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INFLUENCE OF IRON OXIDES ON THE PROPERTIES OF UNFLUORIDATED ENAMEL FRIT GLASS AND COATINGS

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Abstract. The influence of iron oxides on the properties of unfluoridated enamel glass frit and coatings in the system of $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$ has been studied. It has been determined that the introduction of Fe_2O_3 additive in the amount of 0.4 mol % instead of SiO_2 into an unfluoridated glass enamels improves the optical-color characteristics of the coatings, pigmented with selenium cadmium red.

Keywords: unfluoridated glass frit, brightly pigmented coating, iron oxide, microstructure.

1. Introduction

Cookware is the most common type of steel products which are subjected to the enameling. Utilized enamels should not contain harmful ingredients to human health and must be acid resistant. Occupation safety must be ensured for the manufacturing process of glass frit for the enamels [1].

Presently, most enterprises producing enameled products, use fluoride-containing enamels. Despite the improvement of training methods fluoride before blending, a significant number of them disappear in melting. The design of unfluoridated brightly colored enamel coating is quite a challenging task and the most problematic issue is getting enamel coating with stable characteristics of red color.

The red coatings were obtained in the previous research [2]. They were located in purple area of CIE diagram [3] by color tone (λ , nm) and by visual assessment almost all coatings had burgundy-cherry shades that did not match λ pigment No.1024 – 618 nm. As it has been proven [4] the pigment representing the solid solution CdS-nCdSe is oxidized when burning of these enamels resulting in unstable color of products. Obtaining of such unfluoridated glass enamels that would

recreate the color tone of the pigment itself or would be close to it is reasonable. It is expected that this is possible to achieve by introduction of small additive of ferric oxide to glass base to decrease the viscosity of enamels when burning and the amount of this corrective additive should not affect the quality of color characteristics of coatings.

The influence of this oxide on the properties of glasses was studied by many scientists, although the results obtained are hard to compare, since behavior of iron ions in glasses of different compositions is characterized by extraordinary complexity. For instance, the monograph [5] contains the analysis of literature and the results of own research regarding the use of ferric oxides in the ground enamels. In general ferric oxides decrease viscosity, increase the temperature coefficient of linear expansion, facilitates the better adhesion of enamel layer to steel.

However, the data of introduction of ferric oxides to glass enamels used as the basis of brightly colored coatings, are absent in literature.

The purpose of this work is the research of the influence of little additive of Fe_2O_3 on physical and chemical properties and structure of glass enamels that contain no fluorine and optical color characteristics of brightly colored coatings based on them.

2. Experimental

The initial glass frit was taken of the following composition (mol %): $18\text{Na}_2\text{O}$, $13\text{B}_2\text{O}_3$, 52SiO_2 , $17(\text{TiO}_2 + \text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{CaO} + \text{P}_2\text{O}_5)$ [2]. In the researched enamels the amount of the basic components (Na_2O , B_2O_3 , SiO_2) at their constant content (83 mol %) was changed in compliance with simplex lattice plan of Scheffe [3, 4] within the limits showed in Fig. 1. This work features comparative analysis of the properties of unfluoridated glasses and coatings in which the amount of oxides of the

basic sodium-borosilicate system (series I) was changed, and the similar glasses containing Fe_2O_3 in little amount (0.4 mol %) due to SiO_2 (series II).

Boiling of enamels has been implemented under laboratory conditions in electric furnaces with silicon carbonate heaters at 1523 K for 90–120 min. The preparedness of enamels was determined through the test by “thread” and “biscuit”.

Enamel slips on the basis of the researched unfluoridated glass frit were prepared under formulation used at JSC “Novomoskovskiy posud” but with decreased contents of pigment, mass fractions: frit – 100; clay – 4; electrolytes – 1.3; water – 40; red pigment No.1024 – 6. The slip was applied on the grounded plates and has been burning in laboratory muffle furnace at 1053–1093 K for 4 min.

