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 Na₂O – B₂O₃ – SiO₂ has been studied. It has been determined that the introduction of Fe₂O₃ additive in the amount of 0.4 mol % instead of SiO₂ 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 Fe₂O₃ 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 %): 18Na₂O, 13B₂O₃, 52SiO₂, 17(TiO₂+Al₂O₃+K₂O+CaO+P₂O₅) [2]. In the researched enamels the amount of the basic components (Na₂O, B₂O₃, SiO₂) 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 Fe₂O₃ in little amount (0.4 mol %) due to SiO₂ (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 – \( \lambda \), 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 B₂O₃) implied significant opacity (Fig. 1). Glass enamels 1, 11 and 12 (the highest contents of Na₂O) were almost transparent with a slight opalescence; other glasses had the average opacity. At the same time introduction of Fe₂O₃ 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 Na₂O, B₂O₃, SiO₂ (Fig. 2a) in glasses compared to the similar glasses containing 0.4 mol % Fe₂O₃ (Fig. 2b) showed the following. The addition of ferric oxide, firstly, insignificantly impaired the index of water resistance: (0.02 – 0.53) cm³·g⁻¹ – glass enamel of the first series, (0.04 – 0.68) cm³·g⁻¹ – glass enamel of the second series; secondly, shifted location of extremum of maximum leachability from the area of the highest contents of Na₂O to the top of triangle B₂O₃.

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

**Fig. 2.** The water resistance of glass frit (spending of 0.01N HCI, cm³·g⁻¹): series I (a) and series II (b)

**Fig. 3.** Flowability of glass frit, mm: series I (a) and series II (b)
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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 Fe$_2$O$_3$ 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 B$_2$O$_3$ 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 Na$_2$O is not more than 22 mol % and B$_2$O$_3$ – not more than 17 mol % (Table 1).

Table 1

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<tr>
<th>Glass number</th>
<th>DRF, % (coating without pigment)</th>
<th>Color tone $\lambda$, nm</th>
<th>Color purity $P$, %</th>
<th>Brightness $L$, %</th>
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Note: * – $\lambda$ is located in the purple area of CIE diagram
So, introduction of 0.4 mol % of Fe₂O₃ 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 Fe₂O₃ instead of SiO₂ 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 temperature 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 Fe₂O₃.
4. Conclusions

Thus, introduction of Fe$_2$O$_3$ 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.

References