Синтез керамічних пігментів традиційно здійснюється при високій температурі (не нижче 1200 °С). Для її зниження використовують мінералізуючі добавки, які мають різний механізм дії на вихідні компоненти пігментних шихт. Ефективність дії мінералізаторів визначається їх природою, вмістом, ступенем диспергування в реагенті, який активується. Отже, пошук найбільш ефективних мінералізаторів при синтезі, зокрема, силікатно-шпінельних керамічних пігментів має важливе наукове та практичне значення.

Досліджено дію різних мінералізуючих добавок (B_2O_3, $Na_2B_4O_7$, Na_2O, NaF) на процеси формування кристалофазового складу шлаквмісних керамічних пігментів і зміну їх колірних показників. Встановлена пряма залежність між температурою плавлення мінералізаторів та ефективністю їх впливу на утворення шпінельних фаз, які виступають носіями кольору в таких пігментах. Відчутний ефект від введення натрію фториду, що має найвищу температуру плавлення серед дослідних добавок, досягається в результаті випалу пігментів при температурі не нижче 1150 °С. Дія натрію оксиду ефективна починаючи з температури 1100 °С. Найбільш доцільно застосовувати борвмісні сполуки. Їх введення дозволяє знизити температуру випалу шлаквмісних пігментів до 1050 °С при повному зв'язуванні вихідних компонентів в шпінельні тверді розчини. Синтезовані при цьому керамічні пігменти забезпечують формування глазурних покриттів, які за якісними показниками не поступаються покриттям, отриманим з додаванням високотемпературних пігментів (температура випалу 1200–1250 °С). На утворення силікатних фаз (діопсиду і воластоніту), які не є носіями кольору в дослідних пігментах, ефективну мінералізуючу дію чинять добавки NaF і B_2O_3

Ключові слова: керамічні пігменти, мінералізатори, випал, кристалофазовий склад, колірні показники, глазурні покриття

UDC 666.291
DOI: 10.15587/1729-4061.2020.196725

PATTERNS IN THE SYNTHESIS PROCESSES AND THE CHARACTERISTICS OF SILICATE-SPINAL CERAMIC PIGMENTS WHEN INTRODUCING MINERALIZERS

O. Zaichuk
Doctor of Technical Sciences, Associate Professor*
E-mail: zaychuk_av@ukr.net
A. Amelina
PhD*
E-mail amelinaalex1@gmail.com
O. Khomenko
PhD, Associate Professor*
E-mail: elenahtks@ukr.net
N. Sribniak
PhD, Associate Professor**
E-mail: nataliia.sribniak@snau.edu.ua
L. Tsyhanenko
PhD, Associate Professor**
E-mail: liudmyla.tsyhanenko@snau.edu.ua
O. Savchenko
PhD**
E-mail: savushka.sumy@gmail.com
O. Telichenko
Senior Lecturer
Department of Construction Operations***
E-mail: olexander.telichenko@snau.edu.ua
*Department of Chemical Technology of Ceramics, Glass and Building Materials
Ukrainian State University of Chemical Technology
Gagarina ave., 8, Dnipro, Ukraine, 49005
Department of Building Structures*
***Sumy National Agrarian University
Herasyma Kondratieva str., 160, Sumy, Ukraine, 40021

Received date 02.01.2020
Accepted date 13.02.2020
Published date 28.02.2020

1. Introduction

Ceramic pigments are the most widespread and effective dyes when obtaining glazed ceramic, enameled metallic, and glass articles. The base of the structure of ceramic pigments is the sTable colored crystalline compounds in the form of spinel, silicates, willemites, solid solutions such as corundum, phosphates, molybdates, tungstate, vanadate, etc. The use of pigments is associated with high-temperature processes, so they must exhibit thermal and chemical stability. While in the fine-dispersed state, these dyes cause selective absorption and dispersion of light, due to which a glass layer becomes opaque and acquires the color that complements the absorbed color [1].

Ceramic pigments are mostly obtained by solid-phase synthesis at high temperatures from chemically pure reagents. That is why the main trends in the development of the production of ceramic pigments are to extend the base of raw materials and to reduce the temperature of their synthesis. At present, there is a significant scientific and practical

experience of obtaining ceramic pigments using a wide spectrum of anthropogenic raw materials [2–4]. The use of anthropogenic raw materials containing the structure-forming and coloring oxides in order to obtain the pigments would reduce the cost of their production, partly to ensure the recycling of industrial waste. In this case, the qualitative indicators of the obtained dyes often are not inferior, and sometimes superior, to the quality of materials synthesized from conventional, technically pure and natural raw components. At the same time, the firing temperature of such pigments remains quite high and is in the interval of 1,200–1,300 °C [5–7].

In the intensification of solid-phase reactions of the synthesis of ceramic pigments, an important role belongs to mineralizers. The effectiveness of the mineralizers is determined by their nature, content, degree of dispersion in the activated reagent. Therefore, it is a relevant task to study the comparative influence of different mineralizers on the processes of synthesis of ceramic pigments, in particular silicate-spinel. The spinel and silicate pigments are the most common among the available variety of ceramic dyes.

