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HIGH TEMPERATURE SYNTHESIS OF INORGANIC PIGMENTS IN THE ZnO-MgO-CoO-Al(OH)3-Al SYSTEM

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The method of self-propagating high-temperature synthesis (SHS) in the ZnO-MgO-CoO-$Al(OH)_3$-Al system produced pigments with a blue-blue spinel structure.

Spinels are chemical compounds produced by the interaction of divalent metal oxides with amphoteric oxides of three-and four-valent metals.

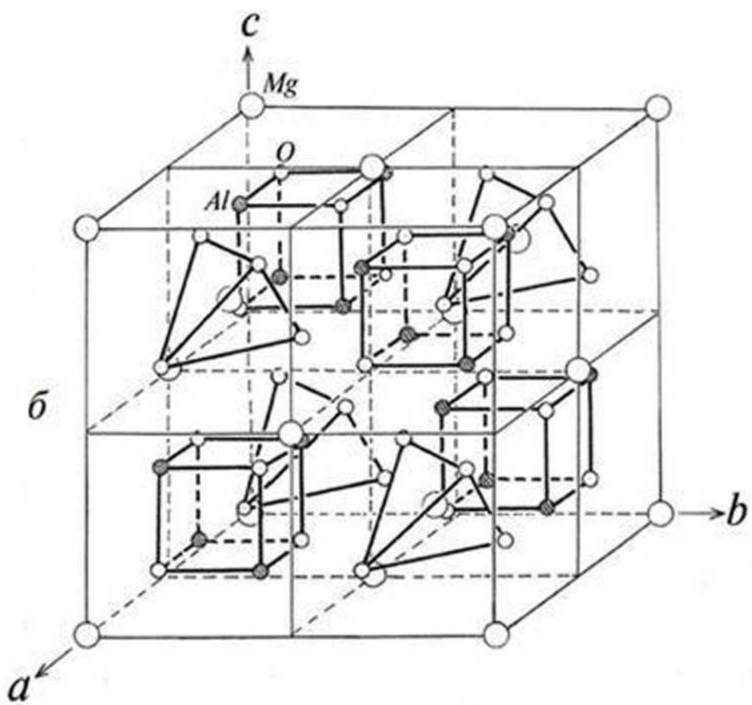

Figure 1. Structure of the spinel

In the unit cell of the spinel structure, 32 oxygen anions form the densest cubic package (three-layer, HCC) with 64 tetrahedral voids (cations occupied 8) and 32 octahedral (cations occupied 16). By the distribution of cations in the occupied tetrahedral and octahedral structures are distinguished: normal (8 tetrahedrons occupied by the cations, A^{2+} , 16 octahedra with cations B^{3+}) addressed (8 tetrahedra occupied by cations B^{3+} ,16 octahedra – B^{3+} and 8 A^{2+} , and these cations in the octahedral voids can be distributed as statistically, and in an orderly manner), and intermediate spinels.