The following properties were determined for researched frits by the known methods: temperature coefficient of linear expansion (TCLE) and softening temperature (ST) – by the dilatometer DKV-5A, flowability – by the method of drop spreading [6], water resistance – by a grain method [7]. The optical and color characteristics of coatings were determined by the comparator KC-3: diffuse reflection factor – DRF, %; color tone – λ , nm; color purity – P , %; lightness (relative brightness) – L , %. Coefficient of specular reflection – CSR, % – was determined using glossmeter FB-2.

3. Results and Discussion

Introduction of ferric oxide additive to the researched glasses had no influence on the process of boiling and damping degree (transparency), the main factors of influence are the components of sodium-borosilicate system. The test by “biscuit” of glasses 4, 14 and 15 (the highest contents of B_2O_3) implied significant opacity (Fig. 1). Glass enamels 1, 11 and 12 (the highest contents of Na_2O) were almost transparent with a slight opalescence; other glasses had the average opacity. At the same time introduction of Fe_2O_3 to researched enamels resulted in the change of frits color: from almost colorless to chartreuse.

Analysis of water resistance index change depending on the amount of basic components Na_2O , B_2O_3 , SiO_2 (Fig. 2a) in glasses compared to the similar glasses containing 0.4 mol % Fe_2O_3 (Fig. 2b) showed the following. The addition of ferric oxide, firstly, insignificantly impaired the index of water resistance: (0.02 – 0.53) $\text{cm}^3 \cdot \text{g}^{-1}$ – glass enamel of the first series, (0,04 – 0,68) $\text{cm}^3 \cdot \text{g}^{-1}$ – glass enamel of the second series; secondly, shifted location of extremum of maximum leachability from the area of the highest contents of Na_2O to the top of triangle B_2O_3 .

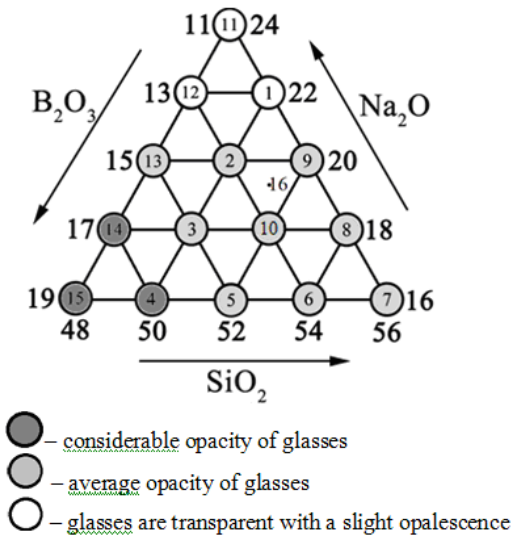


Fig. 1. Contents and characteristics of the basic components of the researched glasses (mol %)

The glasses containing ferric oxide are characterized by somewhat higher temperature coefficient of linear expansion (85–108) 10^{-7} deg^{-1} than similar glasses without this additive (82–100) 10^{-7} deg^{-1} , the softening temperature remains unchanged (823–873 K).

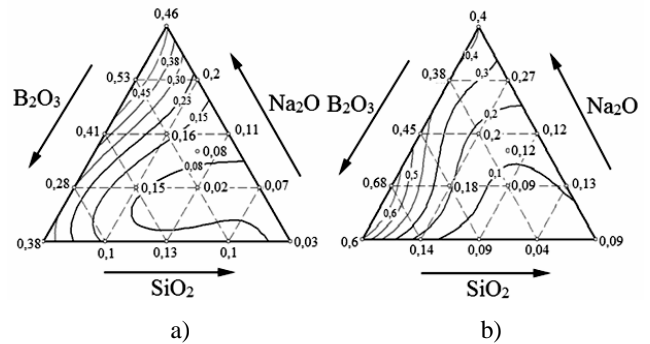


Fig. 2. The water resistance of glass frit (spending of 0.01N HCl, $\text{cm}^3 \cdot \text{g}^{-1}$): series I (a) and series II (b)