2. Literature review and problem statement

Reducing the temperature of the synthesis of ceramic pigments implies the use of various mineralized additives. Mineralizers can, at low temperatures, to form a liquid phase (melt), which significantly affects the crystalline lattice of starting raw materials. This decreases the strength of the crystalline lattice and its transfer to an active state, as well as the increase in the collision surface between the reagents particles, diffusion rate, and the entire process in general [1].

A wide range of compounds is used as mineralizers in pigment technology.

The authors of [8, 9] argue that the introduction of boron oxide into the system leads to the emergence of melt at a relatively low temperature and contributes to the transfer of the crystal structure into an active state, without destroying it.

Using B_2O_3 can also intensify the chromophore properties of ceramic pigments. Moreover, for the effective progress of solid-phase reactions, the amount of the liquid phase in the system should be, if possible, small, because its excess can negatively affect the chromophore properties of ceramic pigments and causes their strong sintering. At the same time, the insufficient content of the liquid phase causes poor wetting of the particulate matter and its subsequent merging, which results in a slower reaction speed in the solid phase [10, 11].

The increase in the purity and intensity of green coloration of uvarovite pigments by the equimolecular replacement of free silicon dioxide in their composition with phosphorus (*V*) oxide was established in paper [12]. The authors noted the introduction of P_2O_5 into the structure of the mineral uvarovite in the form of tetrahedrons $[PO_4]^{3-}$ and a decrease in the firing temperature to 1,100–1,150 °C. At the same time, a considerable effect is achieved with the introduction of a significant amount of P_2O_5 (exceeding 7 % by weight).

The strong impact on the stability of the crystalline lattice of pigments is exerted by the compounds of fluorine and alkali metals.

The authors of [13, 14] argue that the mineralizing effect of fluorine-ions, in particular on silicate pigments, is explained by the fact that they increase the reactivity of the crystalline lattice of the material by weakening the silicon-oxygen frame. This provides for the possibility of diffusion processes in the region of low temperatures, 1,100–1,150 °C.

Effective modifiers of the structure of pigments also include the additives of alkali metal oxides.

In [15], a sol-gel method was used to synthesize a pigment with the structure of olivine (Co_2SiO_4). However, despite the presence of mineralizers (NaCl and KCl), the temperature of pigment synthesis remained high and amounted to 1,200 °C.

It is shown in [16] that LiCl contributes to the transition of the tetragonal form of $Nd_2Si_2O_7$ into monoclinic at a relatively low temperature of pigment thermal treatment (1,100 °C), thereby improving the color indicators. However, it may reduce their temperature resistance.

Thus, the choice of a mineralizer is crucial for the activation of solid-phase reactions during the synthesis of ceramic pigments. At the same time, the lack of detailed studies of the comparative influence of certain mineralized additives on the characteristics of ceramic pigments, specifically spinel and silicate, necessitated our research in this field.

3. The aim and objectives of the study

The aim of this study is to determine patterns in the processes of mineral formation and changing the color indicators of silicate-spinel ceramic pigments when introducing mineralizing additives. This would make it possible to choose the most effective mineralizing additives, thereby significantly reducing the firing temperature of the pigments of a given type.

To accomplish the aim, the following tasks have been set:

– to determine the influence of the nature and content of mineralizing additives on the color indicators of slag-containing silicate-spinel pigments and glass coatings at their introduction;

– to establish features in the formation of the crystal-phase composition of the examined pigments in interrelation with the basic technological factors of their manufacture.

4. Materials and methods to study ceramic pigments with the additives of mineralizers

The examined pigments' main component was the dump open-hearth slag from one of the metallurgical enterprises in the city of Dnipro (Ukraine), which was preliminary magnetically enriched and averaged. In order to obtain brown color, we additionally injected oxides of chromium and nickel; black color – chromium and cobalt oxides in the total amount of up to 23 % by weight.

The formulations of slag-containing pigments that we devised and reported in earlier studies [17, 18] provide for high-quality glass coatings.

The additives of mineralizers involved the introduction to the ground pigment charges of orthoboric acid (H_3BO_3), sodium tetraborate, hydrate ($Na_2B_4O_7{\cdot}10H_2O$), sodium carbonate (Na_2CO_3), sodium fluoride (NaF). Their amount was 2.0 and 4.0 mass fractions in recalculation for B_2O_3, $Na_2B_4O_7$, Na_2O, and NaF, respectively.

Pigment charges were prepared by the joint wet grinding of starting raw components. The moisture content of the prepared suspensions was 35 %. Dried to a residual moisture content of 1 %, the pigment charges were fired in an electric

furnace in the temperature range 1,050–1,150 °C with aging over 1 hour. The ready pigments were finely ground, adding water to a humidity of 35 %. The dispersion of pigments was characterized by the residue on control sieve No. 0056, which should not exceed 0.4 %. The prepared pigments were dried to the humidity not larger than 0.8 %. To obtain colored glass coatings, the synthesized pigments were injected to the ground transparent fritted glaze, intended for the application onto ceramic tiles, in an amount of 8 % by weight. The glaze coatings were fired at a temperature of 1,100 °C.

