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PATTERNS OF COLORING WITH IONIC DYES OF THE BASE GLASS MATRIX AND ENAMEL COATINGS IN THE SYSTEM $R_2O-BaO-ZnO-Al_2O_3-B_2O_3-TiO_2-SiO_2$

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The paper presents the study on the identification of patterns of coloring of a basic glass matrix and enamel coatings based on it in the system $R_2O-BaO-ZnO-Al_2O_3-B_2O_3-TiO_2-SiO_2$ by a number of ionic dyes. Regardless of the dye content, ionic dyes give the same color tone to both glasses and coatings based on these glasses as follows: CuO (1.0–3.0 wt.%) λ=489–494 nm (blue-green), Fe_2O_3 (0.5–2.0 wt.%) λ=575–585 nm (yellow), $K_2Cr_2O_7$ (0.5–2.0 wt.%) λ=570–576 nm (yellow-green), CoO (0.5–1.0 wt.%) λ=441–463 nm (blue-violet), and NiO (0.5–1.0 wt.%) λglass=559'–571' nm, λcoatings=598–629 nm (brown). It is shown that according to the degree of color intensity of glasses and coatings based on them, the dyes are arranged in the following sequence: $CoO>NiO>CuO>K_2Cr_2O_7>Fe_2O_3$. The research was conducted using a special computer program COLOR GLASS. The established patterns are used in the development of lead-free glass enamels for jewelry and decorative products.

Keywords: glass, enamel, coating, ionic dye, coloring.

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Introduction

Our work relates to the problem of the development of lead-free enamel coatings for copper, gold, silver in jewelry and art. This is a separate type of enamel, which has special requirements for gloss, refractive index, transparency and color [1].

The enamels used in this case differ from enamels for ferrous metals not only in the main composition, but also in the method of painting. While enamels for ferrous metals are mostly colored with pigments during the firing stage, enamels for non-ferrous and precious metals are usually colored during melting. Therefore, the coloring mechanisms of such enamels imply the coloring mechanisms of glass. According to up-to-date concepts [2], coloring occurs due to ion-coordination complexes, which form chromophore ions in the structure of a glass.

The degree of oxidation of the ion and its coordination state (tetrahedral or octahedral) are here important. As can be seen form Table, there is no unambiguity in different literature sources about the shades of color of the glass, which are formed by a particular dye. Only the visual characteristics of the color and the subjective assessment of the color intensity are provided.

Formation of the color of enamel coatings, which occurs in a much longer technological process, is even less predictable. The color is influenced by additional factors at the stage of melting of fiberglass, and in the subsequent stages of preparation of a slip, its applying on a metal basis, firing of an enamel layer. Earlier [11], a study of the coloring ability of some ionic dyes (CuO 2.0 wt.%; CoO 0.5 wt.%, and $K_2Cr_2O_7$ 1.0 wt.%) was conducted, depending on the acid-base properties of glasses in the system $Na_2O-BaO-B_2O_3-SiO_2$, which is chosen as the base for the development of lead-free enamels. Ionic dyes over 100 wt.% of the main glass was added to the batch during melting. In glass bases with different chemical composition, and hence different values of acid-base properties, the content of components was widely varied (mol.%): Na_2O (25–55), B_2O_3 (15–45), SiO_2 (24–53), and BaO (5, a constant level). As a result of the performed researches, the dependences of the color tone of glass in the system $Na_2O-BaO-B_2O_3-SiO_2$, colored with copper, cobalt and chromium ions, on the acid-base properties of the glass matrix were established, which were estimated by the coefficient Ψ_B.