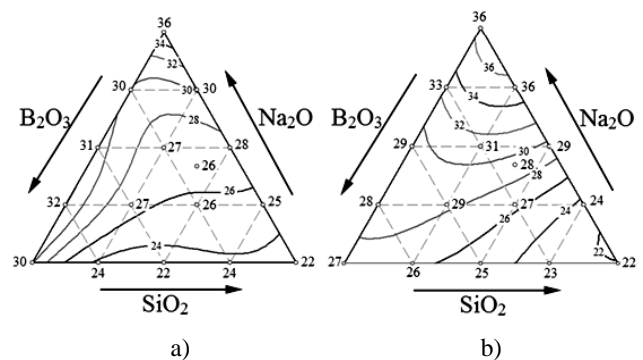


Fig. 3. Flowability of glass frit, mm: series I (a) and series II (b)

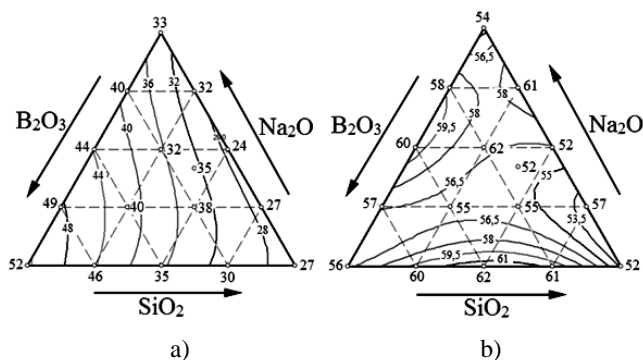


Fig. 4. Diffuse reflection factor of coatings without pigment, %: series I (a) and series II (b)

While adding 0.4 mol % of ferric oxide to the glasses composition delta of flowability insignificantly but stably increases (up to 6 mm) in the area of compositions located in the center of concentration triangle (Fig. 3)

Thus, introduction of 0.4 mol % of ferric oxide additive to the researched unfluoridated enamels resulted in the insignificant change of properties of frits in the direction of fusibility.

Table 1 contains comparative characteristic of optical and color properties of the researched coatings at the burning temperature of 1093 K. Some of them are

changed essentially when using the glass frits containing Fe₂O₃ in insignificant amount.

For example, diffuse reflection factor of coatings without pigments decreases by 1.5–2 times: from 24–52 to 52–62 % for enamels containing ferric oxide. In the glasses of series I DRF of enamels is virtually increased linearly with increasing the B₂O₃ contents (Fig. 4a) that match with the data of opacification of glass frits when boiling. Configuration of DRF isolines of concentration triangle of the glasses of series II indicates the complex nature of dependence of this parameter on the composition on glass enamels (Fig. 4b).

The color tone changes especially qualitatively regarding the red enamels that is located in the area of purple colors of CIE diagram for considerable part of coatings based on glasses of the first series, and for the glasses of series II it changes to the spectral part of red color (Fig. 5). Probably, one of the reasons for this fact is the optical merging of purple color giving selenium cadmium pigment to coating and chartreuse color of frit containing iron.

Color purity, brightness and coefficient of specular reflection of coatings while introducing ferric oxide to glass frit were the best in the contents 1–10, where the amount of Na₂O is not more than 22 mol % and B₂O₃ – not more than 17 mol % (Table 1).

Table 1

Comparative characteristic of optical and color properties of enamel coatings on the basis of glasses without Fe₂O₃ (series I) and glasses with 0.4 mol % Fe₂O₃ (series II)

Glass number	DRF, % (coating without pigment)		Color tone λ, nm		Color purity P, %		Brightness L, %		CSR, %	
	I	II	I	II	I	II	I	II	I	II
1	32	61	≥700*	680	27	37	12	18	52	53
2	32	62	700	645	44	47	14	19	63	54
3	40	55	670	633	47	52	17	20	49	69
4	46	60	660	618	45	58	18	26	50	60
5	35	62	700	618	44	60	16	22	38	55
6	30	61	≥700	647	43	46	14	19	40	64
7	27	52	≥700	680	41	50	12	17	42	64
8	27	57	≥700	690	42	42	11	15	42	59
9	24	52	≥700	670	30	41	12	17	43	64
10	38	55	≥700	645	47	47	14	17	50	58
11	33	54	660	700	42	35	18	18	67	69
12	40	58	630	650	55	45	21	19	58	61
13	44	60	625	628	62	52	26	23	68	55
14	49	57	617	630	62	53	27	22	63	58
15	52	56	618	622	61	53	27	24	50	46
16	35	52	≥700	660	48	46	15	16	46	60