The color indicators of the developed pigments and the glass coatings containing them were studied at the colorimetric device KTs-3. For the brown pigments of series 1.2d, we determined the color indicators (color tone (dominating wavelength – λ), color purity – *P*, lightness – *L*). For the black pigments of series 8d, we determined only the lightness indicator, which in this case characterizes the degree of blackness of the body. The crystal-phase composition of the pigments was determined by X-ray phase analysis at the diffractometer DRON-3.0 in the Cu-Kα radiation.

5. Results of studying ceramic pigments with the additives of mineralizers

5. 1. Results of studying the color indicators of the slag-containing pigments

The objects of our study are the ceramic pigments, synthesized in the system open-hearth slag–Cr_2O_3–NiO (dark brown 1.2d) [17], and open-hearth slag– Cr_2O_3–CoO (black 8d) [18]. A temperature range of 1,200–1,250 °C is the most rational for firing such pigments; it enables the formation of the assigned mineralogical composition in combination with Table color indicators.

To obtain the slag-containing pigments at a lower temperature, it is necessary to bring their crystalline lattice to a more active state by the additional introduction to their composition of the mineralizers. We studied various additives containing boron oxide, alkaline oxide Na_2O, and fluoride-ions. Their characteristic is given in Table 1.

The mineralizers were injected into the ground charge of the examined pigments. Synthesis of the obtained compositions was performed in a temperature range of 1,050–1,150 °C.

The dependences of color indicators of pigments on the nature and amount of the introduced mineralizers at different firing temperatures are given in the form of graphic charts in Fig. 1–3. For the black pigments of series 8d, we determined only the indicator of.

The result of our study has established that sodium fluoride has an effective mineralizing effect on the components of the examined pigment charges only at the firing temperature 1,150 °C. This fact was confirmed by a visual assessment of the color of the pigments obtained, as well as the values of their color indicators. The pigment's color 1.2d under an increase in the temperature of its synthesis from 1,100 to 1,150 °C changes from brown to dark brown. The value of the dominant wavelength, in this case, is shifted from the orange (595–612 nm) to the red (620–645 nm) region of the spectrum. The lightness indicator *L* decreases in total from 13.0–14.9 % to 11.8–12.8 %. The color purity also decreases (from 7–15 to 5–7 %).

For the 8d pigment, the color changes from dark gray to black. The *L* indicator is reduced from 10.3–11.6 % to 9.7–10.2 %.

Table 1

Mineralizers characteristic [19]

Compound chemical formula	Compound title	Color and crystalline shape	Temperature, °C		Water solubility, g/100 cm^3	
			melting	boiling	at 20 °C	at 100 °C
H_3BO_3	Orthoboric acid	colorless hexagonal or triclinic	185 decomposes	–	2.7^0	39
B_2O_3	Boron oxide	colorless cubic or hexagonal	450	>1,700	1.1^0	15.7
B_2O_3	Boron oxide	vitreous	577	–	poorly soluble	soluble
$Na_2B_4O_7{\cdot}10H_2O$	Sodium tetraborate, hydrate	colorless monoclinic	75	$-10H_2O$>200	2.12^0	22.0^{50}
$Na_2B_4O_7$	Sodium tetraborate	colorless crystalline	742	1575 decomposes	1.11^0	52.5
Na_2CO_3	Sodium carbonate	white, crystalline	854	decomposes	21.5	soluble
NaF	Sodium fluoride	colorless cubic	1,040	1,705	4.28	4.96^{94}

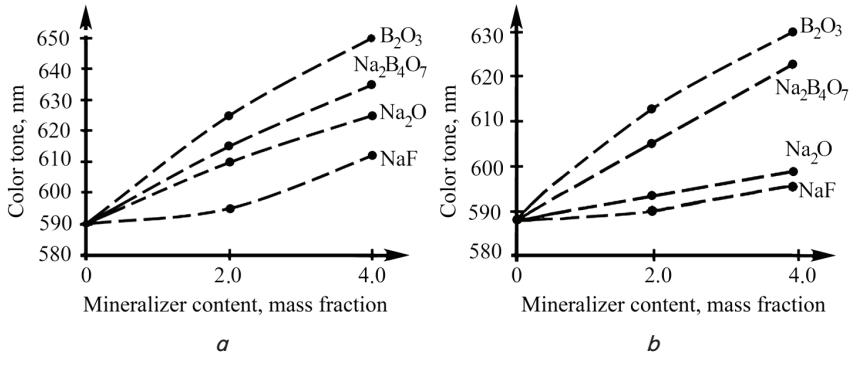
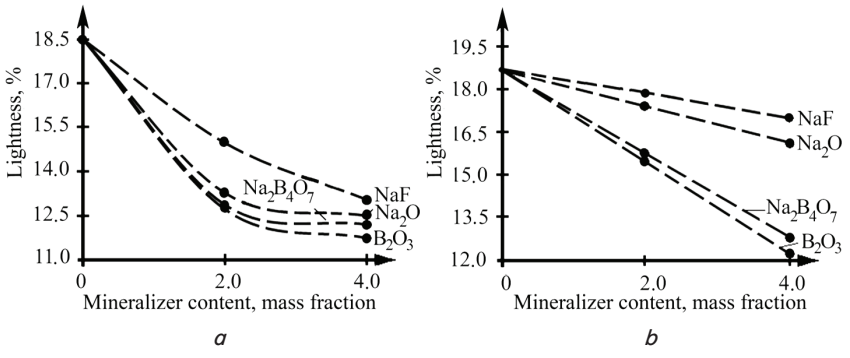
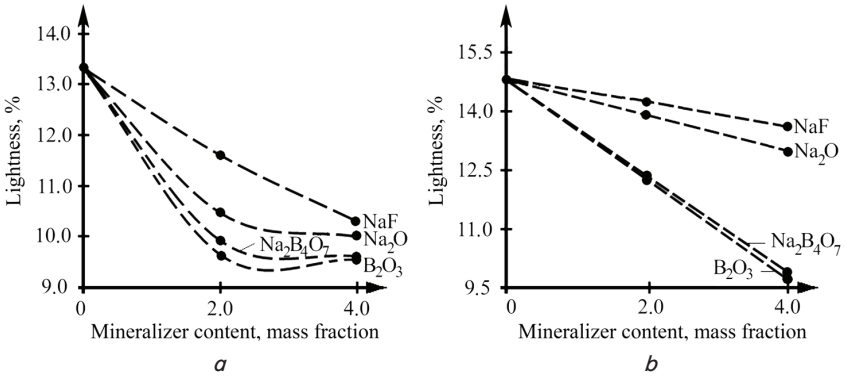