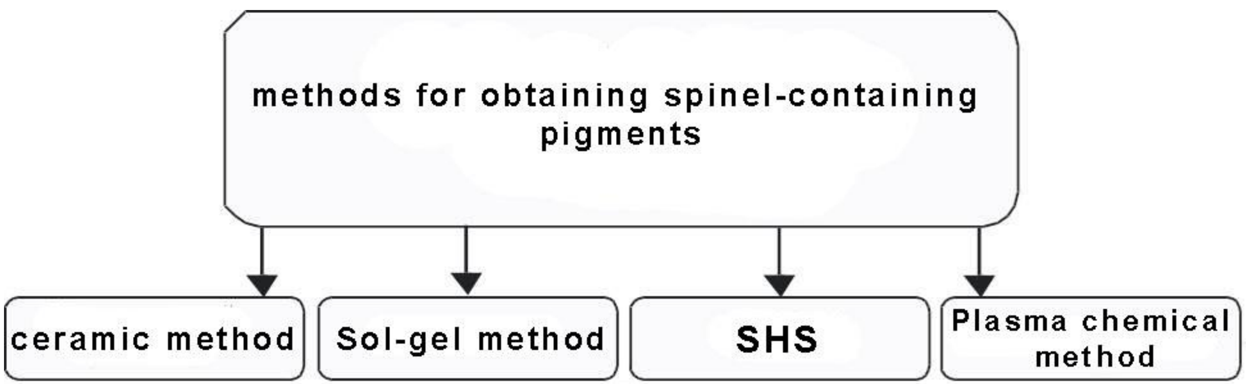

Figure 2. Methods for obtaining spinels

<u>The advantages of the pigments of the spinel type:</u>

1. **thermal stability,**
2. **ability to intensively color glazes with a low concentration of pigment,**
3. **light resistance,**
4. **chemical resistance,**
5. **environmental friendliness**

Spinel synthesis is usually carried out by reaction sintering of the corresponding oxides at temperatures of 1100-1200°C or Sol-gel method followed by annealing, which is associated with high energy costs.

Self-propagating high-temperature synthesis (SHS) is a type of combustion process, in which valuable in practical terms solid substances (materials) of any shape and different sizes are formed. These are powders of different dispersion, loosely bound conglomerates of particles, foams, specks and ingots with different strengths, films, fibers, and crystals.

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SH-synthesis of spinel-type pigments was carried out in a constant air pressure unit at atmospheric pressure.

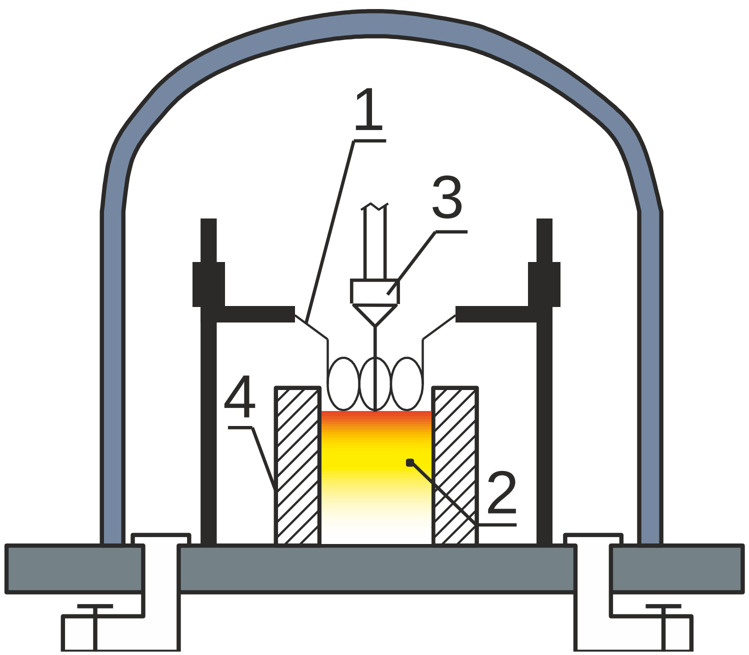

Figure 3. Schematic representation of the SHS-constant pressure installation, where1-molybdenum spiral, which initiates combustion process, 2-sample, 3-thermocouple, 4–resistance furnace.

The efficiency of SHS processes is associated with the use of chemical heat generation, high temperatures and combustion rates, simplicity of hardware design, high quality of products (obtained under optimal synthesis conditions). Combustion process Limitations are related to the need to select inexpensive and non-deficient reagents that ensure exothermic process.

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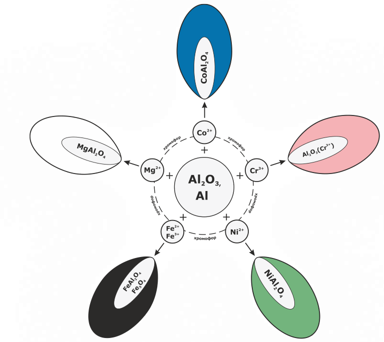

The oxides of cobalt, zinc, magnesium (Co_3O_4, ZnO, MgO) and aluminum hydroxide (high grade) $Al(OH)_3$ were used for the self-propagating high-temperature synthesis of pigments ranging from moderate blue to dark blue. Magnesium nitrate $Mg(NO_3)_2 \cdot 6H_2O$ was used as an oxidizing agent, and aluminum powder of the (ASD-4) was used as a reducing metal.

