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# DEVELOPMENT OF COMPOSITIONS OF PIGMENTED COLORED LEAD-FREE GLAZES FOR IMPROVING CERAMIC PRODUCT DESIGN

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The features of the surface structure of different types of ceramic are determined and their comparative characteristics are presented. The decoration of faience with colored glazes is examined and the composition of lead-free pigmented faience glaze is described.

***Key words:*** faience glaze, ceramic paint, glaze coating.

Glazing consists in the coating of products with glaze in order to improve aesthetic properties and increase decorative qualities. Glaze is an inorganic glassy and transparent coating. The glazing of ceramics gives the latter strength and durability. The main component of any glaze is silica, whose base is silicon dioxide $SiO_2$; alumina $Al_2O_3$ and borax are also present in the glaze. Due to the high melting point of silicon dioxide (1600°C) fluxes are added to the glaze (small amounts of the oxides PbO, CuO, $Na_2O$, ZnO, CaO, and others). The shades of the same color on the ceramic beneath a glaze coating vary depending on the content of lead, boric acid, system pH, and other additives in the glaze [1 – 3].

The fritted glaze suspensions used in manufacturing tend to settle with compacted sediment being formed. Fine grinding of solid components and the addition of such highly dispersed components as bentonite, clay, and kaolin reduce the rate of separation and increase the aggregate stability of the glaze [4].

There are several varieties of ceramics. In particular, faience possesses a fine-pored surface covered with a colorless transparent or dull (opaque) glaze. Majolica is a ceramic consisting of a porous clay body produced at low temperatures. Majolica is made from fired clay (faience waste) with the use of colored glazes. Porous faience and majolica products have different surface structure. Majolica is made from faience bodies with a specific recipe and decorated with colored lead glaze coating (glaze) [5].

The color of the glaze is due to the presence of certain coloring oxides in it. The tint of the color is affected by the content of oxides, such as $Al_2O_3$, BaO, MgO, ZnO, and others, in the glaze.

*Blue glazes* owe their color to the presence of cobalt oxides or salts in their composition. However, the addition of about 15% (by weight) $Na_2O$ to the glaze gives bright ultramarine hues. When $K_2O$ is present in the glaze, cobalt gives a blue spectral color. A multi-alkali glaze with $Na_2O$ and $K_2O$ present together changes the green color of the copper dyes to blue-green, and the blue and cobalt tones become very bright.

*Green glazes* acquire a rich color and shine when copper oxide CuO and zinc oxide ZnO are present together. Bright low-transparent green colors can be obtained by adding chromium oxide $Cr_2O_3$. If the glaze contains > 3% (by weight) $Cr_2O_3$, the glaze becomes completely opaque, like paint.

*Brown glazes* owe their color to the presence of iron oxide FeO. Various hues (red, pink, violet) are obtained when manganese oxide MnO is added to brown glaze. An excess of calcium oxide in faience glaze contributes to the production of bright red hues of pink colors [6].

*Majolic lead glazes* with cobalt oxide weight content 1.0 – 1.5% are dark blue. Borax and alumina are not added in this case, as they make the glaze darker.

*Turquoise and pale-blue glazes* owe their color to the presence of copper, potassium, and sodium oxides in alkaline lead glazes. Zinc oxide imparts a blue-green hue.

*Yellow lead glazes* acquire this color due to the presence of iron oxide or antimony oxide. Hues ranging from yellow-brown to dark brown appear when the amount of iron oxide is increased. However, glazes with high lead content and insufficient silica are known to adversely affect the following color hues: chromium greens turn brown or yellow-brown, and titanium yellows turn dirty-yellow and green.

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Lead oxide has a positive effect on all other colors. Multilead glaze forms a warm palette of tones, but only decorative faience articles such as vases, sculptures, etc. are covered with such glaze. In addition, the use of lead oxide in majolica colored glazes is environmentally unsafe [7].

The purpose of the present studies was to develop colored, pigmented, lead-free glazes for faience. For this, additives of pigments or their mixtures (including coloring oxides) were used in certain quantities in lead-free faience glaze in order to develop a pigmented faience glaze formulation. In experiments, some organic substances were added to assess their effect on the properties of the glaze slip and the color of the glaze coating. The influence of mineral additives such as pegmatite, magnesite, borax, and others on the technological properties of the glaze and the quality of the glaze coating was studied.

## OBJECTS OF STUDY AND PROCEDURE

The following initial components were used to develop pigmented lead-free faience glaze.

