Представлені результати розробки кольорових ювелірних емалей на основі безсвинцевого скла для декоративних, художніх і ювелірних виробів із золота, срібла та міді. Досліджено спільний вплив на оптико-колірні характеристики добавок TiO_2, MoO_3, Fe_2O_3 і барвників NiO, CoO і $K_2Cr_2O_7$+CuO. Отримано зелені, трав'яні, гірчичні, фіолетові, коричневі емалеві покриття з температурою випалу 800 °С. Запропоновано шкалу оцінювання якості емалевого покриття

Ключові слова: ювелірна емаль, склопокриття, гаряча емаль, художнє емалювання, іонне забарвлення, колір скла

Представлены результаты разработки цветных ювелирных эмалей на основе бессвинцового стекла для декоративных, художественных и ювелирных изделий из золота, серебра и меди. Исследовано совместное влияние на оптико-цветовые характеристики добавок TiO_2, MoO_3, Fe_2O_3 и красителей NiO, CoO и $K_2Cr_2O_7$+CuO. Получены зеленые, травяные, горчичные, фиолетовые, коричневые эмалевые покрытия с температурой обжига 800 °С. Предложена шкала оценивания качества эмалевого покрытия

Ключевые слова: ювелирная эмаль, стеклопокрытие, горячая эмаль, художественное эмалирование, ионное окрашивание, цвет стекла

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OBTAINING DYED DECORATIVE ENAMELS FOR PRODUCTS MADE OF GOLD, SILVER AND COPPER

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1. Introduction

Enameling has more than 3000-year history. The ancient objects with enamel, found by archaeologists, date back to the 14th century B.C. The enameling of the precious metals as the decorative enameling was the first to appear [1]. The application of the colored glass as the coating fused to the metallic surface is one of the earliest technologies in the decorative applied art. However, this form of the decoration of different articles made of gold, silver and copper has not lost its popularity until today.

The enameled jewelry articles, dishes, icons, church utensils, picture and mirror frames, vases and elements of the interior decor are becoming increasingly popular.

For many centuries, the decorative enameling was rather an art than an exact science. The secrets of craft were the property of a master and were passed on from generation to generation [2]. In the course of time, many compositions of jewelry enamels were lost. Therefore, the development of new formulations of artistic enamels is an urgent task, which will facilitate the development of decorative applied art and jewelry production.

Nowadays the Ukrainian artists-enamellers mostly use imported enamels. The contemporary world market is presented by the following firms: Tompson (USA), Schauer (Austria), Limoge (France), Milton Bridge (England), the Dulevskiy dye plant (Russia) [3].

The complex technology of manufacturing the artistic enameled articles, the lack of production standards, the enamels of insufficient quality and high percentage of defective finished articles are the main problems with enameling of the nonferrous metals [4].

2. The literature analysis and the problem statement

Traditionally, scientists throughout the world pay considerable attention to the problems of enameling steel, cast iron and aluminum, which is testified by the materials of the international congresses of enamellers [5]. The existing world standards applied to the enamel coatings [6] are developed considering the enamels for steel, cast iron and aluminum. There is no standardization of jewelry enamels. Those few contemporary works [1, 4, 7–9], which present the results of research into jewelry enamels mostly focus on the compositions, which contain lead oxide.

For obtaining the articles made of gold, silver and copper, the lead silicate enamels (PbO up to 65 %) are applied. For obtaining highly artistic articles, the application of enamels of different colors is conducted step by step depending on the enamel fusing temperature. Therefore, their firing is carried out repeatedly (up to 15 times) [9]. The lead compounds contribute to spreadability and high luster of enamels. It was established as a result of the conducted studies [10] that many lead containing enamels for noble metals do not ensure a quality enamel coating because of high firing temperature (exceeding 800 °C) or because of low chemical stability. In different countries there are corresponding limitations to the use of lead compounds in the production. The transition to the lead-free enamels is especially urgent because of lead's high toxicity and sublimation in the process of founding [11].