The aim of this work is to establish the dependences of color characteristics of glasses and coatings based on the matrix transparent lead-free

Ion-coordination complexes and glass color

Ion	Coordination complex	The color of the glass according to literature data	Color intensity
Cr^{3+}	$[Cr^{3+}O_6]$	Green [3,4]	High
Cr^{6+}	$[Cr^{6+}O_4]$	Yellow [3,4]	Average
Fe^{2+}	$[Fe^{2+}O_6]$	Blue-green [5], blue [3]	Average
Fe^{3+}	$[Fe^{3+}O_4]$ $[Fe^{3+}O_6]$	Yellow-green [3,6], yellow, brown [5]	Low
	$[Fe^{3+}O_3S]$	Amber [6]	
Co^{2+}	$[Co^{2+}O_4]$	Blue [7,8]	Very high
	$[Co^{2+}O_6]$	Pink [7,8]	
Ni^{2+}	$[Ni^{2+}O_4]$	Purple [5], yellow-brown [3], yellow [7]	High
	$[Ni^{2+}O_6]$	Brown, yellow-brown, green [3]	
Cu^{+}	$[Cu^{+}O_6]$	Colorless [7], dirty yellow or brown [9]	No information
Cu^{2+}	$[Cu^{2+}O_4]$	Green [7], yellow [10], blue [3,10], blue [9]	Average
	$[Cu^{2+}O_6]$	Blue or bluish green [3], purple or green [5]	

glass enamel on the content of the most common ionic dyes CoO, NiO, CuO, $K_2Cr_2O_7$ and Fe_2O and develop the coatings of different colors for decorative products.

Experimental

The matrix lead-free transparent glass No. 33–10 in the system R_2O–BaO–ZnO–Al_2O_3–B_2O_3–TiO_2–SiO_2 [12] was chosen for experimental study. Matrix enamel glass (matrix enamel) is an enamel glass (enamel) in which the ratio of basic oxides remains constant, and additional components (opaque, dyes), which depending on the set task provide technological, operational or decorative qualities of a coating, are entered into its structure [13].

For the preparation of raw materials of experimental glasses, we used finely ground quartz sand as well as the following raw materials of the brand «chemically pure» and «clean for analysis»: soda ash (Na_2CO_3), potassium nitrate (KNO_3), barium carbonate ($BaCO_3$), zinc oxide (ZnO), alumina (Al_2O_3), boric acid (H_3BO_3), titanium dioxide (TiO_2). The following dyes were added in the amount of more than 100 wt.% with respect to the main composition of the glass (wt.%): CoO 0.5, 1.5, and 2.0; NiO 0.5, 1.5, and 2.0; CuO 0.5, 1.0, 2.0; and 3.0, $K_2Cr_2O_7$ 0.5, 1.5, 1.0; and 2.0; and Fe_2O_3 0.5, 1.0, and 2.0. Melting of the glass was performed in a corundum crucible in an electric furnace with silicon carbide heaters at the temperature of 1250^0C for 60 minutes, and fried dry on iron rolls.

To obtain coatings, all test glasses were ground to pass through a 0063 sieve, prepared an organic bond slip, applied to a white surface in the form of titanium enamel on primed steel plates, dried at 80^0C and fired at 800^0C for 3 minutes. The average thickness of the fired coating layer was $0.2 \cdot 10^{-3}$ m.

The color coordinates (XYZ) of the glasses and coatings based on them were determined in the reflected light of source A using a color comparator CC-3. Given the fact that the characteristics of transparent enamels, which are applied directly to the metal substrate, is influenced by the color of the base (brick red – copper, yellow – gold, silver – silver), colored enamel coatings were studied on a white background (titanium enamel), and glass samples $1 \cdot 10^{-3}$ m thick were placed on the surface of the reference sample of white color. Using a specially developed computer program COLOR GLASS, the color coordinates (xy), color tone (l, nm) and color purity (P,%) were calculated according to the color coordinates (XYZ) defined on the CC-3 color comparator. Automatic visualization on the graph of ICL color points of the studied materials makes it possible to establish the patterns of their color.

Results and discussion

As a result of melting, a wide range of colors was obtained depending on the type of dye and its concentration. Thus, the introduction of different dyes provides the following colors: CuO (0.5–3.0 wt.%) – from light to dark blue; CoO (0.5–2.0 wt.%) – from dark blue with a purple tinge to blue-black, slightly transparent; $K_2Cr_2O_7$ (0.5–2.0 wt.%) – from lettuce yellow to lettuce green; NiO (0.5–2.0 wt.%) – from brown with a purple tinge to black-brown, opaque; and Fe_2O_3 (0.5–2.0 wt.%) – from yellowish-green to khaki.

