process also indicate the expediency of using this method.

For many years, attempts have been made to obtain oxide pigments by the low-temperature method [10–14], but systematic studies have not been carried out. The resulting products in most cases are compounds that are poorly reproducible in composition. In this regard, it is of interest to carry out the synthesis in such a mode that would make it possible to obtain pigments with good color characteristics in a finely dispersed state, excluding the laborious stage of grinding.

In addition, at present, the developers of paints and varnishes are faced with the task of replacing toxic anticorrosive chromium-containing and lead-containing pigments that are part of most modern inhibitory-type primers [15–17]. Traditional anticorrosive pigments containing lead or chromium cations are currently limited in use due to their negative impact on humans and the environment [18–22].

An alternative to such pigments is precisely the spinel pigments, including aluminum ferrites, cobalt and nickel aluminates, zinc ferrites, copper ferrites, magnesium aluminates, zinc aluminates, etc. Spinel structures are characterized by high chemical stability, a variety of colors, in some cases by magnetic properties, specific optical and anticorrosive properties [23–25].

Important technological properties of pigments are their optical-color characteristics, which depend on the chromophore ions that make up the structure of the compounds obtained [26–27]. In pigments, including spinels, as is known, the main chromophores are transition metal ions, the use of which also makes it possible to vary the pH of the aqueous extract and thus additionally regulate the anticorrosive properties of the pigments. [28].

The purpose of this work was to study the regularities of the formation of anticorrosive properties, develop compositions for obtaining spinels using the method of co-precipitation and further heat treatment in the Fe-Al-Mg-O system.

Materials and methods

To obtain co-precipitated hydroxides, 0.5 M aqueous solutions of iron (II) sulfate, aluminum sulfate, and magnesium sulfate were used. Sodium hydroxide was used as a precipitant. The ratio of cations was varied in accordance with Table 1. The obtained hydroxides were washed and dried at a temperature of 60 °C, and then calcined at a temperature of 800 °C.

The pH of aqueous extracts of pigments was determined using a laboratory pH-meter pH-150 MI with a combined glass electrode. The procedure for preparing an aqueous extract of the pigment is as follows: 15 g of the pigment was placed in a 150–300 ml beaker, 50 ml of distilled water was added, heated to boiling and boiled for 30 min. The suspension was cooled, filtered. Then it was quantitatively transferred into a volumetric flask and the volume was brought up to 50 ml with distilled water [29]. The main technological characteristics were determined both for dried samples and for those calcined at a temperature of 800 °C.

The anticorrosive activity of pigments was assessed by the potentiodynamic method by comparing the anodic and cathodic polarization curves, as well as the curves of potentials and corrosion currents calculated on the basis of the Tafel sections of curves. Polarization curves were obtained on a setup consisting of a Potentiostat / Galvanostat / ZRA Gamry potentiostat connected to a PC using the Gamry Framework program. Scan rate of potential 50 mV/s. As a working electrode, we used plates of St. 3 steel with an area of 1 cm^2. Before the experiment, the electrodes were polished, degreased, kept in a HCl solution (1 : 1 vol.) for a minute. A platinum wire served as an auxiliary electrode.

Electrode potentials were measured relative to a saturated silver-silver chloride electrode. The experiment temperature was 298 ± 1K.

The degree of protection was determined by the formula:

$$z = \left(\frac{I_0 - I_{pig}}{I_0} \right) \times 100, \qquad (1)$$

where: z – degree of protection, %;

I_0 — corrosion current in the background solution, A/cm^2;

I_{pig} – corrosion current in a water extract, A/cm^2.

X-ray diffraction patterns of pigments were obtained on a DRON-2.0 device in monochromatic copper radiation with a nickel filter. The determination of color characteristics and color purity was carried out using an FKTsSh-M color comparator.