The danger of lead for a human is determined by its toxicity and ability to be accumulated in the organism. In many countries the pollution of air, water and soil with lead is an ecological issue. Its content in the cities exceeds maximum permissible concentration by dozens of times. Lead is the main anthropogenic toxic element in the group of heavy metals. In the report to the World Health Organization in 2002 [12], the influence of lead and its compounds is defined as one of the 20 factors, which cause diseases in humans. Thus, the problem of environmental pollution with lead is very urgent nowadays. In this case, the most radical protection is the transition to the lead-free technologies. Besides, the lead compounds are the expensive and deficit components.

In connection with this, a number of studies aimed at obtaining the low-lead and lead-free compositions of jewelry enamels were conducted. It should be noted that the studies of the development of enamels without application of lead are not numerous.

In the work [9], the fusible (780–800 °C) enamels of sky-blue color for copper and its alloys were obtained. The enamel coatings were developed on the basis of alkali-containing silicate glass with a low amount of boron and lead.

Barium oxide was introduced for the purpose of obtaining lead-free fusible enamel instead of lead oxides. As the base of the glass matrix, the system SiO_2–Na_2O–K_2O–B_2O_3–BaO–CaO–Al_2O_3 [13] was selected. As a result, the enamels for artistic products made of copper were obtained. The temperature of their applying was 850 °C, which hampers their wide application.

The known [2, 14] jewelry enamels of different color tones are also distinguished by chemical composition. This leads to essential difference in the values of temperatures of firing enamels of different colors: from 800 to 950 °C [15].

In the source [16], a new method of applying the enamels to the jewelry articles with the use of 3D technologies is suggested. In connection with this, the task of obtaining colored enamels of different colors on one glass base was set.

Thus, colored glasses of a wide palette, close in their properties, which will be fired at the same temperatures, are necessary for contemporary artistic enameling. The content of lead compounds in their compositions must be excluded.

3. The purpose and the tasks of the research

The purpose of this work was obtaining light-colored enamel coatings of a various color range on one lead-free glass base, which will make it possible to simplify the technology of production of decorative and jewelry articles.

To achieve this purpose, the following tasks should be solved:

– to study combined influence of the additives, which impart white achromatic color to glass and the components, which ensure specific chromatic color, on the optic and color characteristics of coatings on the copper base layer;

– to determine the best additives and their rational content for obtaining the opacified coatings;

– to estimate the quality of obtained enamel coatings.

4. Materials and methods of the study of the optic and color indices of enamel coatings during the introduction of dyes and additives TiO_2, MoO_3, Fe_2O_3

As the glass base for obtaining dyed coatings, the base enamel 10N, which was developed at the Department of Chemical Technology of Ceramics and Glass of the Ukrainian State Chemical-Engineering University (the city of Dnipro, Ukraine), was accepted. Its chemical composition is, mass %: SiO_2+TiO_2–44,5; Na_2O+K_2O–26,0; B_2O_3+Al_2O_3–14,5; BaO+ZnO–15,0. The main properties are: leaching – 2,0 cm^3/g, temperature of the beginning of softening (TBS) – 550 °C and temperature coefficient of the linear expansion (TCLE) – $110 \cdot 10^{-7}$ $degree^{-1}$.

Into a basic composition of the glass 10N, there were additionally introduced above 100 mass % the additives TiO_2 in the quantity of 10,0; 12,5 and 15 mass %, MoO_3 – 1,5; 2,25 and 3,0 mass %, Fe_2O_3 – 0,25; 0,5 and 0,75 mass % as the components, which influence glass transparency. Titanium dioxide opacifies glass as a result of its crystallization with the enamel coating firing in the form of anatase or rutile modification. Molybdenum oxide is the dispersion opacifier [14]. It is known [17] that iron oxide in small amounts is the modifying additive, which changes the microstructure of glass. Due to the intensification of liquation processes, the introduction of Fe_2O_3 leads to an increase in the coefficient of diffuse reflection (CDR) of enamel coatings. All enumerated additives must give white color to the glass and the coating.

