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UTILIZATION OF DTA FOR TWO-STEP SYNTHESIS OF Cu–Mn–Cr SPINEL

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The novel two-step synthesis method decreasing the calcining temperature necessary for formation of spinel lattice and as well for reaching of bright and clear hue of the pigments prepared were investigated. This work aims to utilization of DTA for synthesis monitoring. Influence of raw materials and temperature of calcination on color properties were observed. The characterization of the samples was performed by X-ray diffraction and colorimetry in the CIE $L^*a^*b^*$ system. It was proved that the black spinel pigment $Cu_{2.3}Mn_{2.8}Cr_{4.9}O_x$ can be prepared at finally temperature 700°C as one-phase system with high quality black hue.

Keywords: *ceramic pigments, optical properties, spinel pigments, thermal analysis*

Introduction

Ceramic pigments, especially mixed metal oxides, are compounds insoluble and inert in glazes, ceramic pastes and plastic. Pigments with the spinel structure belong to the mixed metal pigments group. Each pigment has a defined crystal structure which is defined by the host lattice [1]. Other oxides interdiffuse at high temperature into the host lattice structure by forming either a solid state solution or a new compound [2].

The quality of the ceramic pigments depends on its optical and physical properties. These properties are directly related to the crystalline structure of the pigment, its chemical composition, purity, stability and some physical characteristic such as particle size distribution, particle shape, surface area, etc. [3].

The most general method to prepare spinel pigments involves solid state reaction of the mechanically mixed parent metal oxides. However, for complete reaction a temperature about 1300°C or higher has to be maintained for long time periods [1, 4]. Second industrially used method of spinel pigment preparation is precipitation from aqueous solution of raw materials [5, 6]. The main advantage of this process is that the size and shape of precipitated pigment can be controlled by the reaction conditions, such as the rate and order of the reactants addition, pH, stirring, reactor size and shape and reaction temperature. This method is also suitable for nanoparticles preparation. There are lot of possibilities of laboratory spinel pigments preparation including Pechini method (polymeric precursor method) [7–9], sol-gel process and others [10, 11].

The novel two-step synthesis method for mixed metal oxide pigments synthesis represents in the first step forming of the intermediate product at medium temperature. The second step represents classical calcinations in an electric furnace [12].

Spinel compounds are used not only as ceramic pigments, but also as gas-sensitive materials [13], magnetic materials [6] and catalytic materials [14].

Experimental

The pigments were prepared by a two-step method [15]. The first step represents the formation of semi-product at medium temperature. The semi products were obtained by mixing of raw materials in aqueous suspensions (approx. 70%) in a porcelain mortar and were calcinated at 400°C on an alloy steel plate. The second step represents a classical calcination in an electric resistance furnace with an increase of temperature 10°C min^{-1}. The calcination temperature of the second step range from 600 to 1000°C was maintained for 2 h. After that, the fired samples were decanted in hot distilled water, filtrated and dried.

As a precursor we used for all reaction mixture $Na_2Cr_2O_7 \cdot 2H_2O$ (Lachema, CZ) and Na_2CO_3 (Lachema, CZ). Reaction mixture No. 1 further contains: $CuCO_3$ (Shepherd Color Comp., USA) and $MnSO_4 \cdot H_2O$ (Lachema, CZ), reaction mixture No. 2 $CuSO_4 \cdot 5H_2O$ (Lachema, CZ) and $MnCO_3$ (Shepherd Color Comp., USA) and reaction mixture No. 3 $CuSO_4 \cdot 5H_2O$ (Lachema, CZ) and $MnSO_4 \cdot H_2O$ (Lachema, CZ). All mixtures contained foaming agents, i.e. fumaric acid and urea.

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The solid semi-products were analyzed by simultaneous thermal analysis TG/DTA [16]. The equipment STA Jupiter 449C (NETZSCH, Germany) was used in the temperature range from 30 to 1250°C at heating rate 10°C min^{-1}. The analysis was carried out in an open ceramic crucible under air and α-Al_2O_3 was used as a reference material.

The powder pigments were studied by X-ray diffraction analysis. The X-ray diffractograms in the range from 10 to 80° were obtained using the diffractometer D8 Advance (Bruker, GB), CuK_α radiation and scintillation detector.

The color properties were described in terms of CIE $L^*a^*b^*$ system (1976). The values a^* (the axis red-green) and b^* (the axis yellow-blue) indicate the color hue. The value L^* represents the lightness or darkness of the color as related to neutral scale. In the $L^*a^*b^*$ system it is described by number from zero (black) to hundred (white). The pigments color properties were measured after their application into organic matrix. Color properties were measured in the visible region of light (400–700 nm) using MiniScan MS/S (Hunterlab, USA). The measurement conditions were following: Illuminant D65 (6500K), 10° complementary observer and measurement geometry *d*/8°.