The main reactions that provide the SHS process are the reactions of exothermic oxidation of aluminum, realized through the thermite reaction and direct oxidation of aluminum:

$$\mathbf{CoO+2Al+O_2=Al_2O_3+Co}$$

$$\mathbf{Co_3O_4+4Al+O_2=3Co+2Al_2O_3}$$

$$\mathbf{2Al(OH)_3 \xrightarrow{^\circ C} Al_2O_3+3H_2O}$$

$$\mathbf{4Al+3O_2=2Al_2O_3+3350}\ \textbf{кДж}$$

As a result of their flow, the initial reagents are heated to a temperature of ~ 1000°C, above which the process of synthesis of spinel itself begins, which is also accompanied by the release of heat.

$$\mathbf{MeO+Al_2O_3=MeAl_2O_4}\textbf{, где (Me=Co, Mg, Zn)}$$

X-ray phase analysis of compositions with different ratios of $Al(OH)_3$:Al=10 and $Al(OH)_3$:Al=11, other things being equal, showed that they have almost the same composition and consist mainly of spinel $Mg_xZn_yCo_{1-x-y}Al_2O_4$ (figure 4). At the noise level, cobalt and various modifications of aluminum oxide are detected. Therefore, further studies are given for the ratio with a lower content of aluminum in the charge, where the synthesis products contain a smaller amount of cobalt.

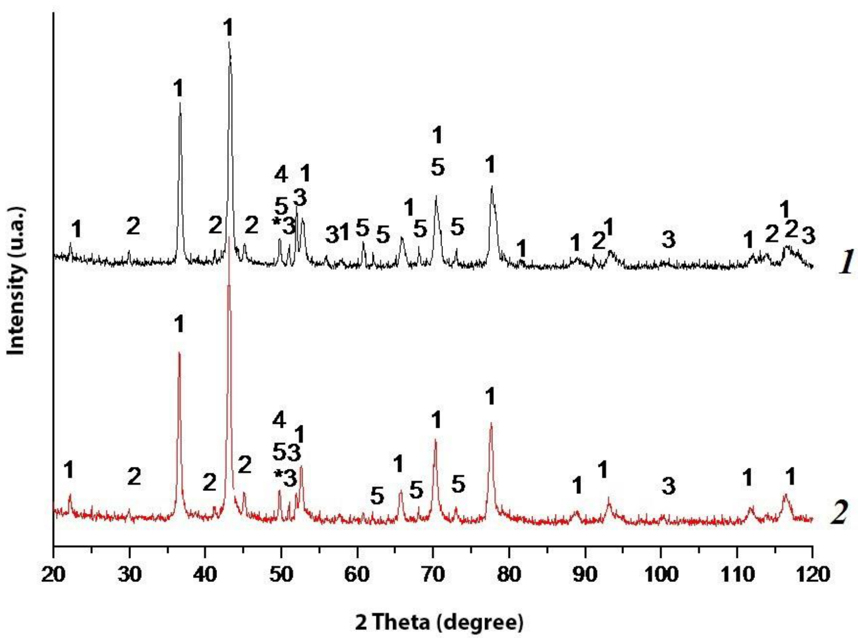

Figure 4. X-ray diffraction patterns of pigments based on alumocobalt spinel synthesized using $Al(OH)_3$: curve 1 - ratio $Al(OH)_3$: Al_2O_3= ~ 10, curve 2 - ratio $Al(OH)_3$: Al_2O_3= ~ 11, where (1) aluminium-cobalt spinel $Zn_xCo_{1-x}Al_2O_4$, (2) α- Al_2O_3 (Rhombohedral), (3) Co (Hxgonal), (*3) Co (Cubic), (4) $Al(OH)_3$ gibbsite, (5) θ-Al_2O_3

Thermogravimetric studies performed on the STD Q-600 thermal analyzer allowed us to analyze the main pathways of chemical reactions and identify various stages of chemical reaction in the initial mixture during synthesis. The gases released during the heating process were determined using the Rgolab VG mass spectrometer combined with the thermal analyzer.