The measurement results were processed using the simplex-lattice planning method. When studying the properties of a mixture, depending on the content of components in it, the factor space was presented in the form of a correct (q-1) - dimensional simplex. In order to study the dependence of the indicated physicochemical and optical characteristics of pigments on the composition and temperature of annealing of pigments using the simplex-lattice planning method, corresponding experiments were carried out. The response surface on the "composition-property" diagrams was depicted using isolines, which were performed using mathematical models.

Results and discussion

The results of measuring the characteristics of pigments in the Fe-Al-Co-O systems before and after annealing are shown in Table 1 and in Fig. 1 and 2.

Table 1

Color characteristics of Fe-Al-Mg-O pigments before and after calcination

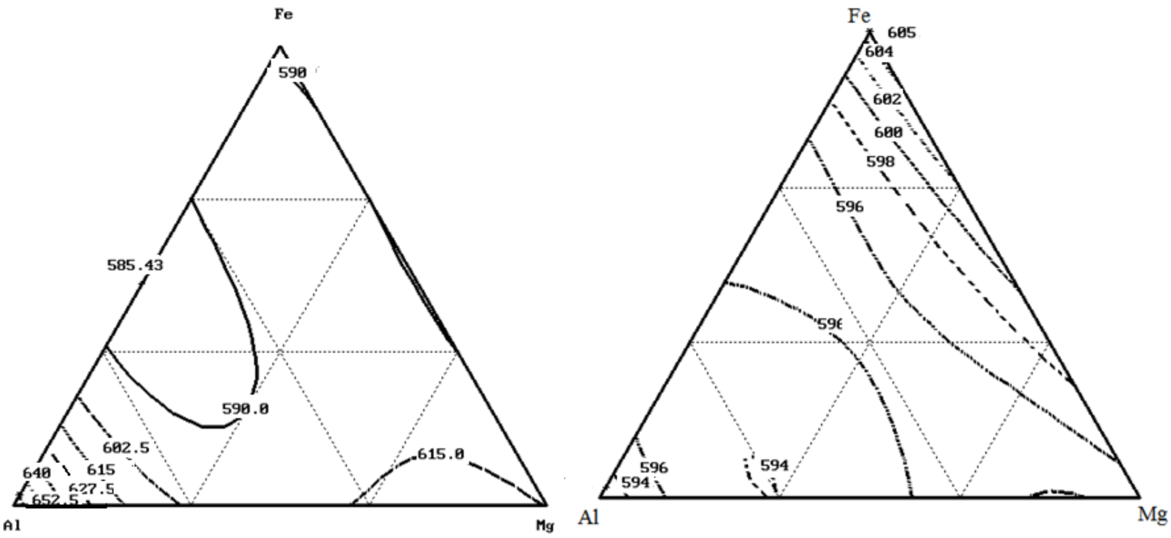
№	composition			DRC, %	λ,nm	P,%	DRC, %	λ, nm	P, %
	Fe_2O_3	Al_2O_3	MgO		uncalcined			calcined	
1	1			36.49	588	69	12.76	630	10
2	1/3	2/3		33.24	596	40	24.47	601	45
3	2/3	1/3		33.85	599	50	20.66	602	45
4		1		94.25	700	1	85.85	700	0
5		1/3	2/3	62.68	605	10	12.12	579	1
6		2/3	1/3	79.97	700	5	19.16	400	1
7			1	26.15	591	15	10.61	500′	0
8	2/3		1/3	18.76	595	30	9.48	510′	0
9	1/3		2/3	28.33	596	40	9.34	560′	1
10	1/3	1/3	1/3	25.23	595	35	10.19	499	4

*** DRC - diffuse reflection coefficient, % ; λ -wavelength, nm; P – purity, %**

The characteristics of the synthesized compositions are given in Table 1. The dependence of the color indicators presented in the form of composition-property diagrams is shown in Fig. 1–3.