For dyeing glasses in the mass, the d-elements are mostly used, each of which exists in several valence-coordination states, and depending on this, has selective absorption of the luminous radiation in the strictly fixed spectral range [18]. Dye ions mainly carry out the functions of modifiers, being located in the glass matrix cavities, connecting through oxygen with the silica-oxygen network. The color the chromophore ions give to glass depends on their valence state and the coordination number in the chromophore complexes [19].

According to the known data from the literature [20], the following dyes are added to the glass for obtaining the color:

– NiO – dyes the glass into violet, brown and rarely yellow or green colors;

– CoO – gives dark-blue, gray or pink color to basic glass;

– the combination of $K_2Cr_2O_7$+CuO – dyes the glass into blue-green colors depending on their ratio.

The indicated dyes were introduced above 100 mass % of the basic glass 10N and to all the glasses, containing the additives TiO_2, MoO_3 and Fe_2O_3. NiO, CoO and $K_2Cr_2O_7$+CuO were added to the charge for founding in the amount of 0,75 mass p., 0,37 mass p., 0,45+0,52 mass p., accordingly.

Founding of the experimental glass was carried out under laboratory conditions in the furnace with the silit heaters at the temperature of 1250 °C for 1 hour. During the process of observing the fusion, the active gas generation and foaming were not noticed. The readiness of the glass was checked against the thread and the flat cake. It was fritted by a dry method, passing the fusion through the iron shafts. All the obtained frits were dyed evenly and had good luster.

The frit was ground in the agate mortar until it was able to pass through the sieve No. 0063. The dross was prepared by the following recipe: 100 mass p. of frit, 40 mass p. of water, 3,3 mass p. of organic bond. They were applied by a wet method, by the method of pouring onto the copper degreased samples, dried at the temperature of 100–120 °C until complete moisture removal and fired in the muffle furnace at the temperature of 800 °C for 3 min. 3 layers of the enamel were applied.

The visual estimation of the coatings quality was conducted in accordance with the characteristic scale, developed at the Department of Chemical Technology of Ceramics and Glass of the Ukrainian State Chemical-Engineering University (the city of Dnipro, Ukraine) (Table 1).

Table 1

Scale of the coating quality evaluation

Points	Enamel description
1	The coating is not fused, numerous defects, lack of luster
2	The coating is insufficiently fused, the surface is not smooth, numerous defects, unsatisfactory luster, uneven dyeing
3	The coating is fused, there are single defects: pricks (“pockmarks”, “pimples”), internal cracks and breaks, insignificant burnouts or foaming of enamel; the luster is satisfactory, uneven dyeing
4	The coating is well fused, the smooth and even surface, there are small single pricks (“pimples”, “pockmarks”), good luster, insignificant change of the enamel color over the surface
5	The coating is well fused, the smooth and even surface, without any defects, high luster, the even dyeing of the surface

The luster of the obtained coatings was determined with the instrument BF-2 [21] and the color characteristics were determined with the color comparator CC-3 [22] by the standard colorimetric system XYZ, proposed by the International Commission of Illumination (ICI) [23].

The differential-thermal analysis of the glass frits was carried out with the derivatograph Q-1500D, the X-ray phase analysis was carried out with the plant DRON-3.

5. Results of the studies of enamel coating and glass frits properties

The optic color characteristics of the obtained enamel coatings were determined. The results of the studies are given in Table 2.

The analysis of the characteristics of the obtained coatings was carried out in comparison with the characteristics of the dyed basic composition of 10N, which does not contain the components influencing the transparency of glass.

With the use of cobalt oxide as a dye, the coatings of dark-blue color with the low purity of 1–5 % were obtained, in this case the wavelength of coatings ranges from the violet spectrum area λ=443 nm to the blue-azure area λ=489 nm during the introduction of the opacifying additives to the basic glass 10N.

The combination of different opacifying additives and the nickel oxide dye to the basic glass leads to the formation of various colors and shades (Table 2). In this case, the color purity of 5 % in the basic glass 10N rises considerably with the introduction of the opacifying additives, for example, to 39 % with 1,5 mass % MoO_3. The coatings are characterized by λ from 482 nm to 605 nm, which corresponds to the green, yellow and orange spectrum area.