Color coordinates (XYZ) were determined for the experimental glasses on the CC-3 color comparator. Using the COLOR GLASS program, the color points of the research objects were plotted on the ICL graph according to the chromaticity coordinates (xy). To take into account the value of the third component of color, lightness, color points were transformed into a color line. The length of

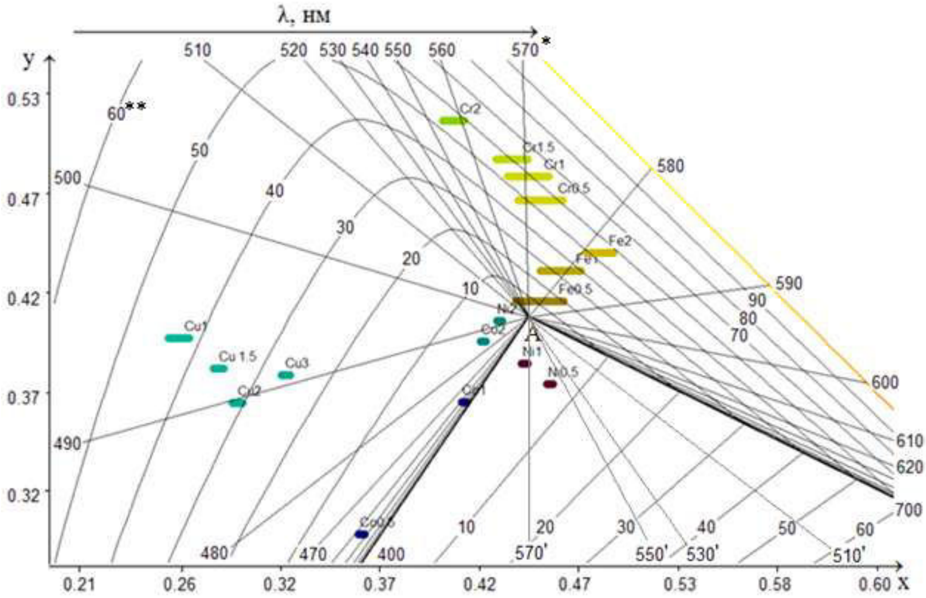

Fig. 1. ICL graph showing color characteristics of matrix enamel glass 33-10 which is colored with CuO, CoO, $K_2Cr_2O_7$, NiO, and Fe_2O_3. Here, x and y are the chromaticity coordinates, source «A»; 570* – color tone λ, nm; 570' – additional wavelength, nm; 60** – color purity P,%, Cu1 – dye and its quantity

the horizontal lines corresponds to the value of the brightness of each glass, and the left end of the line corresponds to the values of the chromaticity coordinates (xy) (Fig. 1).

Figure 1 shows how the color of the matrix glass 33-10 varies depending on the type of dye and its quantity. All test samples were visually transparent except for the sample with NiO and CoO in the amount of 2.0 wt.%. Since the XYZ color coordinates were determined from the surface of the sample, which was located on the white standard, the degree of lightness can be used to estimate the degree of glass color: the lower the light value, the more intensely colored glass and the smaller the proportion of white achromatic color in the reflected light flux.

Figure 2 shows that oxides of cobalt and nickel color the glass most intensely, and regardless of their amount: L=7.43–6.31% and 7.25–6.41%, respectively. The values of lightness here and hereafter are placed from a larger value to a smaller one, which corresponds to an increase in color intensity.

CuO dye provides less intense color of the glass: with increasing the amount of this dye from 1 wt.% to 3.0 wt.% the lightness decreases, and the color intensity, correspondingly, increases by about 2.5 times: L=25.37%–10.65%. $K_2Cr_2O_7$ (L=54.31–26.24%) and Fe_2O_3 (L=58.33–33.05%) dyes ensure the least intensely colored glass.