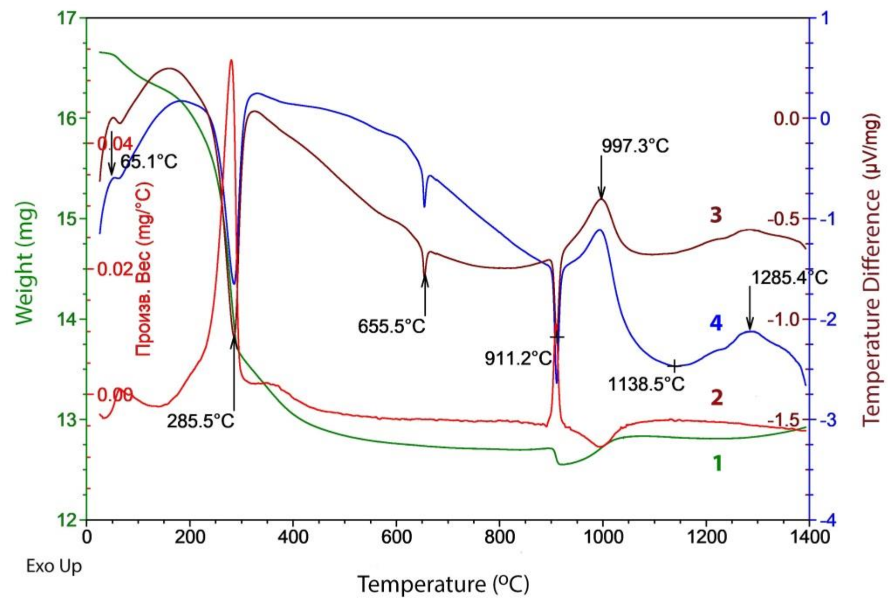

Figure 5. Complex thermal analysis of the ZnO-MgO-CoO-Al_2O_3 pigment, where TG (1-green) is the thermal analysis weight curve, DTG (2-red) is the derivative of the weight, DTA (3-brown) is the differential thermal analysis curve and DSC (4-blue) is the differential scanning colorimetry curve. The weight reduction is directed upward on the DTG curve.

Figure 5 shows that water from $Al(OH)_3$ when heated, according to mass spectroscopic data, is removed as molecules and ions by 17 and 18 masses, respectively, in the temperature range of 220÷310°C with a maximum at 290°C. The adsorbed water is removed earlier-at 65°C. At temperatures of ~250 °C, 290°C, the following reactions occur:

$$\mathbf{Al(OH)_3\ (bayerite) \rightarrow \eta\text{-}\ Al_2O_3}$$

$$\mathbf{Al(OH)_3\ (gibbsite) \rightarrow \gamma\text{-}AlOOH\ (boehmite)}$$

A slight decrease in mass and a weak endoeffect in the range of 350-400°C are associated with the decomposition of magnesium nitrate.

$$\mathbf{2\ Mg(NO_3)_2 \cdot 6H_2O \rightarrow 2MgO + 4NO_2 + O_2 + 6H_2O}$$

Melting of aluminum occurs at 655.5°C. At a temperature of 911.2°C, the process of endothermic decomposition of $Co_3O_4 \rightarrow CoO$ is observed.

The energy efficiency of SHS processes in the synthesis of spinel-containing pigments is associated with exothermic reactions of aluminum oxidation, which includes two processes – an alumothermic reaction with cobalt oxide and direct aluminum oxidation.

$$\mathbf{2Co_3O_4 \rightarrow 6CoO + O_2\uparrow}$$

$$\mathbf{3CoO + 2Al = Al_2O_3 + 3Co + 1196{,}8\ кДж}$$

$$\mathbf{4Al + 3O_2 = 2Al_2O_3 + 3350\ кДж}$$

At a temperature of 1138.5°C, the synthesis of spinel itself begins according to the equation presented below, with the formation of solid substitution solutions.