Fig. 1. Color tone dependence (nm) of the examined pigments of series 1.2d on the nature and content of the mineralizers fired at temperature: *a* – 1,100 °C; *b* – 1,050 °C



a *b*

Fig. 2. Lightness dependence (%) of the examined pigments of series 1.2d on the nature and content of the mineralizers fired at temperature: *a* – 1,100 °C; *b* – 1,050 °C



a *b*

Fig. 3. Lightness dependence (%) of the examined pigments of series 8d on the nature and content of the mineralizers fired at temperature: *a* – 1,100 °C; *b* – 1,050 °C

The pigments synthesized at a temperature of 1,150 °C with the addition of Na_2CO_3, $Na_2B_4O_7{\cdot}10H_2O$, especially H_3BO_3, were in the sintered form, which made it difficult to grind them. They were not used to determine the color indicators.

Increasing the firing temperature of the pigments, which contained sodium oxide as a mineralizing additive, to 1,100 °C and increasing the concentration of Na_2O to 4 mass fractions form the dark brown and black coloration of compositions from series 1.2d and 8d, respectively. Consequently, the chrome-nickel pigment 1.2d demonstrates a shift of λ from the orange (599–610 nm) to a longer wave area of the visible region of the spectrum – red (625 nm) – Fig. 1, *a*. This is also accompanied by a decrease in the values of *L* from 13.2–16.1 % (Fig. 2, *a*) to 12.5 %; and *P*, from 8–16 % to 7 %, respectively. The synthesized chrome-cobalt pigment 8d is characterized by the enlarged degree of blackness (*L* falls to 10.0 %) – Fig. 3, *a*.

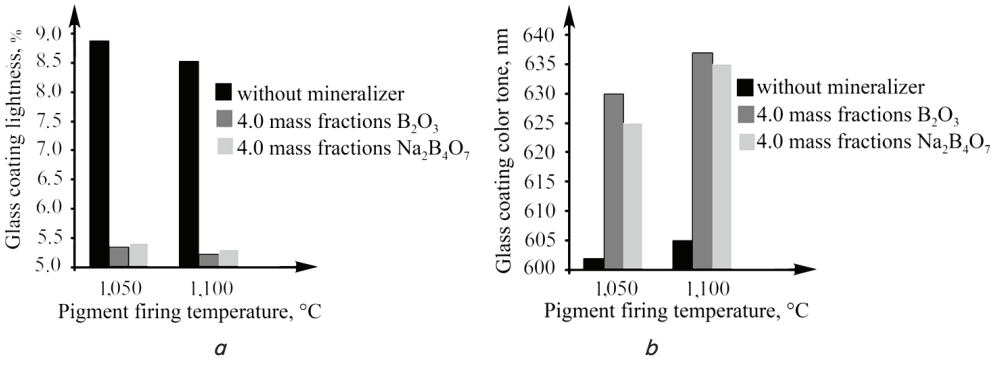
More substantial changes in the color indicators (color tone – Fig. 1, and lightness – Fig. 2, 3) of the examined pigments occur at the introduction of boron-containing compounds (H_3BO_3, $Na_2B_4O_7{\cdot}10H_2O$). This allows us to assert that such compounds are the most effective mineralizing additives in the examined systems. The most effective mineralizing additives in the examined systems are the boron-containing compounds. Their introduction makes it possible to lower the firing temperature of the slag-containing pigments B_2O_3 or $Na_2B_4O_7$) to 2 mass fractions at a synthesis temperature of 1,100 °C. Such pigments, in terms of their qualitative parameters, are not inferior to the pigments fired at 1,200–1,250 °C. The values of color tone for the pigments from series 1.2d in this case are within 625–630 nm (Fig. 1) and correspond to the red region of the spectrum, lightness – 12.2–12.7 % (Fig. 2), and the color purity is 7 %. The ceramic pigment from series 8d in turn, after firing in the interval 1,050–1,100 °C, is characterized by a high degree of blackness (*L*=9.5–9.7 %) – Fig. 3.