According to the ideas of color science in relation to conventional paints [14], with the increase in the amount of dye, the color tone should not

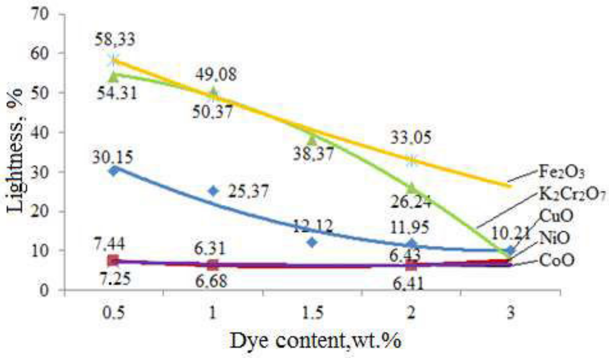

Fig. 2. Dependence of lightness (color intensity) of glass on the type and amount of dye

change, and the purity of color should increase. However, in relation to glass, this postulate is correct only with respect to Fe_2O_3 (Fig. 1): at all studied concentrations the color tone is almost constant λ=581–585 nm, and the purity of color P increases from 20.2 to 58.2% with increasing Fe_2O_3 content in the glass. Analysis of the characteristics of quality indicators of color (i.e. color tone and purity) of other dyes showed that the statement used for conventional paints «the more dye–the more color» cannot be applied to «hot painting». During melting, complex redox processes and the formation of the structure of the glass and ionic coloring complexes occur, which affects the final color. For example, with increasing $K_2Cr_2O_7$ concentration from 0.5 to 1.5 wt% the wavelength and color purity change slightly λ=573→575 nm, P=61.3→65.4%; and a further increase in the concentration of this dye up to 2.0 wt.% leads to both a shift in wavelength toward the green part of the spectrum (λ=560 nm) and a decrease in P up to 59.2%. This means that the equilibrium between the coloring complexes $[Cr^{3+}O_6]$ (green) and $[Cr^{6+}O_4]$ (yellow) shifts towards Cr^{3+} with an increase in the $K_2Cr_2O_7$ content in glass. In addition, this is a completely different «dye» with a different wavelength, the purity of which cannot be equated with the purity of the previous λ.

In the case of staining glass with copper oxide at different concentrations, there is a small fluctuation λ=489–493 nm, and the purity of color gradually decreases from P=41.4% to 25.65% in the transition from the CuO content from 1.0 wt.% to 3.0 wt.%, respectively. Thus, we can assume that the ratio between the content of complexes $[Cu^{2+}O_4]$ (yellow) and $[Cu^{2+}O_6]$ (blue) changes with increasing the concentration of the coloring ion copper (2+), which practically does not affect the color tone, but affects the purity color, i.e. the share of the dominant blue wavelength in the total luminous flux increases.

Analysis of qualitative color characteristics (color tone and color purity) for glass stained with cobalt and nickel oxides is quite difficult due to the extremely high intensity of staining with these components as well as due to the peculiarities of the ICL graph. The essence is that the disadvantage of this graph is the unevenness of the color space: the area of green is stretched as compared to the areas of blue-purple and magenta. Unambiguously, we can say that the color tone of glass stained with CoO (0.5 and 1.0 wt.%) is in the range of 441–463 nm (violet-blue part of the spectrum); the color of the glass with 2.0 wt.% CoO cannot be considered reliable due to the opacity of the sample. Glass with NiO (0.5 and 1.0 wt.%) in terms of color is located in the purple part of the ICL graph λ=559', 571' nm. The color values of the glass with 2.0 wt.% NiO cannot be considered reliable due to the opacity of the sample.

The effect of dyes on the color of coatings was also studied. Figure 3 shows the location of the color characteristics of the obtained coatings on the ICL graph. In the analysis of experimental data, a parallel comparison of the color characteristics of the glass and the coating based on it was performed. The following patterns were established. For CuO-colored coatings, the color varied from light blue to dark azure; the value of the color tone almost does not depend on the dye content, λcoating=491–494 nm, and practically coincides with λglass=489–494 nm. The amount of CuO has almost no effect on the color purity of coatings (Pcoating=17.4–21.8%), while in glass this effect is more noticeable (Pglass=29.4–41.4%).