The weight content of the components of faience frit was a follows, %: quartz sand — 29.7; feldspar (pegmatite) — 19.1; borax — 14.4 (boric acid, $B_2O_3$ content — 37 – 57%); fired glazed faience body — 10; strontium carbonate — 13.3; soda — 5.4; chalk — 6.2; magnesite (dolomite) — 1.9. Sodium sulfate (up to 1.0%), cobalt color (alloy of oxides Co–Cr–Zn–Fe up to 0.032%), and borax (1.2 – 1.9%) were used to modify the frit so as to improve the appearance of products and reduce post-firing streaking on the glaze surface and to increase the heat resistance of the products. The result was the following formulation for finished faience glaze (weight content, %): faience frit 72 – 73; clay 7.5 – 10.0; quartz sand 4.5 – 6.5; pegmatite 15.0; sodium sulfate — 1.0; and, lime (burnt chalk) — 0.075. The latter is added to regulate the coagulation properties of the faience glaze. Pegmatite (75% silicon dioxide $SiO_2$ with admixtures of Ca, Al, Si, Be, Li, Pb, Cs, Zr) is introduced to improve the drying of aqueous glaze after application to a porous surface. Colored pigments were used to give color hues — brown and green (an alloy of oxides of Co, Cr, Zn) in amounts up to 25% (by weight) faience glaze.

In other experiments an aqueous solution of urea-formaldehyde resin KF-Zh was added into the formulation (following GOST 14231–88).

Mixtures of ceramic colors was used in the investigation:

No. 1 — brown + orange + pink;

No. 2 — turquoise + green + cobalt color;

No. 3 — pink + cobalt color + brown.

Ceramic paint is a mineral paint based on mineral dyes (metal oxides). However, due to the high melting temperature > 1450°C, to obtain frit the metal oxides are mixed with a flux after the melt of the mineral components cools.

Several methods were used to prepare colored glazes for both faience glaze and majolica with a high content of strontium, borax, and $Na_2O$. The first method is to simply mix the glaze with the underglaze color. The second method is to fuse the ready ceramic paint with glaze, followed by wet (water) grinding. Fusion of dry faience glaze with green paint was performed at ratio 3% paint to dry glaze material. Wet (water) milling lasted for 40 h in a laboratory mill with uralite balls.

The technology for preparing the pigmented lead-free faience glaze consisted of the following: a mixture of ceramic pigments was passed through a sieve with 3600 holes/$cm^2$. The faience glaze was taken in the form of a thick aqueous suspension with moisture content 48% and density 1.5 g/$cm^3$. Pigments or their mixture were added to a part of the glaze aqueous suspension and, after mixing, was added to the rest of the glaze and passed twice through a finer sieve (4900 holes/$cm^2$). To eliminate the stratification of the suspension a 5% aqueous solution of polyvinyl alcohol (PVA) was introduced in the amount 0.03% (by weight) into the prepared glaze suspension to increase its aggregate stability, which additionally gives the tone of the colored suspension.

To obtain colored glazes, mixtures of green, cobalt, and brown pigments were added in amounts 3% (by weight) with the ratios 5.0 : 5.0 : 2.0, respectively, and subsequently magnesite $MgCO_3$ was added in amount 0.5 g. a uniform glaze surface was obtained after thorough mixing, application on a porous ceramic surface by dipping, and subsequent firing at 1140 – 1160°C.

The dry matter in the glaze was determined by the pycnometric method [8, 9]. An organoleptic method was used to assess the quality of the glaze coating.

The quality of the ready glaze was checked against GOST 4.69–81 and GOST 28390–89 indicators. The gloss and surface cleanliness were determined and a flame test was performed.

## EXPERIMENTAL PART

**Introduction of pigments or their mixtures into lead-free faience glaze.** An aqueous suspension of faience glaze with moisture content 45 – 50% and density 1.35 – 1.40 g/$cm^3$ was prepared from the components of the specified composition. Mineral substances (pegmatite, borax, alumina, dried quartz suspension, ceramic paint) were added in excess of 100% (to the dry residue of the aqueous dispersion of faience glaze) to obtain the formulations indicated in Table 1.

It follows from Table 1 that due to the difference in the mineralogical composition of these pigments both formulations of the brown, lead-free, strontium glaze (compositions1 and 2) have a better quality coating than the green glaze. Therefore, it can be concluded that the use of a mixture of brown pigment with other pigments will have a beneficial effect on the quality of the technological glaze.

**TABLE 1.** Compositions of Colored Lead-free Unfritted Faience Glazes

| Composition number and glaze color | Weight content of components, % | | | | | | | | Quality of glaze coating (visual determination) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Colorless faience glaze | Pegmatite | Borax | Alumina | Dried quartz suspension | Ceramic paint* | Brown and dark-brown pigment | Green pigment | Gloss, GU** | Coverage | Surface cleanliness — presence of pinholes pinched |
| 1 — brown | 100 | – | – | – | – | 5–6 | 25 | – | 40 | – | Absent |
| 2 — dark-brown | 100 | – | 1 | 1 | 1 | 5–6 | 25 | – | 44 | – | Absent |
| 3 — green | 100 | 10 | 1 | – | – | 2–3 | – | 25 | 36 | – | Present |

* Contains ceramic pigments.