The pigments with boron-containing mineralizing additives were injected into the composition of transparent fritted glaze in the amount of 8 mass fractions followed by the firing of coatings at a maximum temperature of 1,100 °C.

The dependence of color indicators of the obtained glass coatings on the amount of boron-containing additives, introduced to the pigments, is shown in Fig. 4 and Fig. 5.

It was established experimentally that the dynamics of change in the coloration of the ceramic pigments, obtained with the introduction of boron-containing compounds as mineralizers, and the pigment-containing glaze coatings are similar. Namely, the introduction of such pigments to the ground base fritted glaze causes a significant increase in the intensity of the brown and black coloration of a glass layer. Moreover, the most significant intensification of coloring takes place in the case of applying the examined pigments, synthesized using B_2O_3, which is introduced by boric acid. And the most significant intensification of coloring takes place when applying the examined pigments, synthesized by using boric acid.

In this case, the glass layer containing the 2d pigment is characterized by the increased brown color. This is confirmed by shifting the λ values from the orange (602–605 nm) to a longer wave region of the spectrum – red (630–637 nm), Fig. 4, *b*. The black color of glazed coatings, following the introduction of the 8d pigment, synthesized by adding the boron-containing compounds, is also greatly enhanced. This is accompanied by a fall in the lightness indicator values from 5.2–5.6 % (for the glass layer containing the examined pigment without a mineralizer) to 3.8–3.9 and 3.9–4.1 % (when introducing the pigment obtained by using B_2O_3 and $Na_2B_4O_7$ as a mineralizing additive) – Fig. 5.



a *b*

Fig. 4. Dependence of the color indicators of glass coatings on the type of mineralizers and the firing temperature of ceramic pigments from series 1.2d: *a* – lightness, %; *b* – color tone, nm

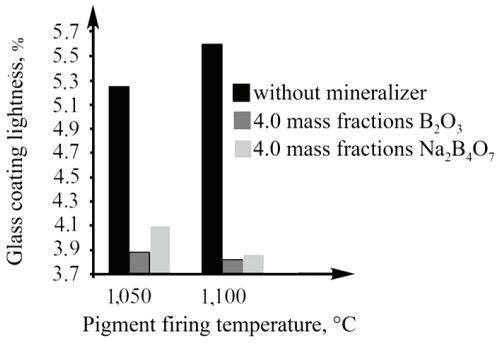


Fig. 5. Dependence of the lightness (%) of glass coatings on the type of mineralizers and the firing temperature of ceramic pigments from series 8d

5. 2. Results of studying the mineralogical composition of slag-containing pigments

To analyze the mineralizing effect of B_2O_3, $Na_2B_4O_7$, Na_2O, and NaF, we compared the absolute intensity of the main diffraction maxima that are characteristic of the spinel and the main silicate phase (diopside) – Fig. 6.

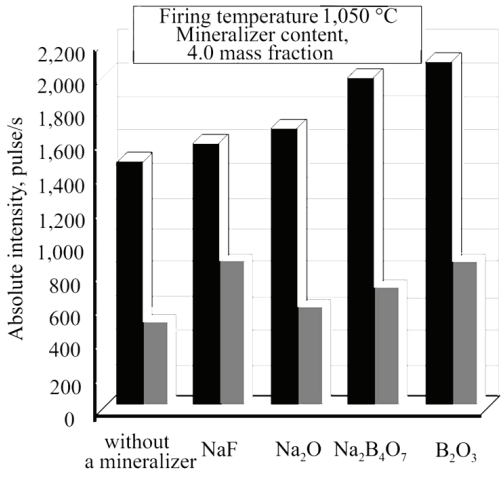
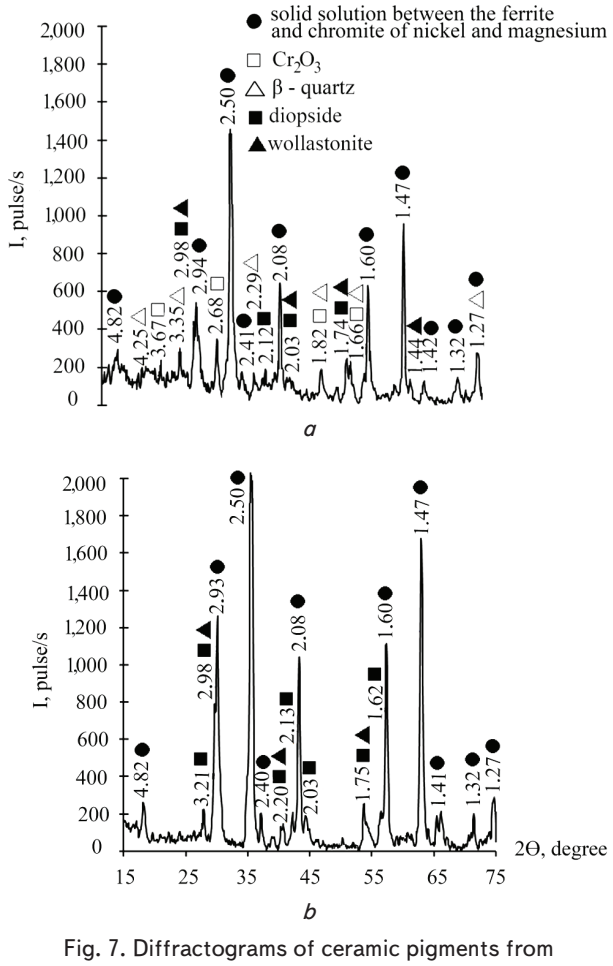