The color of the coatings, which were stained with iron (III) oxide, varied from ivory to light brown. The color tone almost does not depend on the dye content (λcoating=575–581 nm) and practically coincides with λglass=581–585 nm. In addition, as in glass, the purity increases with increasing the Fe_2O_3 content (Pcoating=11.1–21.2%), but the value of this indicator is much smaller than for glass

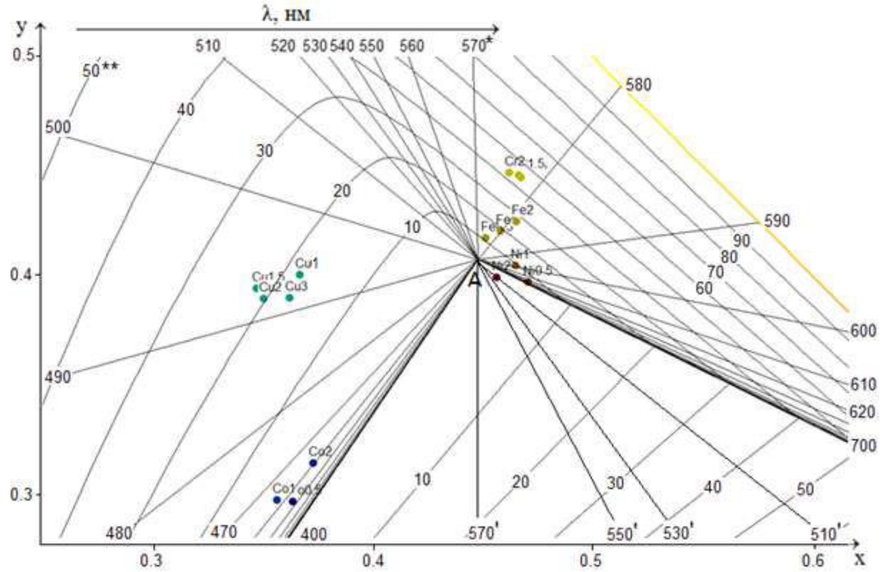

Fig. 3. ICL graph showing the color characteristics of coatings based on matrix enamel glass No. 33-10, which is colored with CuO, CoO, $K_2Cr_2O_7$, NiO, and Fe_2O_3. Here, x and y are the chromaticity coordinates, source «A»; 570* – color tone λ, nm; 570' – additional wavelength, nm; 50** – color purity P,%, Cu1 – dye and its quantity

(Pglass=20.2–58.2%).

The color tone and color purity of coatings colored with $K_2Cr_2O_7$ almost does not depend on the dye content, the coating is light green: λcoating=576–577 nm, and Pcoating=39.34–44.65%. The color of the coatings painted with CoO changes from light blue with a purple tinge to blue-black. The color points of the cobalt oxide-colored coatings, in contrast to the glass color points, are quite close to each other and the color tone values are quite homogeneous: 453–463 nm, the color purity of both glass and coating is low (up to about 3.0%) (Figs. 1 and 3).

Nickel (II) oxide stains the matrix enamel glass No. 33-10; and the coating based on it is brown with a purple tinge. The color tone of NiO-colored glass falls into the purple part of the ICL graph λglass=559'–571' nm, and λcoating=598–629 nm falls into the long-wavelength part of the main spectrum.

Figures 2 and 4 show that the dependences of the lightness of the glass and the lightness of the coating on the dye content is the same (i.e. L decreases with increasing the content of the coloring ion), and the ranking of the intensities of individual dyes is the same.