Note: * – λ is located in the purple area of CIE diagram

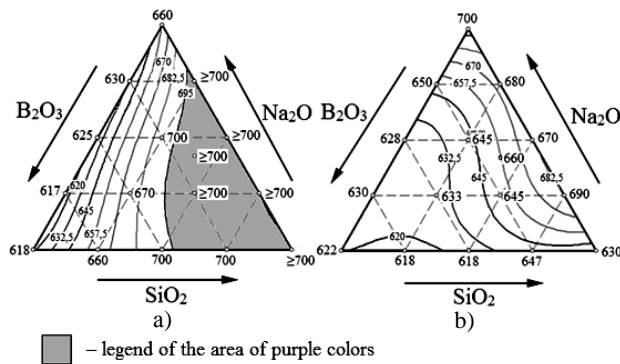


Fig. 5. Color tone of coatings with red pigment, nm: series I (a) and series II (b)

So, introduction of 0.4 mol % of Fe_2O_3 to the compositions of glass enamels changes the characteristics of coatings dramatically, such as diffuse reflection factor of enamels without pigment and color tone of coatings with red selenium cadmium pigment. These facts may indicate the change of microstructure of the investigated glasses which research is exemplified by the glass 10, located in the center of concentration triangle where the maximum level of change of optical and color characteristics of coatings is observed with the introduction of ferric oxide in its composition.

Fig. 6 shows the photos from the surface of glass 10 and the same glass with 0.4 mol % of Fe_2O_3 instead of SiO_2 after pickling 2 % HF for 40 sec. The photos were made using scanning electron microscope REM-106Y at the enlargement by 10000 times. Fig. 7 shows the curves of differential and thermal analysis of these glasses obtained by derivatograph Q-1500D.

The research results (Fig. 6a) show the presence of liquating structure of drop appearance in the initial glass [8]. The bifurcation of softening endoeffect of this glass – 848 K and 933 K and one peak of full melting at the tem-

perature of 1063 K are observed at the curve of differential and thermal analysis (Fig. 7a). Introduction of ferric oxide additive to the glass base results in the enlargement and merger of drops (Fig. 6b). Two peaks of softening endoeffects are observed more clearly and their temperature decreases – 823 K and 893 K and the endoeffect of full glass melting featured bifurcation of the DTA curve within the temperature peaks of 1053 and 1128 K (Fig. 7b). That is, the present research results indicate activation of the process of glass differentiation at the introduction of Fe_2O_3 .

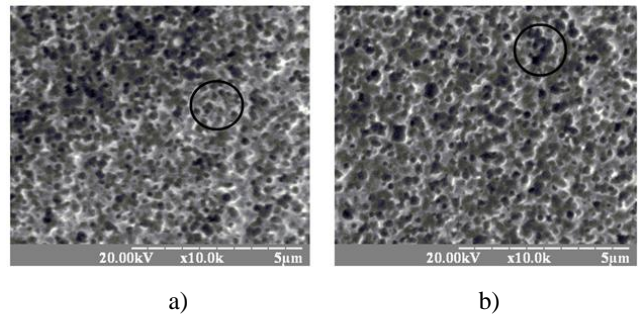


Fig. 6. Microstructure of researched glasses: 10 (a) and 10 with 0.4 mol % Fe_2O_3 instead of SiO_2 (b)