Fig. 6. Chart of change in the intensity of the main diffraction maximum of the 1.2d pigment: ■ – spinel solid solution between ferrites and chromites of nickel and magnesium (d=2.50 Å); ■ – diopside (d=2.98 Å)

The results of our X-ray phase analysis of ceramic pigments agree well with the research into their color indicators.

The dynamics of change in the intensity of a diffraction maximum d=2.50 Å indicate that in the reactions to form the spinel solid solution the most effective mineralizing action is exerted by the additives of boron-containing compounds, which are the most fusible (Table 1).

Consequently, at a low temperature of 1,050 °C, there is a complete binding of the starting components of pigment charge in the spinel phase, which act as color carriers. In the dark brown 1.2d pigment, this is a solid solution between the ferrite and chromite of nickel and magnesium with their characteristic lines (d=4.82; 2.93; 2.50; 2.08; 1.60; 1.47 Å) – Fig. 7.



a

b

Fig. 7. Diffractograms of ceramic pigments from series 1.2d, fired at a temperature of 1,050 °C: *a* – no mineralizing additive; *b* – with the addition of 4.0 mass fractions B_2O_3

In the chrome-cobalt 8d pigment, the black coloring is due to the formation of spinel ($MgFe_2O_4$, $CoFe_2O_4$, and $CoCr_2O_4$), which, due to the similarity of their structure, also produce a solid solution of substitution (Fig. 8).

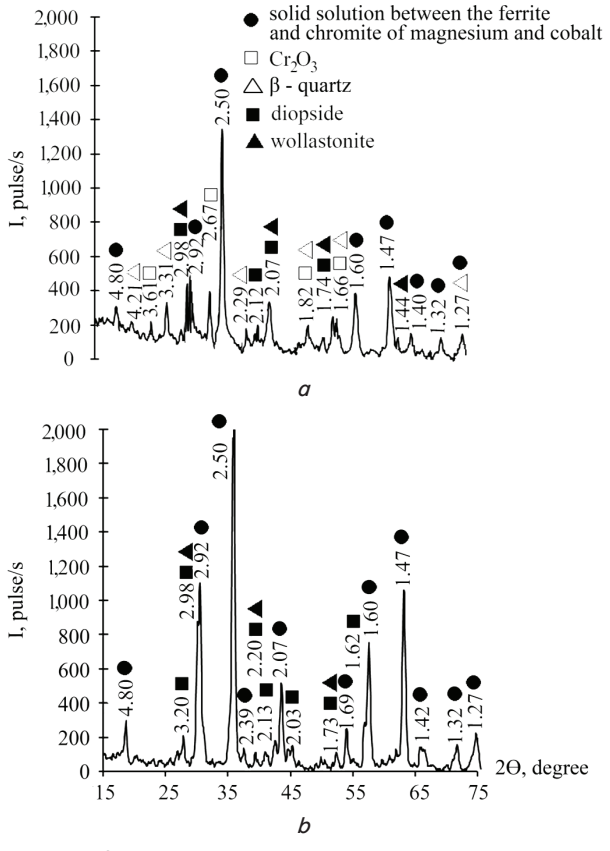


Fig. 8. Diffractograms of ceramic pigments from 8d series, fired at a temperature of 1,050 °C: *a* — no mineralizing additive, *b* — with the addition of 4.0 mass fractions of B_2O_3

In the presence of B_2O_3 at a temperature of 1,050 °C, along with the compounds-chromophores, there is a complete formation of silicates in the form of diopside (d=3.20; 2.98; 2.13; 2.03 Å) and wollastonite (d=2.98; 2.20; 1.73 Å), Fig. 7, 8.

A weaker action, compared to the boron-containing compounds, is exerted by NaF and Na_2O. At the same time, in the reactions to form the silicate phase (diopside), the NaF additive, along with B_2O_3, is the most active (Fig. 6).

6. Discussion of results of studying the influence of mineralizers on the processes of synthesis and the color indicators of slag-containing pigments

In the course of our study, it was established that the color indicators of the examined ceramic pigments, their qualitative and quantitative crystal-phase composition, are determined by the nature and content of mineralizing additives. Moreover, there is a direct dependence between the melting point of mineralizers and their influence on the processes that cause the formation of the predetermined spinel phases in the composition of the examined compositions.