$$\mathbf{MeO + Al_2O_3 = MeAl_2O_4 \quad (Me = Co,\ Zn,\ Mg)}$$

Rapid heating of the starting mixture destroys the crystalline structures of aluminum hydroxide and magnesium nitrate with the release of gaseous reaction products and the formation of finely dispersed and active oxides of aluminum and magnesium. During the SHS process, the high propagation velocity of the combustion wave prevents the sintering of Al_2O_3 particles. High temperatures lead to the formation of a finely dispersed spinel structure confirmed by scanning electron microscopy (Philips SEM 515)

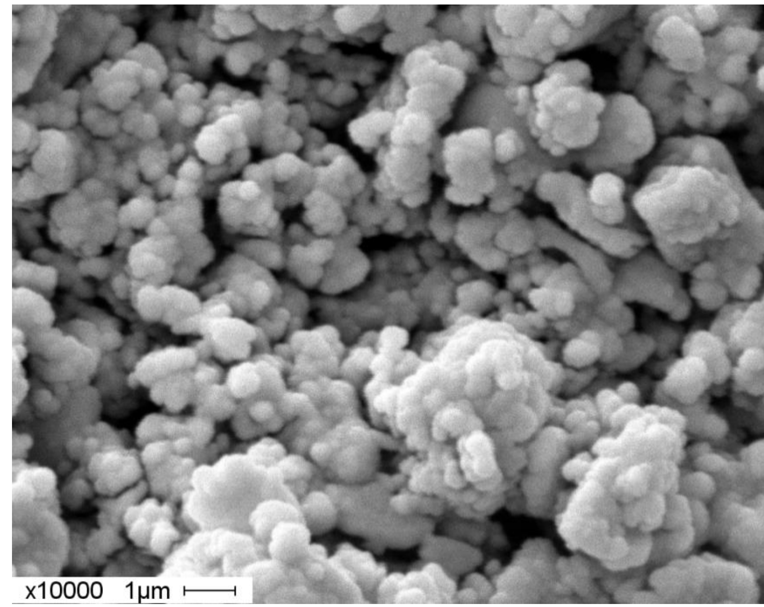

Figure 6. Micrograph of the pigment obtained in the ZnO-MgO-CoO-$Al(OH)_3$-Al system, raster image (Philips SEM 515)

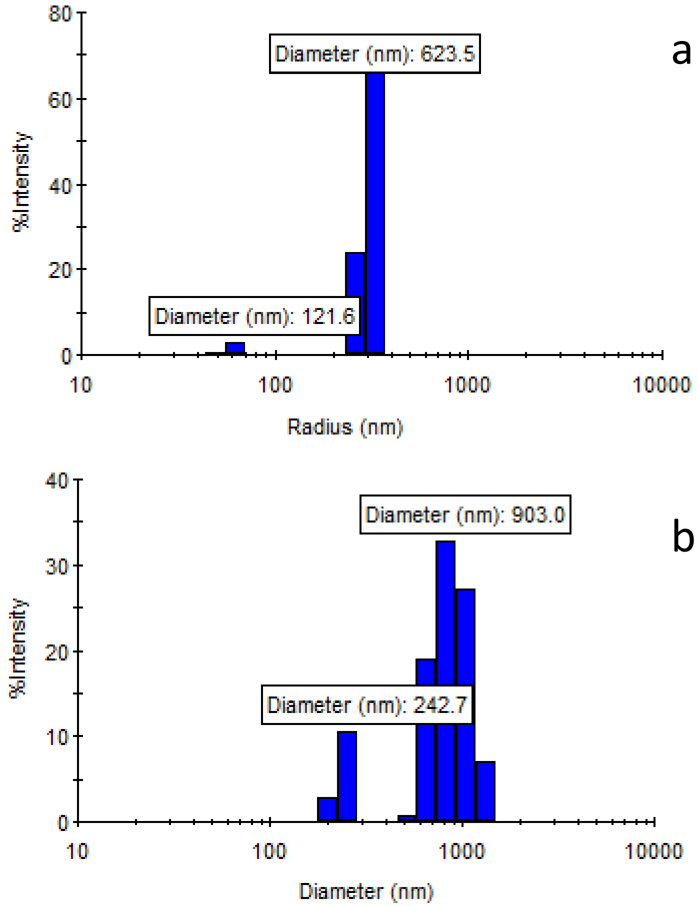

Figure 7. Histogram of particle size distribution: a) - in $Al(OH)_3$ after heating to 500°C, b)-in the spinel-containing pigment of the ZnO-MgO-CoO-$Al(OH)_3$-Al system.