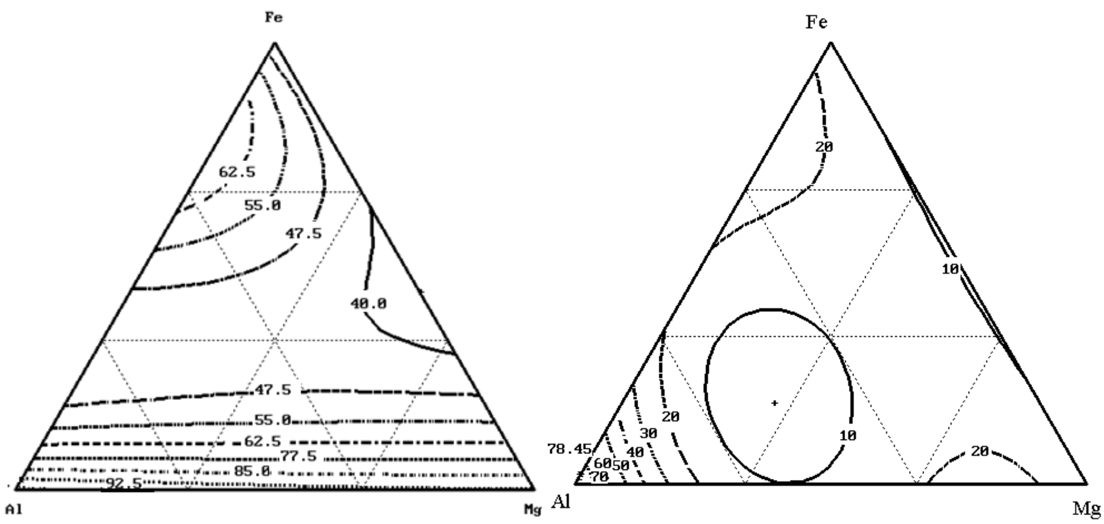
Analyzing the data obtained, it can be said that the color is due to the phase composition of the resulting hydroxides and oxyhydroxides, as well as the treatment temperature of the compositions. The yellow color of sample No. 1 corresponds to the formation of iron oxyhydroxide. The change in the saturation of the yellow color along the Fe-Al side of the triangle depends on the aluminum content. Moreover, color formation occurs according to the law of additivity. The presence of aluminum leads to the formation of solid solutions of iron and aluminum oxyhydroxides. Composition 4 corresponds to the formation of white aluminum hydroxide. Samples 5 and 6 correspond to different magnesium content and predetermine the beige and milk colors of the products formed.

Magnesium hydroxide has a milky color - the wavelength of 591 nm corresponds to the yellow-green part of the spectrum. Combinations of magnesium and iron give brown colors, the dominant wavelength of which (596 nm) corresponds to the red region of the spectrum. The increase in iron content gives the pigment a dark brown color. The composition corresponding to the triple point (Fe - Al - Mg) is also brown.



a) b)

Fig. 1 Color characteristics of pigments of the Fe-Al-Mg-O system
a) treatment temperature 60 °C b) treatment temperature 800 °C



a) b)

Fig. 2 RC of pigments of the Fe-Al-Mg-O system a) treatment temperature 60 ° C b) treatment temperature 800 °C