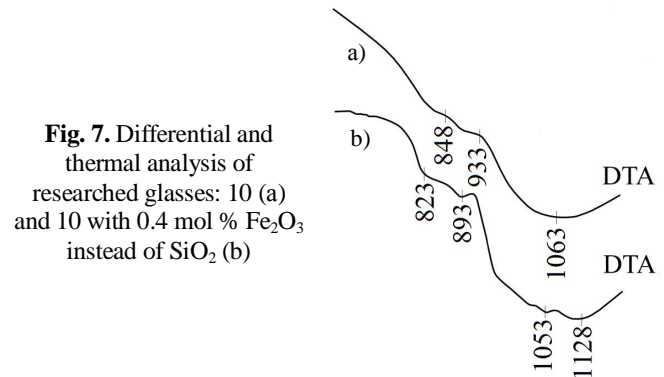


Fig. 7. Differential and thermal analysis of researched glasses: 10 (a) and 10 with 0.4 mol % Fe_2O_3 instead of SiO_2 (b)

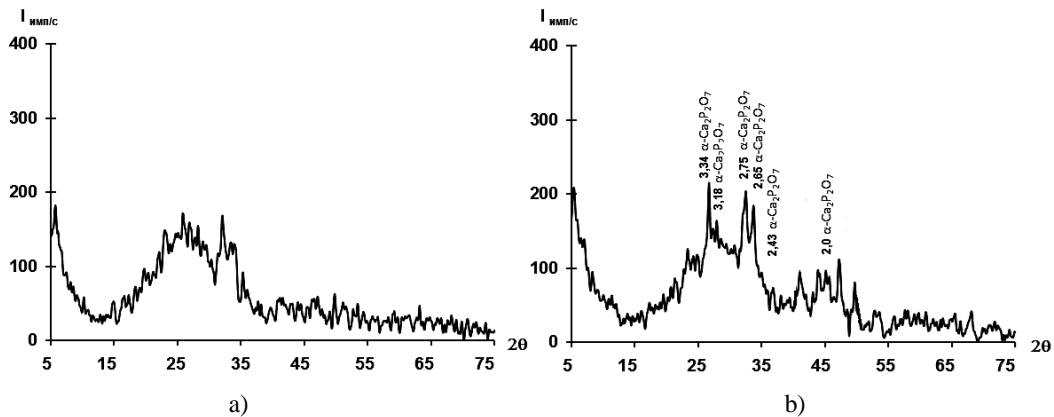


Fig. 8. X-ray phase analysis of researched coatings: 10 (a) and 10 with 0.4 mol % Fe_2O_3 instead of SiO_2 (b)

Such changes in microstructure of glasses are represented in the rapid growth of coatings opacification (the increase of diffuse reflection factor) since burning is the actual additional heat treatment of liquating glasses. The X-ray unit DRON-3 obtained the diffraction pattern of slip burnt at 1093 K for 4 min (burning mode of coatings). Enamel 10 is characterized by expressed amorphous halo (Fig. 8a) and the enamel containing Fe_2O_3 has quite expressed peaks on diffraction pattern referring to $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$ (Fig. 8b).

4. Conclusions

Thus, introduction of Fe_2O_3 additive in the amount of 0.4 mol % instead of SiO_2 to glass enamel containing no fluorine allows to obtain the red coatings with stable color characteristics. The data of TCLE and water resistance meet the requirements of standards [6, 7] for coating enamel frits and depending on the class of water resistance such frits can be used for external or internal enameling.

It should be also noted that optimum temperature of the present coatings burning is 1073–1093 K that is by 30–50 K lower than the burning temperature of industrial fluorine containing enamel. Accordingly, two urgent issues in the field of enameling are solved: economics and ecology.

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ВПЛИВ ОКСИДІВ ЗАЛІЗА НА ВЛАСТИВОСТІ БЕЗФЛУОРИСТИХ ЕМАЛЕВИХ СКЛОФРИТ ТА ПОКРИТТІВ

Анотація. Досліджено вплив оксидів заліза на властивості безфлуористих емалевих склофрит та покриттів в системі $\text{Na}_2\text{O}-\text{V}_2\text{O}_5-\text{SiO}_2$. Встановлено, що введення додатку Fe_2O_3 у кількості 0,4 мол.% замість SiO_2 в безфлуористій склоемалі покращує оптико-колірні характеристики покриттів, забарвлених червоним селенокадмієвим пігментом.

Ключові слова: безфлуористі склофрити, яскраво забарвлені покриття, оксид заліза, мікроструктура.