Table 2

Optic color characteristics of the obtained coatings

Enamel name	Color tone λ, nm	Color purity P, %	Luminosity L, %	Coefficient of mirror reflection (CMR), %	Visual estimation, color/ points
Additive CoO – 0,37 mass p.					
10N	443	1	8,1	60	blue/5
10N–10TiO_2	479	5	7,9	93	blue/4
10N–12.5TiO_2	478	3	7,7	95	blue/4
10N–15TiO_2	489	4	10,0	67	blue/4
10N–1.5MoO_3	474	4	8,7	89	blue/4
10N–2.25MoO_3	475	5	8,8	74	blue/4
10N–3.0MoO_3	467	2	9,3	65	blue/5
10N–0.25Fe_2O_3	440	1	6,6	81	blue/5
10N–0.5Fe_2O_3	455	1	9,1	65	blue /5
10N–0.75Fe_2O_3	470	3	9,4	61	blue /5
Additive NiO – 0,75 mass p.					
10N	605	5	8,6	82	brown/5
10N–10TiO_2	588	24	18,2	97	mustard/4
10N–12.5TiO_2	587	30	20,4	95	mustard /4
10N–15TiO_2	573	32	35,0	98	mustard /4
10N–1.5MoO_3	482	39	24,7	99	violet/5
10N–2.25MoO_3	530′*	20	21,2	91	violet /5
10N–3.0MoO_3	510′	17	28,9	72	violet /5
10N–0.25Fe_2O_3	537	21	15,2	87	brown /5
10N–0.5Fe_2O_3	536	21	14,2	63	brown /5
10N–0.75Fe_2O_3	517	16	13,9	65	brown /5
Additive $K_2Cr_2O_7$ –0,45 mass p.+CuO–0,52 mass p.					
10N	521	20	19,4	66	grassy/5
10N–10TiO_2	583	44	15,9	66	mustard/3
10N–12.5TiO_2	589	26	19,3	60	mustard/3
10N–15TiO_2	584	34	23,4	57	mustard/3
10N–1.5MoO_3	502	10	11,8	98	green/4
10N–2.25MoO_3	502	10	13,5	86	green/5
10N–3.0MoO_3	507	19	31,7	74	green/5
10N–0.25Fe_2O_3	517	23	10,5	98	grassy/5
10N–0.5Fe_2O_3	512	23	10,2	95	grassy/5
10N–0.75Fe_2O_3	511	21	10,2	99	grassy/5

*Note: * – 530′ is the designation of the wavelength in the purple area of the color graph ICI*

With the use of combination of the potassium dichromate and the copper oxide dyes, the coatings of the complex colors, in which green and yellow shades with the wavelength of 502–589 nm are mixed up, were obtained.

Luminosity, the quantitative indicator of color, is the ratio of brightness of the luminous flow reflected by a body to the brightness of the flow falling onto a body. In connection with this, this characteristic can be used for the comparison of chromatic colors of one tone, achromatic (white, gray, black) colors among themselves, chromatic colors relating to different spectrum areas as well as chromatic colors with the achromatic ones.

Analyzing the luminosity of the studied enamel coatings, the dependencies represented in Fig. 1–3 were obtained.

It should be noted, that in spite of significant addition of “classical opacifier” TiO_2 to the basic glass 10N, only with its content higher than 10 mass %, the clarification of the coatings, dyed with NiO and $K_2Cr_2O_7$+CuO was observed (Fig. 1).