Thus, the tangible effect from the introduction of sodium fluoride, which has the highest melting point (1,040 °C, Table 1), is achieved only as a result of firing the pigment charges at a temperature not lower than 1,150 °C. This defines its inappropriate use as a supplement that intensifies the progress of solid-phase reactions in the specified system, where the main phase is spinel.

Using sodium oxide as a mineralizer, introduced with the help of its carbonic acid salt, is feasible in the amount of 4 mass fractions at the firing temperature of pigments not less than 1,100 °C.

The most effective action on the processes of mineral formation in the examined pigments is exerted by the additives of boron-containing compounds, due to their high fusibility (Table 1). The result is the intensified synthesis reactions involving the liquid phase. Moreover, the action of boron oxide, introduced by orthoboric acid, is, in this case, is more pronounced compared to sodium tetraborate.

The mechanism of the influence of compounds containing boron oxide is, first, the formation of the liquid phase (melt) at relatively low temperatures. In addition, B_2O_3 acts on the crystalline lattice of the components of pigment charges, bringing it to an active state without destruction. The reason for this phenomenon lies in the fact that the B^{3+} boron ion has a large charge and a small ionic radius (0.02 nm). In this regard, the ion boron has a stronger ability to polarize (deformation) compared to the single-charge ions of alkaline metals, and it significantly influences the reduction in the stability of the crystalline lattice [1]. In addition, it is known that boron oxide positively affects the chromophore properties of the pigments themselves. The role of the main chromophores in the examined dark-brown pigment belongs to the ions of transition metals Ni^{2+}, Cr^{3+} and Fe^{3+}. Their electronic shell is not fully completed and has a high polarization ability. Their coloration varies depending on the polarization ability of ion, specifically oxygen, which is included in the complexes of ions of transition metals. In the presence of B^{3+} ions, there is an increase in the ability to polarize the oxygen anion in such complexes, so that the absorption of light in the visible spectrum is increased resulting in the coloration of ceramic pigments.

In general, it follows from the analysis of the acquired experimental data that the introduced mineralizers, in terms of their effect on enhancing the coloration and intensification of spinel-forming reactions of the examined ceramic pigments, can be arranged in the following sequence:

$$NaF<Na_2O<Na_2B_4O_7<B_2O_3.$$

The effect of the considered mineralizers on the formation of silicate phases differs from the above series. The effectiveness of NaF and B_2O_3 additives in this case is almost equivalent.

The presence of fluoride ions, according to literary data [13, 14], increases the reactivity of the crystalline lattice of the material due to the weakening of the of the silicon-oxygen frame, which causes the progress of diffusion processes in the region of low temperatures.

Thus, we have established patterns of change in the crystal-phase composition and color indicators of silicate-spinel ceramic pigments, depending on the nature of the mineralizers, which allowed us to recommend the most effective ones. This makes it possible to significantly decrease the firing temperature of such pigments (up to 1,050 °C). At the same time, the application of the established patterns is limited to spinel and silicate pigments. Therefore, it is advisable in the future to consider the comparative effect of different mineralizers on the processes of synthesis of ceramic pigments with the structure of other types.

7. Conclusions

1. Our study has determined the peculiarities of change in the color indicators of silicate-spinel ceramic pigments, which were obtained on the basis of open-hearth slag, depending on the content and nature of additives-mineralizers. It was established that the tangible effect of the introduction of sodium fluoride, which has the highest melting point among the examined additives, is achieved as a result of firing the pigments at a temperature not lower than 1,150 °C. The effect of sodium oxide is effective starting at a temperature of 1,100 °C. The most expedient is to use additives of boron-containing compounds. Their introduction makes it possible to lower the firing temperature of slag-containing pigments to 1,050 °C or reduce the concentration of the mineralizer (B_2O_3) to 2 mass fractions at the synthesis temperature 1,100 °C. The synthesized pigments ensure the formation of glaze coatings, which, in terms of their qualitative indicators, are not inferior to the coating obtained with the addition of high-temperature pigments (the firing temperature is 1,200–1,250 °C).

2. A direct dependence between the melting point of the mineralizers and their influence on the processes that determine the formation of the predetermined spinel phases in the composition of examined compositions has been established. The introduction of B_2O_3 as a mineralizer provides for the complete binding of the starting components in the spinel solid solutions as early as at a temperature of 1,050 °C. In the brown pigments from series 1.2d, this is a solid solution between the ferrite and chromite of nickel and magnesium. In the black pigments from series 8d, this is a solid solution between the ferrites of magnesium and cobalt, as well as cobalt chromite. This allows us to argue about the effectiveness of using the boron-containing mineralizers to accelerate the spinel-forming reactions in the synthesis of ceramic pigments.

The formation of silicate phases (diopside and wollastonite), which are not color carriers in the examined pigments, is significantly affected by the mineralizing action exerted by the additives of NaF and B_2O_3.

