SYNTHESIS OF PIGMENTS BASED ON THE CuO – Cr2O3 – Al2O3 SYSTEM USING THE PRECIPITATION METHOD

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The purpose of the present work is to study a possibility of producing pigments based on CuO – Al2O3 and CuO – Al2O3 – Cr2O3 systems.

In the synthesis of pigments using the traditional powder method, Al2O3, Cr2O3, and CuO (analytical grade) were pulverized and fired in crucibles in a laboratory furnace at temperature 1100 C with holding at the maximum temperature of 30 min. For the purpose of comparison, pigments were obtained using the precipitation method. The authors used aqueous solutions of salts Cu(NO3)2 • 3H2O, AlCl3 • 6H2O, Cr(NO3)3 • 9H2O (analytical grade, concentration 0.5 mole/liter), since in this case the use of ammonium solution would result in the formation of soluble ammonium copper complex. The obtained precipitate was filtered, dried, and fired. After firing, the pigment was pulverized until it passes through a No.0056 sieve with residue 0.5 – 1.5%.

In order to test the pigments with respect to their color parameters, they were introduced into LG-10 fritted glaze in the amount of 3 – 10%. The glaze composition (wt.%) was as follows: 96 frit (LG-19), 2 – 4 Veselovskoe clay, and 0 – 2 kaolin. The following additives were introduced above 100%: 0.1 – 0.4 sodium nitrate, 0.03 – 0.1 sodium polyphosphate or tripolyphosphate, and 0.1 – 0.2 technical sodium carboxymethylcellulose. The moisture content in the glaze was 35 ± 2 wt.%

The pigment suspension was poured on the surface of facing tiles. The tiles were fired in a laboratory surface at temperature 950 ± 10°C with 30 min holding. After firing, the color of the pigment was visually determined (Table 1). The brightest were glaze coatings with pigments of compositions 1, 7, and 10.

The paste was prepared from flux based on LG-19 frit (45 – 55%) and transformer oil (45 – 55%). The pigment was introduced in an amount up to 5% into the components metered in accordance with the formula. The resulting paste was applied to wet glaze and fixed in a two-tier roller furnace at temperature 890 ± 20°C.

The investigation results indicated that pigment 7 in the paste has a light-gray color, and pigment 10 has a greenish-gray color.

Since this technology for pigment production is very energy-consuming and involves high-temperature synthesis, mixtures were prepared by the coprecipitation method: composition 7' and 10', respectively, corresponded to compositions 7 and 10.

In order to determine the precipitation pH and the required amount of precipitator, pH-metric titration was performed on a EV-74 universal ionometer with glass (ESL-43-07) and silver chloride (EVL-1M3) electrodes. Based on the
titration data, titration curves were constructed, and equivalence points were found from them (Fig. 1). One discontinuity can be identified on the titration curves of compositions 7' and 10', whereas the equivalence point of Al(OH)₃ dissolution (pH 12) is absent on the curves, which is evidence of a "loss of identity" of aluminum(III) in this precipitate. Copper hydroxide(II) in the precipitates is not dehydrated, i.e., copper also loses its "identity." This points to the fact that the resulting precipitate is not a mixture of individual hydroxides, but a hydroxide precipitate containing all three ions (Cu²⁺, Al³⁺, and Cr³⁺). The completeness of precipitation was verified by qualitative reactions to ions Al(II), Cr(III) and Cu(II) in the filtrate. The specified ions were not identified in the filtrate. Therefore, quantitatively all of the ions pass to the precipitate.

The calculation showed that three titration discontinuities ought to be seen on the titration curve [1]. The absence of the second and third discontinuity is evidence of the fact that the precipitate is not a mechanical combination of hydroxides, but a chemical compound containing all three ions.

The required amount of precipitator was found from the titration curves. It was found that a slight excess of the precipitator, when pH of the mixture reaches 9.0 – 9.5, is sufficient.

The sequence of pouring solutions is of great importance for the precipitation method. That is why two precipitates of each composition were prepared, using both direct and reverse pouring of solutions. The precipitates matured in mother liquor for 3 days, then were filtered with subsequent washing of the precipitate on the filter to remove adsorbed Na⁺, Cl⁻, NO₃⁻ ions, since the latter degrade the properties of the product.

Next, the precipitates were dried and fired at temperature 1100°C. To determine their color parameters, the obtained pigments in specified quantities were introduced into fritted glaze LG-19 and paste. The results of firing of pigments obtained by coprecipitation are given in Table 2.

With the aim of attempting to combine the process of firing the precipitate and the process of fixing glaze on the crock, which would allow a significant saving in fuel, the behavior of non-fired precipitates in glaze melt and in paste was investigated as well.

On introducing fired pigments and non-fired precipitates in the glaze and paste, good colored coatings without visible defects were obtained.

The structure, phase composition, and color parameters of pigments synthesized using the powder technology and the coprecipitation method were investigated using differential thermal, thermodynamic, and x-ray phase analysis and the reflection spectra.

Study of the pigments produced on the basis of the powder technology indicated that there are three endothermic effects on the DTA curves of compositions 7 and 10 (Fig. 2). The first effect is related to the loss of nonstructural water (85 and 120°C, respectively), the second is associated with the loss of structural water (262 and 276°C), and the third is determined by the conversion of CuO to Cu₂O with formation of two-layer scale (CuO + Cu₂O; 865 – 983 and 895°C). The total weight loss in pigment 10 was 2.7%, and in pigment 7 it was 0.8%. When pigments are produced by the precipitation method, more substantial weight losses are registered. For direct pouring of solutions, the total weight loss in pigment 10' was 42%, in pigment 7' it was 35%, and for inverse pouring it was 40.75 and 37%, respectively. In this context, the yield of the end product was calculated. It was found that in the case of inverse pouring of solutions, the yield of the finished product is greater.

An analysis of DTA curves of the precipitates and individual hydroxides showed that they are not additive. Consequently, the obtained precipitates are chemical compounds containing Cr³⁺, Cu²⁺, and Al³⁺ ions.

Additional data on processes occurring in synthesis of pigments were obtained from thermodynamic calculations performed according to the method described in [2]. It was found that formation of spinels CuO · Al₂O₃, CuO · Cr₂O₃, and CuO · Cr₂O₃ is possible in the given system. In this case,