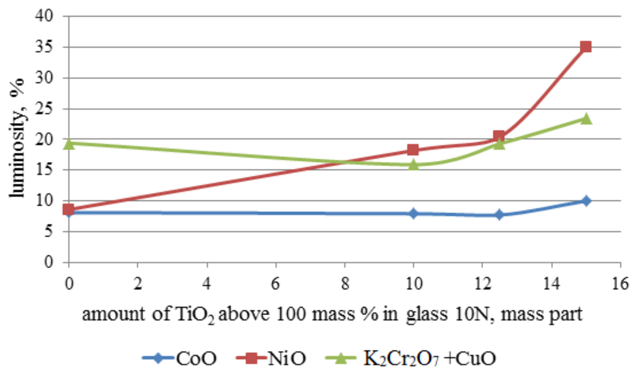

Fig. 1. Dependence of the enamel coatings luminosity on the TiO_2 concentration in basic glass

The combination of the dispersion opacifier MoO_3 with the dyeing NiO is manifested in the tendency of stable coatings clarification with an increase in the dyeing additive. At the same time, with the combination of dyes $K_2Cr_2O_7$+CuO, molybdenum oxide noticeably clarifies coatings with its content higher than 2 mass % (Fig. 2).

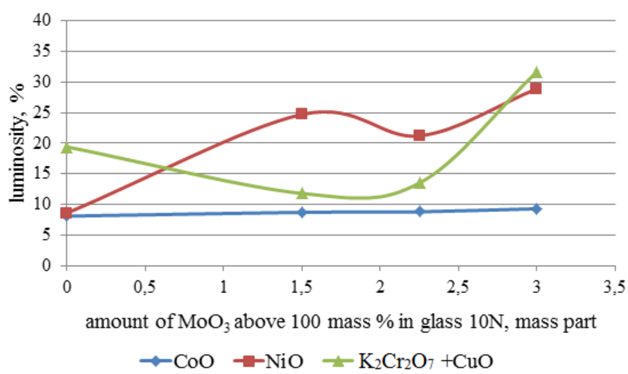

Fig. 2. Dependence of the enamel coatings luminosity on the concentration of MoO_3 in basic glass

Adding Fe_2O_3 to the studied basic glass 10N did not lead to noticeable clarification of coatings with all the studied dyeing components (Fig. 3).

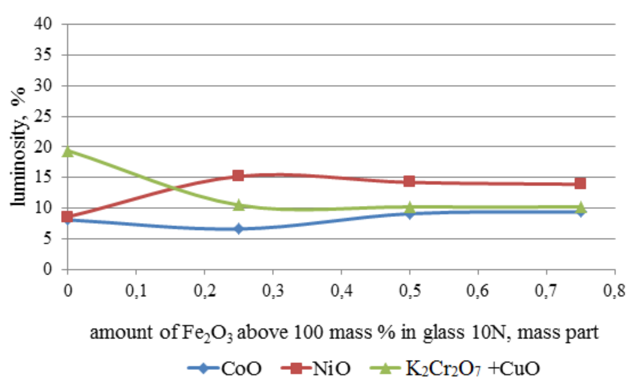

Fig. 3. Dependence of the enamel coatings luminosity on the concentration of Fe_2O_3 in basic glass

Moreover, based on the graphs, represented in Fig. 1–3, it is possible to assert that the luminosity of the enamel coatings dyed with CoO does not depend on the additives and the concentration of TiO_2, MoO_3, Fe_2O_3 in basic glass.

In the analysis of the obtained dependencies of CMR of the painted coatings on the content of titanium oxide in the glass 10N (Fig. 4), it was noted that the introduction of 10 mass % of TiO_2 to the compositions, which contain cobalt and nickel oxides, leads to an increase in luster. With the content of 15 mass % of titanium dioxide in the glass with CoO, the abrupt decrease in luster occurs, whereas with NiO this index remains at a constant level. For the compositions dyed with the combination of dyes $K_2Cr_2O_7$+CuO, the introduction of TiO_2 into the basic composition of glass and the subsequent increase in its content does not practically influence the value of CMR.