The particle size distribution was determined on a DelsaMax PRO analyzer. Figure 7 shows the histograms of the particle size distribution in aluminum hydroxide after heat treatment at 500°C and in the obtained pigment. As can be seen, heating aluminum hydroxide to 500–550°C leads to the formation of particles with a main γ-Al_2O_3 phase of the same size ~ 0.6 µm. Submicron active aluminium oxide exposed to high temperatures reacts with cobalt, zinc, and magnesium oxides and forms finely dispersed spinel, the particle size of which has a maximum at 0.9 µm (Fig. 7-b). Long keeping Al(OH)3 in a furnace at a temperature of ~ 500°C or heating to ~ 1000°C makes these particles coarser.

The technological scheme for the production of SHS pigments by the method consists of the following stages: dosage, mixing (mechanical activation), SH-synthesis, disaggregation, classification and packaging

Figure 8. Appearance of the SHS installation

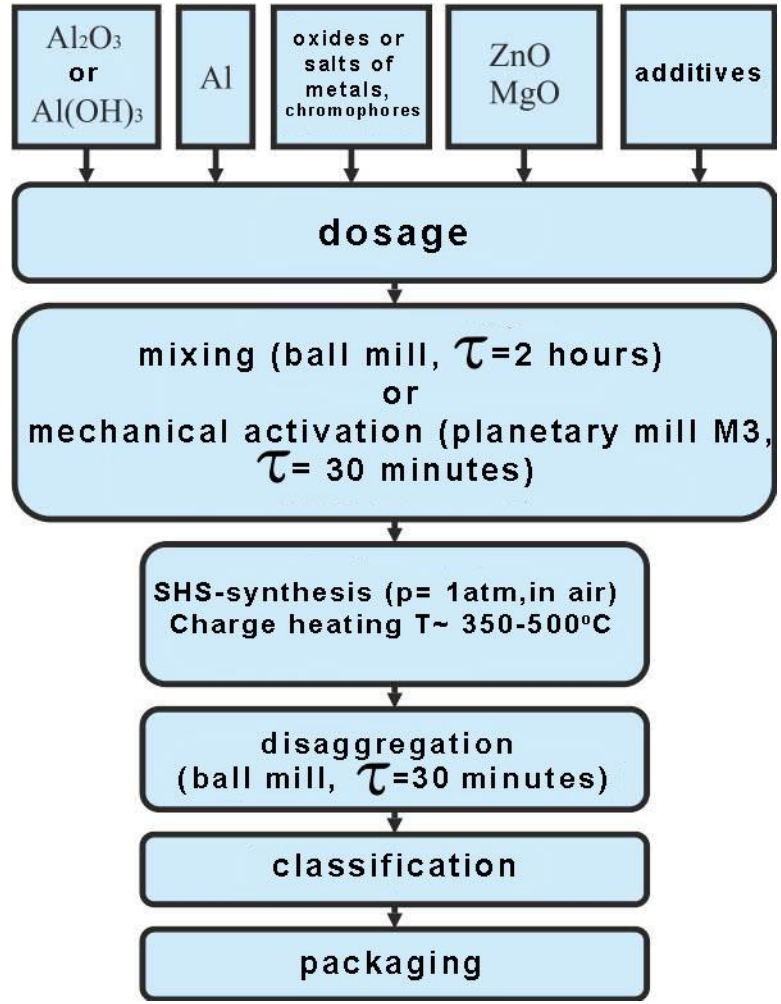

Figure 9. Technological scheme of SH-synthesis of spinel-containing pigments

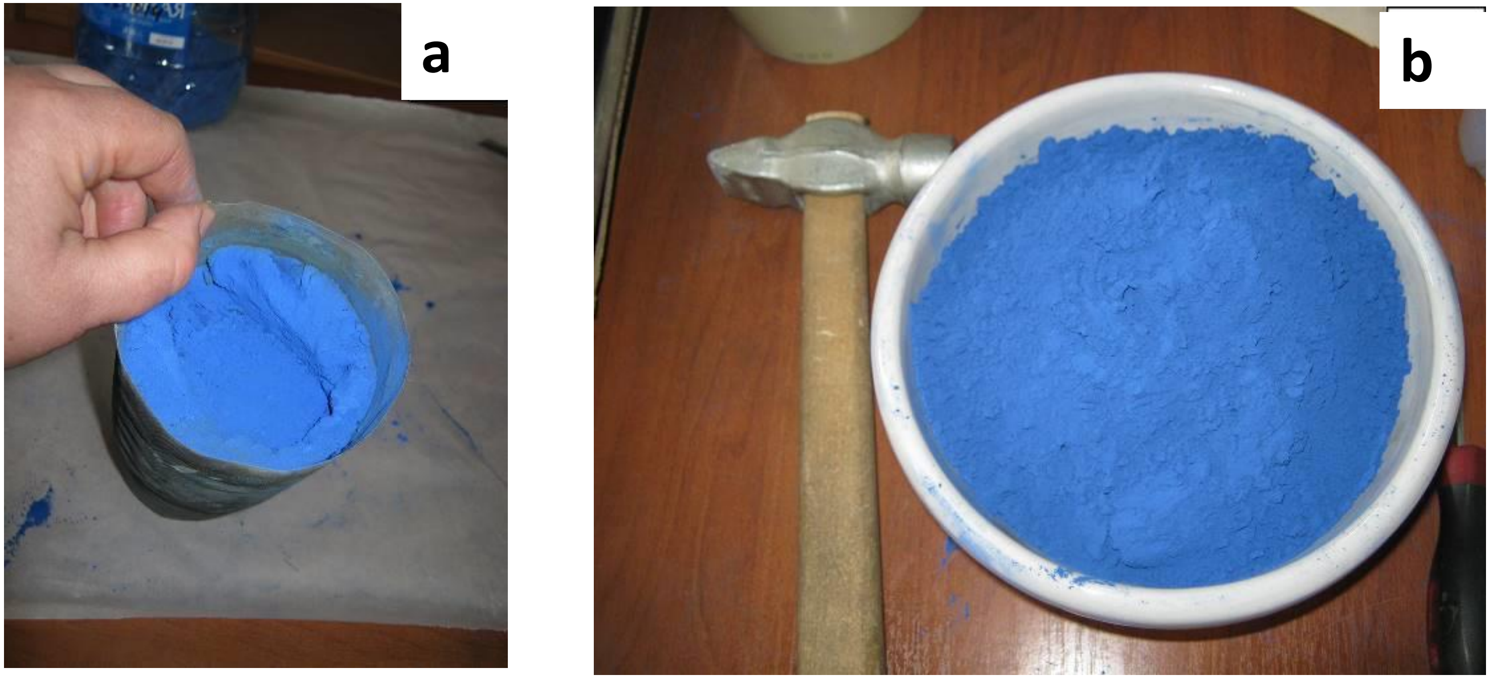

Figure 10. Type of sample immediately after SHS synthesis (diameter 80 mm): a)– blue pigment of the ZnO-MgO-CoO-$Al(OH)_3$-Al system in a glass of mesh (stainless steel), b)– pigment after removing it from the glass without further grinding

Figure 10 shows the synthesized blue pigment of the ZnO-MgO-CoO-$Al(OH)_3$-Al system. As you can see, immediately after SH-synthesis, it is a fine powder that does not require grinding. Just disaggregating it is enough.

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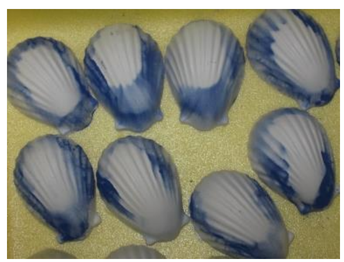
Cobalt-containing pigments of the spinel type

Overglaze painting

Painting with paints based onacrylic varnish and spinel-containingpigment



Gypsum-based materials