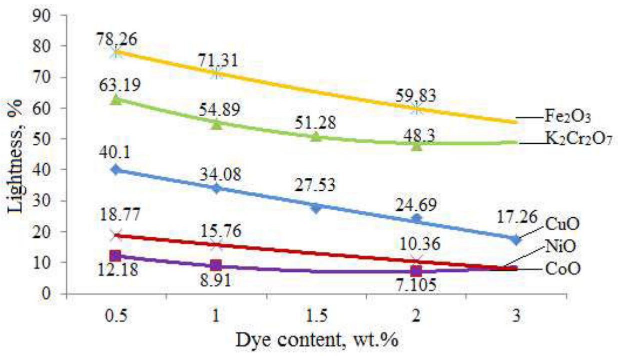

Fig. 4. Dependence of lightness (color intensity) of coatings on the type and amount of dye

Thus, a sequence of dyes, depending on the intensity of the color of the glass and coatings based on this glass with a content of 1.0 wt.% dye, is as follows:

$$CoO>NiO>CuO>K_2Cr_2O_7>Fe_2O_3$$

Iglass,% (intensity)←6.31<6.68<25.3<50.37≈49.08→ →Lglass,% (lightness)

Icoating,% (intensity)←8.91<15.75<34.17<54.89<71.31→ Lcoating,% (lightness)

The relative coloring ability of the studied dyes can be estimated from the values of lightness L (an indicator of inversely proportional color intensity). For example, cobalt (II) oxide colors a coating based on a transparent matrix enamel in the system $R_2O–BaO–ZnO–Al_2O_3–B_2O_3–TiO_2–SiO_2$ ~8 times more intense (71.31:8.91) than iron (III) oxide, and, for example, potassium dichromate yields 1.6 times more intense (54.89:34.17) color of the enamel coating than copper (II) oxide.

Conclusions

We established the dependences of color characteristics of glasses and enamel coatings based on matrix transparent glass in the system $R_2O–BaO–ZnO–Al_2O_3–B_2O_3–TiO_2–SiO_2$ on the type of ionic dye and its amount. It is proposed to evaluate the coloring ability of chromophore components in specific units with the help of the series «color intensity I–lightness L». As a result of the conducted research, the compositions of glass enamels for non-ferrous metals, which do not contain lead, have been developed. New enamels of a wide palette of colors, created on the basis of matrix transparent enamel, are characterized by the same firing interval of 780–820^{0}C. Enamels were tested in the workshop of the Museum of Ukrainian Painting (Dnipro), at the jewelry factory Diadema (Vinnytsia) and recommended for implementation in the production of art and jewelry.

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ЗАКОНОМІРНОСТІ ЗАБАРВЛЕННЯ ІОННИМИ БАРВНИКАМИ БАЗОВОЇ СКЛОМАТРИЦІ ТА ЕМАЛЕВИХ ПОКРИТТІВ У СИСТЕМІ $R_2O-BaO-ZnO-Al_2O_3-B_2O_3-TiO_2-SiO_2$

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У роботі наведені результати дослідження щодо виявлення закономірностей забарвлення однієї базової скломатриці та емалевих покриттів на її основі в системі $R_2O-BaO-ZnO-Al_2O_3-B_2O_3-TiO_2-SiO_2$ низкою іонних барвників. Незалежно від вмісту барвників, вони надають однаковий колірний тон як стеклам, так і покриттям на основі цих стекол, а саме: CuO (1,0–3,0 мас.%) λ=489–494 нм (синьо-зелений), Fe_2O_3 (0,5–2,0 мас.%) λ=575–585 нм (жовтий), $K_2Cr_2O_7$ (0,5–2,0 мас.%) λ=570–576 нм (жовто-зелений), CoO (0,5–1,0 мас.%) λ=441–463 нм (синьо-фіолетовий), NiO (0,5–1,0 мас.%) λскла=559'–571' нм, λпокриттів=598–629 нм (коричневий). Доведено, що за ступенем інтенсивності забарвлення стекол і покриттів на їх основі барвники розташовуються в наступній послідовності: $CoO>NiO>CuO>K_2Cr_2O_7>Fe_2O_3$. Дослідження здійснювались за допомогою розробленої спеціальної комп'ютерної програми COLOUR GLASS. Встановлені закономірності застосовано при розробці безплюмбатних склоемалей для ювелірних та художньо-декоративних виробів.

Ключові слова: скло, емаль, покриття, іонний барвник, забарвлення.

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Keywords: glass; enamel; coating; ionic dye; coloring.

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