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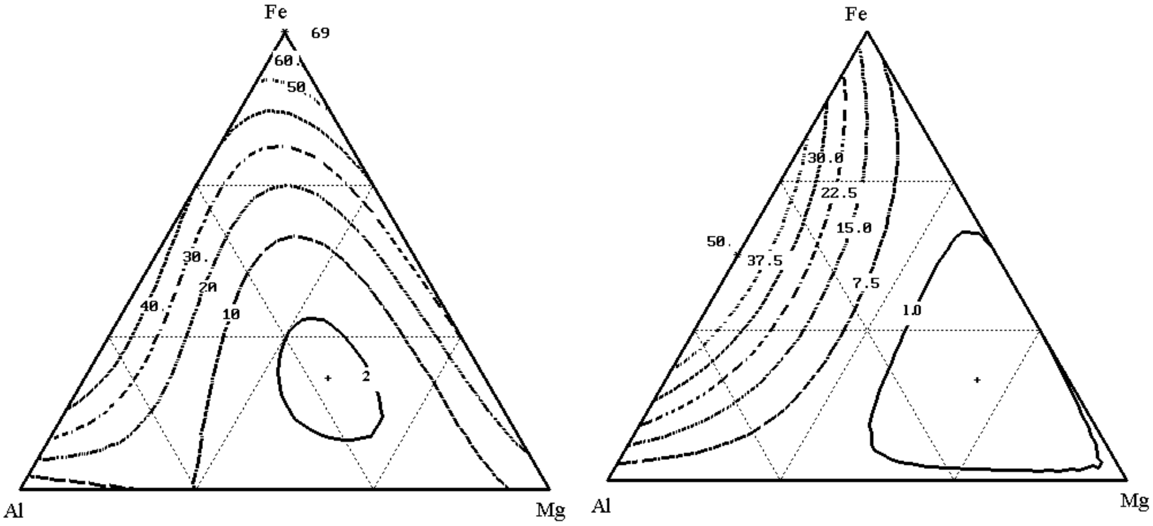
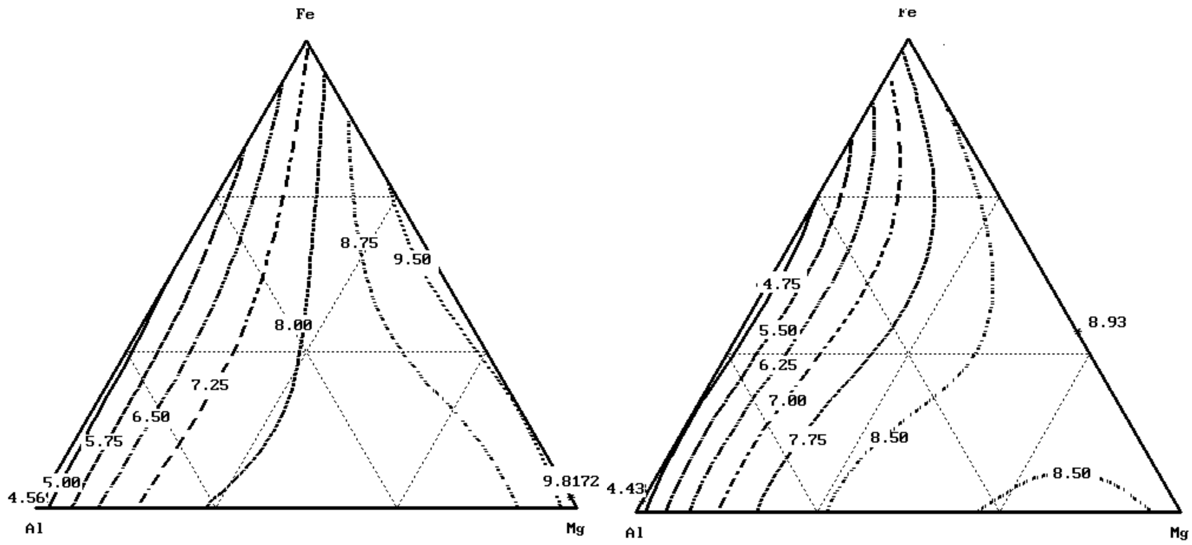


a) b)

Fig. 3. Color purity of pigments of the Fe-Al-Mg-O system a) treatment temperature 60 ° C b) treatment temperature 800 °C



a) b)

Fig. 4. pH of the aqueous extract of pigments of the Fe-Al-Mg-O system a) treatment temperature 25 ° C b) treatment temperature 100 °C

The highest DRC (diffuse reflection coefficient) indicates high gloss values for sample 4 (94.25–94.62). Using the simplex lattice planning method, the positive influence of aluminum on the gloss of pigments was revealed. It was found that iron (III) oxyhydroxide with Mg and Al cations form compositions with a color purity of approximately 20–25 % more than the original. To study the effect of heat treatment, the pigments were calcined at 780–800 °C. After calcination, color formation occurs in accordance with the formation of spinel compounds. The brightness and gloss index decreased, but remained rather high for pigments of the Fe-Al-O system, which include aluminum (2/3 Al – 24.47 ... 24.24 %; 1/3 Al – 20.66 ... 20.52 %). As the color purity increases, the reflectance also increases.