** Gloss Units in accordance with GOST 31975–2017 (ISO 2813–2014).

**TABLE 2.** Composition of Formulations of Unfritted, Lead-free, Faience Glazes with Added Pigments

| Composition number and glaze color | Weight content of pigment, % | | | | | Quality of glaze coating (visual determination) | | |
|---|---|---|---|---|---|---|---|---|
| | Green | Cobalt | Brown | Turquoise | Rose | Gloss, GU | Coverage | Surface cleanliness – presence of pinholes pinched |
| 1 — blue-green | 1.0 | 1.5 | 2.0 | – | – | 36 | Good | Absent |
| | 1.0 | 2.0 | 2.0 | – | – | | | |
| | 1.0 | 1.0 | 3.0 | – | – | | | |
| 2 — grey | 2.4 | 2.4 | 4.9 | – | – | 36 | Good | Absent |
| | 1.5 | 3.0 | 6.0 | – | – | | | |
| | 2.0 | 3.0 | 4.9 | – | – | | | |
| 3 — brown | – | – | 10.0 | – | – | Good color, shine, and coverage by glaze | | |
| 4 — turquoise | – | – | 10.0 | 10.0 | – | Uneven surface coverage after firing | | |
| 5 — rose | – | – | 9.0 | – | 8.0 – 10.0 | Good color and coverage of the surface by glaze | | |

We performed experiments with compositions having different contents of brown pigment in the mixture, and so on. Compositions of colored, unfritted, lead-free, faience glazes with added pigments are presented in Table 2.

It is evident from Table 2 that colored glazes with 3 – 4% content of a mixture of green, cobalt, and brown pigments, in which the content of green pigment is greater than in the composition of Table 1, differ little in color, gloss, and glaze coverage. The glaze coating is uniform, but the glaze itself has become darker (muted) in color. On replacement of the cobalt pigment with pure cobalt oxide the tone of the glaze after firing changes, and non-uniformity of the glaze surface is noted.

### Study of the Effect of the Combined Presence of Mineral Additives — Pegmatite, Magnesite, Borax, and Urea-Formaldehyde Resin KF-Zh on the Quality of the Glaze Coating

Experiments were performed with the addition of urea-formaldehyde resin KF-Zh into the glaze composition to obtain a high-quality coating and improve its technological properties. An aqueous solution of urea-formaldehyde resin KF-Zh was introduced to prevent possible stratification due to the loss of aggregate stability. Magnesite $MgCO_3$ was additionally added to the formulations of colored lead-free faience glazes. Subsequent application of an aqueous suspension of glaze to the faience by dipping and firing at 1140 – 1160°C gives a coating of good quality with an even, smooth, and shiny surface. The compositions of lead-free, unfritted, faience glaze and its technological properties are presented in Table 3.

It can be concluded from the data in Table 3 that the criteria for the quality and selection of the final formulation for colored faience glazes are:

1) manufacturability (aggregative stability) of the selected composition, imparted by the KF-Zh resin present in the formulation;

2) decorative appearance of the glaze surface after firing, the result being an even, smooth, homogeneous, shiny surface with a glossiness of at least 46%, taking into account the composition of the glaze (the amount of mineral additives and ceramic pigments and the selected color and tone) and the ceramic surface.

**TABLE 3.** Composition of Gray Glaze Formulations and Quality of Glaze Coating with the Presence in it of Urea-Formaldehyde Resin KF-Zh

| Glaze color | Weight content of the pigments of dry faience glaze, % | | | | Water dispersion of KF-Zh resin, dry residue | | Technological and decorative properties of glaze based on an aqueous dispersion of glaze with density $d_{gl}$ = 1.38 g/cm$^3$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Green | Cobalt | Brown | Magnesite | 67 ± 2 | 22 ± 2 | Mass content of 22 ± 2% KF-Zh resin solution, % | Coagulation | Gloss and coverage | Color tone |
| Gray | 2.4 | 2.4 | 4.9 | 0.5 | – | 22.5 | 2 | Absent | Good | Lightened |
| Gray | 2.4 | 2.4 | 4.9 | 0.5 | – | 22.5 | 5 | Absent | Good | Gray |
| Gray | 2.4 | 2.4 | 4.9 | 0.5 | – | 22.5 | 7 | Absent | Good | Dark-gray |

## CONCLUSIONS

Today, coating ceramics with colored lead-free glazes remains one of the methods used to improve the quality and design of ceramic products and make them stronger and more durable.

Experimental results have shown that the addition of pigments or their mixtures in certain quantities (for example, a mixture of brown pigment with other pigments) in lead-free faience glaze beneficially affects the quality of technological glaze. The glaze coating is uniform, with excellent gloss and coverage, which surpasses the quality of decoration with colored lead glazes and is also promising from an environmental standpoint.

The simultaneous introduction of mineral additives — pegmatite, magnesite, borax, and urea-formaldehyde resin KF-Zh into the formulation of pigmented unfritted, lead-free, faience glaze improves the decorative properties of the glaze coating.

Research has shown that colored faience glazes with additives can be prepared without fritting (fusing), which is economically beneficial. On replacing cobalt pigment with pure cobalt oxide it becomes necessary to frit (fuse) this composition due to the heterogeneity of the glaze surface.

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