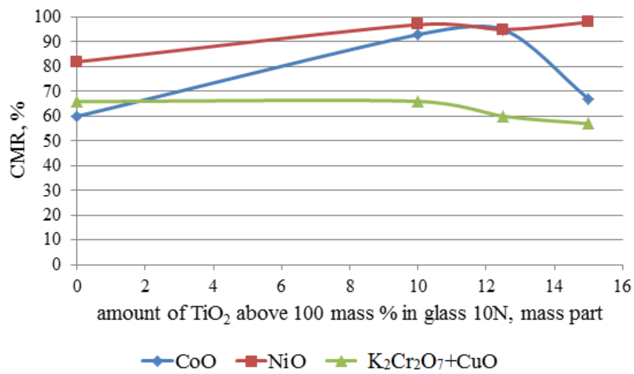

Fig. 4. Dependence of the enamel coatings CMR on the concentration of TiO_2 in basic glass

During the introduction of 1,5 mass. % of molybdenum oxide into the basic composition of 10N, the CMR value for the obtained coatings increases considerably (Fig. 5). But the following increase in the content of MoO_3 reduces this index, probably due to crystallization of glass covering.

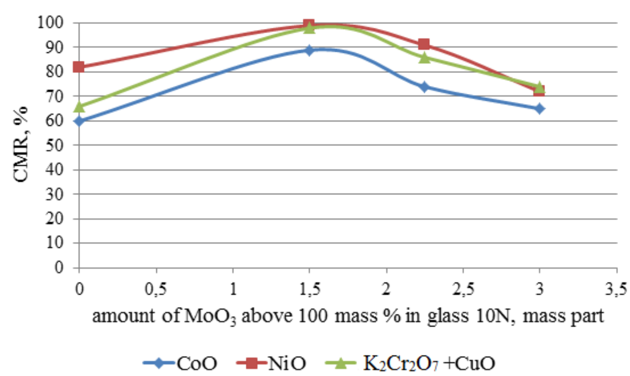

Fig. 5. Dependence of the enamel coatings CMR on the concentration of MoO_3 in basic glass

Adding 0,25 mass % of Fe_2O_3 influences the luster of basic glass in the same way as TiO_2 and MoO_3, i.e. increases it (Fig. 6). The further increase in the content of Fe_2O_3 in combination with CoO and NiO leads to a decrease in CMR, and in combination with the dyeing composition of $K_2Cr_2O_7$+ +CuO, the coatings luster does not practically change.

The visual estimation according to the scale of Table 1 was carried out for the obtained enameled copper samples. The results of the coatings quality are given in Table 2. All coatings scored 4 and 5 points, except for the titanium containing compositions, dyed with the combination of the dyes $K_2Cr_2O_7$+CuO. The chromium compounds in certain compositions can act not only as dyes, but also as opacifiers [19]. This was presumably the cause of the poor quality of the titanium containing coating as a result of its high crystallization.

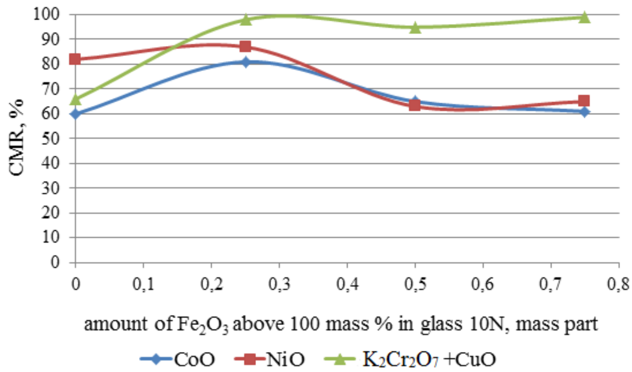

Fig. 6. Dependence of the enamel coatings CMR on the concentration of Fe_2O_3 in basic glass

6. Discussion of the changes in the optic color indices with the introduction of dyes and additives TiO_2, MoO_3, Fe_2O_3

For examining the processes occurring during the enamel coating firing, a differential-thermal analysis of the compositions containing maximal quantity of additives TiO_2, MoO_3, Fe_2O_3 in combination with dyes $K_2Cr_2O_7$+CuO was carried out (Fig. 7).