During heat treatment of two-component pigments, the color tone changed: in combinations with aluminum it increased (579–630 nm), in combinations with iron it decreased (400–560 nm). An increase in covalence after heat treatment leads to a shift in color to longer wavelengths and to an increase in color intensity. For example, the total presence of iron and aluminum in the solution resulted in the terracotta red color of the pigments. The pigments, which included iron and magnesium, changed from yellow to orange. Combinations of aluminum with magnesium had a beige tint. The degree of color saturation of a pigment is determined by its color purity. The color purity remained high only in pigments that included iron and aluminum (P = 45 %).

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Spinel pigments are classified as anodic inhibitors that impede the process of metal ionization, forming passivating films on the surface of the anodic areas that isolate the surface. It is assumed that the corrosion inhibiting process in the presence of spinel compounds is associated with their hydrolysis, leading to an increase in pH under the pigmented paintwork. In addition, ferrites enhance the barrier to diffusion of water and oxygen due to the formation of complexes with acidic groups of film-forming agents.

The anticorrosive activity of the pigments was determined by comparing the anodic polarization curves. Comparison of the anticorrosive properties of pigments obtained by calcining and dried with the same ratio of components makes it possible to assess the contribution to the anticorrosive effect of the pH of the aqueous extract, and the electrochemical component due to the presence of hydrolyzing spinels (Table 2).

Table 2

Composition of pigments of the Fe-Al-Mg-O system and their characteristics

№ п/п	pH	z,%	χ, $Ohm^{-1}\ m^{-1}$	φ, mV	pH	z,%	χ, $Ohm^{-1}\ m^{-1}$	φ, mV
	uncalcined				calcined			
1.	4.95	63.21	5.56	–371	6.56	66.78	4.20	–458
3.	6.68	69.88	5.82	–268	7.41	25.88	4.95	–503
2,	7.9	79.81	5.62	–251	7.09	33.00	4.13	–493
4.	4.45	55.08	5.27	–438	7.04	39.36	4.10	15
6.	8.35	69.88	5.27	–148	9.13	63.16	3.96	116,3
5.	8.34	59.35	5.5	–255	10.68	88.93	3.49	37
7.	10.14	63.23	5.27	–108	10.69	95.89	1.19	98
9.	9.00	63.21	5.21	–125	10.8	95.02	4.03	–38
8.	8.95	86.47	5.21	–165	10.00	39.36	4.17	2
10	8.53	63.21	5.38	–168	7.28	69.85	3.99	–58

*** pH - pH of the aqueous extract; z - protective effect,%; χ - electrical conductivity, $Ohm^{-1}\ m^{-1}$; φ - corrosion potential, mV**

Analysis of Figures 5a and 5b shows that low corrosion potentials correspond to high pH values, i.e. the anticorrosive effect is explained by the action of the formed spinels $MgAl_2O_4$, $FeAl_2O_4$; it is the formation of high-temperature aluminates from co-precipitated aluminum and iron or magnesium hydroxides that provides a high protective effect.