References

1. Maslennikova, G. N., Pishch, I. V. (2009) Keramicheskie pigmenty. Moscow: OOO RIF «Stroymaterialy», 224.
2. Doynov, M., Dimitrov, T., Kozhukharov, S. (2016). Alternative technological approach for synthesis of ceramic pigments by waste materials recycling. Boletín de La Sociedad Española de Cerámica y Vidrio, 55 (2), 63–70. doi: https://doi.org/10.1016/j.bsecv.2016.01.002
3. Hajjaji, W., Costa, G., Zanelli, C., Ribeiro, M. J., Seabra, M. P., Dondi, M., Labrincha, J. A. (2012). An overview of using solid wastes for pigment industry. Journal of the European Ceramic Society, 32 (4), 753–764. doi: https://doi.org/10.1016/j.jeurceramsoc.2011.10.018
4. Costa, G., Della, V., Ribeiro, M., Oliveira, A., Monros, G., Labrincha, J. (2008). Synthesis of black ceramic pigments from secondary raw materials. Dyes and Pigments, 77 (1), 137–144. doi: https://doi.org/10.1016/j.dyepig.2007.04.006
5. Li, Z., Du, Y., Chen, Z., Sun, D., Zhu, C. (2015). Synthesis and characterization of cobalt doped green ceramic pigment from tannery sludge. Ceramics International, 41 (10), 12693–12699. doi: https://doi.org/10.1016/j.ceramint.2015.06.101
6. Prim, S. R., Folgueras, M. V., de Lima, M. A., Hotza, D. (2011). Synthesis and characterization of hematite pigment obtained from a steel waste industry. Journal of Hazardous Materials, 192 (3), 1307–1313. doi: https://doi.org/10.1016/j.jhazmat.2011.06.034
7. Chen, Z., Du, Y., Li, Z., Sun, D., Zhu, C. (2015). Synthesis of black pigments containing chromium from leather sludge. Ceramics International, 41 (8), 9455–9460. doi: https://doi.org/10.1016/j.ceramint.2015.04.001
8. Chavarriaga, E. A., Jaramillo, L. J., Restrepo, O. J. (2012). Ceramic Pigments with Spinel Structure Obtained by Low Temperature Methods. Characterization of Minerals, Metals, and Materials, 155–162. doi: https://doi.org/10.1002/9781118371305.ch19
9. Minakova, N. A., Zaichuk, A. V., Belyi, Y. I. (2008). The structure of borate glass. Glass and Ceramics, 65 (3-4), 70–73. doi: https://doi.org/10.1007/s10717-008-9017-2
10. Yongvanich, N., Supanichwatin, K., Penglan, J., Triamnak, N. (2018). Synthesis and Characterizations of $(CoxMg(2–x))SiO_4$ Forsterite Ceramic Pigments from Mirror Waste. Materials, 11 (7), 1210. doi: https://doi.org/10.3390/ma11071210
11. Zaichuk, A. V., Amelina, A. A. (2019). Blue-green spinel-type ceramic pigments prepared from the slag of aluminothermal production of ferrotitanium. Voprosy Khimii i Khimicheskoi Tekhnologii, 4, 46–54. doi: https://doi.org/10.32434/0321-4095-2019-125-4-46-54
12. Zaichuk, A. V., Amelina, A. A. (2017). Production of Uvarovite Ceramic Pigments Using Granulated Blast-Furnace Slag. Glass and Ceramics, 74 (3-4), 99–103. doi: https://doi.org/10.1007/s10717-017-9937-9
13. Gargori, C., Cerro, S., Fas, N., Llusar, M., Monrós, G. (2017). Red-brown ceramic pigments based on chromium doped ferrian armalcolite, effect of mineralizers. Ceramics International, 43 (7), 5490–5497. doi: https://doi.org/10.1016/j.ceramint.2017.01.065
14. Pishch, I. V., Maslennikova, G. N., Podbolotov, K. B., Karizna, Y. A., Belyakovich, I. V. (2011). Silica based pigments. Glass and Ceramics, 68 (3-4), 71–75. doi: https://doi.org/10.1007/s10717-011-9324-x
15. El Hadri, M., Ahamdane, H., El Idrissi Raghni, M. A. (2017). Effect of sol–gel method on colour properties of the classical cobalt olivine (Co_2SiO_4) ceramic pigment. Bulletin of Materials Science, 40 (2), 375–382. doi: https://doi.org/10.1007/s12034-017-1378-0
16. Ke, S., Wang, Y., Pan, Z. (2014). Synthesis of $Nd_2Si_2O_7$ ceramic pigment with LiCl as a mineralizer and its color property. Dyes and Pigments, 108, 98–105. doi: https://doi.org/10.1016/j.dyepig.2014.04.031
17. Zaichuk, A. V., Belyi, Y. I. (2012). Brown ceramic pigments based on open-hearth slag. Russian Journal of Applied Chemistry, 85 (10), 1531–1535. doi: https://doi.org/10.1134/s1070427212100072
18. Zaichuk, A. V., Belyi, Y. I. (2012). Black ceramic pigments based on open-hearth slag. Glass and Ceramics, 69 (3-4), 99–103. doi: https://doi.org/10.1007/s10717-012-9423-3
19. Lidin, R. A., Molochko, V. A., Andreeva, L. L. (1997). Himicheskie svoystva neorganicheskih veshchestv. Moscow: Himiya, 480.