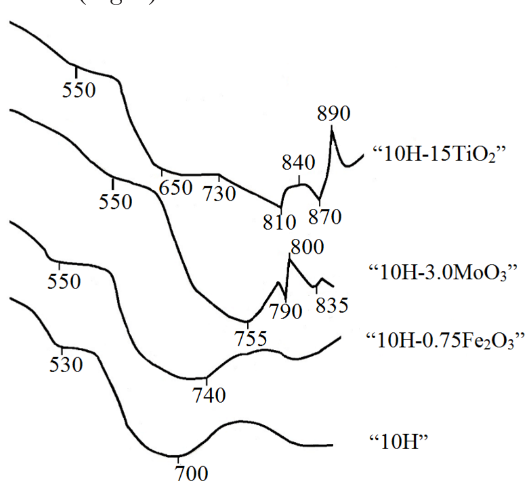

Fig. 7. Curves of glass DTA with addition of $K_2Cr_2O_7$+CuO

As we see, the basic glass 10N and 10N with adding 0,75 mass % Fe_2O_3 has the classical form of a DTA curve without crystallization, whereas in the DTA curve of glass with 3,0 mass % of MoO_3, the sharp deep endo-effect at the temperature of 790 °C is observed, the form of which testifies to the melting of crystalline phase, which must have been formed in the glass at the moment of fritting. The exo-effect in the form of the distinct maximum at the temperature of 800 °C can testify to the distinguishing of a crystalline phase.

With adding 15 mass % of TiO_2 to the glass, the sharp small but explicit endo-effects of melting are observed in the DTA curve, or which is more probable, dissolution in the fusion of glass of two crystalline phases at temperatures of 810 °C and 870 °C. Judging by the well-known facts of the behavior of titanium dioxide in the glass, there can be two polymorphous TiO_2 modifications – anatase and rutile, formed in the glass at the stage of fritting. The sharp exo-effect of crystallization appears at the DTA curve at a higher temperature – 890 °C. Consequently, at the temperature of enamel coatings firing of 800 °C, according to the data of glasses, there cannot be any distinct opacifying of the titanium containing coatings, which is confirmed by the low values of luminosity of titanium containing coatings with all dyes.

With the help of the X-ray phase analysis, crystalline phases, which are distinguished during the investigated coatings firing, were established (Fig. 8).