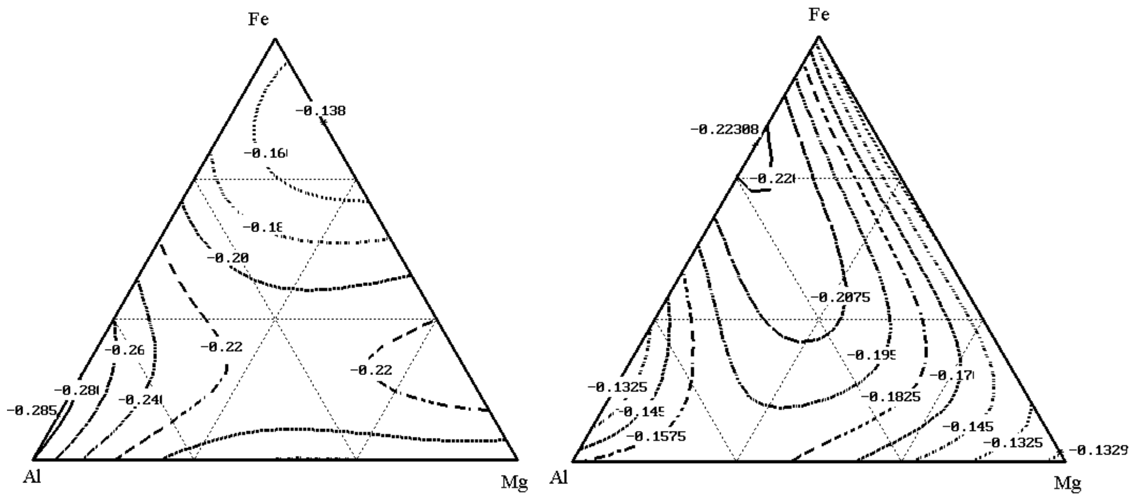

Fig. 5. Steel corrosion potential of a) Fe-Al-Mg-O system, treatment temperature 60 ° C b)) Fe-Al-Mg-O system, treatment temperature 800 °C

The potential and rate of corrosion of steel in solutions prepared from extracts of the studied powder pigments depends both on the nature and composition of these pigments and on the method of their treatment.

Table 2 shows the results obtained by processing the polarization curves for aqueous extracts of calcined powder pigments, consisting of Fe, Mg, Al in different ratios. Composition No. 2 (1/3 Fe and 2/3 Mg) has the greatest inhibitory effect, as evidenced by a more positive potential for the onset of corrosion (-0.2 V). Compositions No. 4, 5, 9 differ in approximately the same action.

Solutions No. 7, 8, 1 have the least inhibitory effect. After calcination, the nature of the dependence changes somewhat. The potentials of the onset of corrosion shift towards more positive potentials, which indicates an improvement in the inhibitory effect. The lowest corrosion rate is observed for composition No. 4 (100% Mg). A high inhibitory effect is observed for compositions No. 5, 3.

Conclusions

The synthesis of composite oxides, including ferrites, by combination of corresponding salts, followed by co-precipitation and heat treatment makes it possible to obtain promising materials. The conducted studies allow us to conclude that dispersed composite hydroxides and oxides are effective anticorrosive pigments with a color gamut in the range of white yellow brown for hydroxides, and white terracotta crimson for complex oxides. In addition, the combination of various colors and anticorrosive activity of complex oxides makes it possible to use them as effective fillers for paints and varnishes.

The main technological properties of pigments are determined by the anionic and cationic composition. Color characteristics are determined by the cation occupying the tetrahedral position in the crystal lattice. For all considered systems, an increase in covalence after heat treatment leads to a shift in color to the long-wavelength region of the spectrum and to an increase in color intensity. The anticorrosive properties of uncalcined pigments are largely determined by the presence of hydroxyl ions formed as a result of hydrolysis of compounds. The greatest effect is observed in the case of using metal compounds, the dissociation constants of which differ significantly. In the case of calcined pigments, the properties depend on the anionic composition. Spinels, garnets, ferrites, the hydrolysis of which passes through the anion, have a low protective effect even in the presence of alkaline earth cations in tetrahedral positions. The protective effect is mainly determined by the deceleration of the anodic process. In this case, anions containing aluminum atoms accelerate corrosion processes.

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