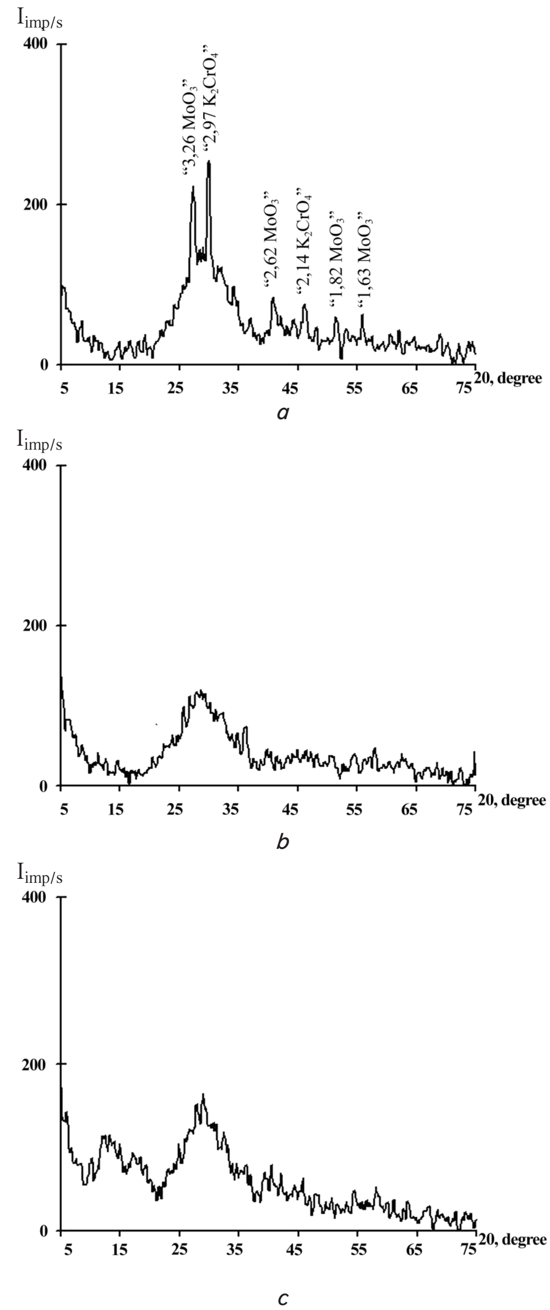

Fig. 8. Diffractograms of examined glasses: *a* — glasses 10N—3, 0MoO3 (hold time — 3 minutes); *b* — glasses 10H—15TiO_2 (hold time — 3 minutes); *c* — glasses 10H—15TiO_2 (hold time — 30 minutes)

For the molybdenum containing glass the hold time was 3 minutes at the temperature of 800 °C (the mode of experimental coatings firing), in this case the presence of two crystalline phases – MoO_3 and K_2CrO_4 is fixed on the diffractogram (Fig. 8, *a*). The titanium containing glass was held at the coatings firing temperature of 800 °C for 3 and 30 minutes (Fig. 8, *b, c*). The form of diffractograms, amorphous halo, testifies to the fact that the content of crystalline phase in the coating is less than 2–10 % (the sensitivity of the Debye-Ferrer powder method).

As a result of the conducted studies, it was established that in this type of glass, adding Fe_2O_3, in contrast to the data of the source [17], does not make it possible to reach the enamel opacifying at the expense of liquation processes. Titanium and molybdenum oxides are promising additives for obtaining the enamel coatings of bright tones. Using a glass base of one chemical composition, it is possible to obtain the enamel coatings of different colors for decorative, jewelry and artistic articles, which are fired in a narrow temperature range. This will considerably simplify the technology of obtaining enameled articles.

The developed colored enamel coatings do not contain lead oxide. This makes it possible to reduce the cost of jewelry enamel due to the use of a cheaper raw material. Furthermore, the synthesis and the introduction of lead-free enamels contribute to the solution of ecological problems, connected with the environmental pollution by lead compounds.

All studies were conducted on the lead-free glass base 10N, which had been developed earlier. Subsequently, the studies aimed at the color range expansion are planned.

7. Conclusions

1. The enamels dyed with cobalt oxide relate to the dark-colored ones according to the work [24], since they have low luminosity of 6,6–10 % and low color purity of 1–5 %. Cobalt oxide is the component with high dyeing power and in the amount of ~1,0 mass % ensures intensive dark-blue color in the thickness of the glass layer of 0,6 mm [20], whereas in the work, the intensive dark-blue dyeing the glass with the thickness of 0,7–0,8 mm with cobalt oxide concentration of 0,37 mass % was obtained. During the combination of nickel oxide and titanium oxide as an opacifier in the basic composition 10N, the bright colored coatings with luminosity of 20,4–35,0 % and the color purity of 30–39 % were obtained. The additives MoO_3 and Fe_2O_3 in combination with the dye NiO make it possible to obtain the coatings, which belong to the dark-colored ones by their color characteristics (Table 2). While introducing the combination of the dyes of potassium dichromate and copper oxide and adding 15 mass p. of titanium oxide, the bright colored coating with the luminosity of 23,4 % and the color purity of 34% was obtained. With the other opacifying additives, this combination of dyes makes it possible to obtain only dark-colored coatings (Table 2).

2. By introducing the additives TiO_2 to 15 mass % or MoO_3 to 3,0 mass % to the glass dyed with ionic dyes, it is possible to vary the shade of the obtained color due to "brightening" of the basic glass. Adding iron oxide to 0,75 mass % does not influence the basic glass 10N opacifying and does not make it possible to obtain bright tone coatings.

3. The developed colored lead-free enamel ensures faultless, smooth and transparent glass coating on the copper samples at the firing temperature of 800°C, which makes it possible to apply it to both gold and silver.

As a result, green, mustard, violet, dark-blue, brown and grassy enamel glass coatings with the luster of 57–99 % were developed, which have good cohesion with the copper samples; they can be recommended to be tested under production conditions.

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