Results and discussion

Reaction mixtures after first step were analyzed by simultaneous thermal analysis. The reaction mixture No. 1 contains $MnCO_3$, $CuSO_4 \cdot 5H_2O$, $Na_2Cr_2O_7 \cdot 2H_2O$ and Na_2CO_3. Processes such as dehydration and conversion reaction (Fig. 1), i.e. formation of Na_2SO_4 and simple and binary oxides, were identified in temperature region below 400°C (corresponding with temperature of the first step of preparation). Decomposition of $Na_2Cr_2O_7$ and reduction of Cr^{6+} to Cr^{3+} starts at the same time. Initiate reaction is finished by repeated heating of semi-product in second step of preparation in temperature region from 30 to 400°C. The non-crystalline character of the sample after the first step was proved by X-ray diffraction (Fig. 5), so the exothermic peak with the maximum at 429°C indicates the sample crystallization. $MnCO_3$ itemizes high temperature stability and its final decomposition is indicated by endothermic peak with minimum at 485°C. The melting of attendant Na_2SO_4 starts at the temperature higher than 900°C (endothermic peak with minimum at 907°C). Two almost indiscernible peaks, exothermic with maximum at temperature 1044°C and endothermic with minimum 1068°C, correspond to partial oxidation of Mn^{2+} to Mn^{3+} and reduction of Cu^{2+} to Cu^{+}. These processes coincide at the almost same time. The last exothermic peak (1247°C) on DTA curve probably corresponds to partial oxidation of Cr^{3+} to Cr^{6+}. This peak was also detected on the DTA curve of the pure product (Fig. 4). Total mass loss for reaction mixture No. 1 was determined on 15.17%.

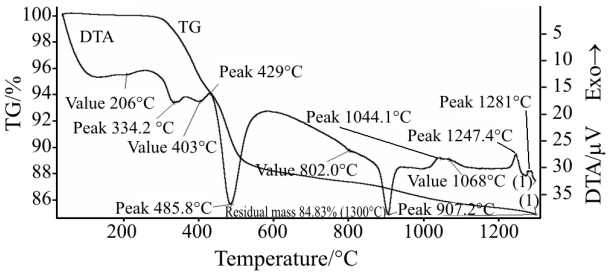

Fig. 1 DTA and TG curves of the reaction mixture No. 1 (sample mass: 313 mg)

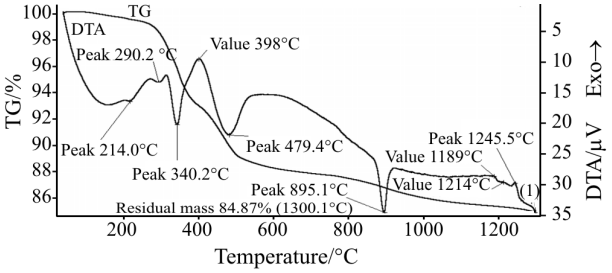

Fig. 2 DTA and TG curves of the reaction mixture No. 2 (sample mass: 327 mg)

Figure 2 shows record of simultaneous TG and DTA of sample No. 2 after first step of preparation. The noticeable endothermic peaks with minimum at temperatures 340 and 479°C are connected with unreacted carbonates decomposition. These processes are attended by noticeable mass loss. The melting of Na_2SO_4 corresponds to endothermic effect on DTA curve (minimum 895°C). The effects at temperatures 1189 and 1214°C relate with manganese oxidation and copper reduction, similar as for reaction mixture No. 1. Last exothermic effect on DTA curve agrees with Cr^{3+} partial oxidation. Total mass loss was determined in this case on 15.13%.

In temperature region from 30 to 400°C, dehydration and conversion reactions are under way during calcination of the solid semi-product of reaction mixture No. 3 (Fig. 3). Peak of crystallization and spinel-phase formation is registered at temperature higher than 400°C. Endothermic peak with minimum at 891°C corresponds again with Na_2SO_4 melting and follow peaks with the oxidation state changes which were described before. Total mass loss on 10.49% was determined on the basis of TG measurement.

Final product, pigment $Cu_{2.3}Mn_{2.8}Cr_{4.9}O_x$, was also analyzed by thermal analysis (Fig. 4). The DTA measurements prove the pigment thermal stability at temperatures up to 950°C. Exothermic peak with maximum at 1034°C indicates compound decomposi-

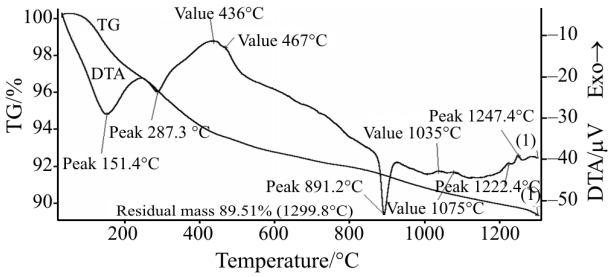

Fig. 3 DTA and TG curves of the reaction mixture No. 3 (sample mass: 306 mg)

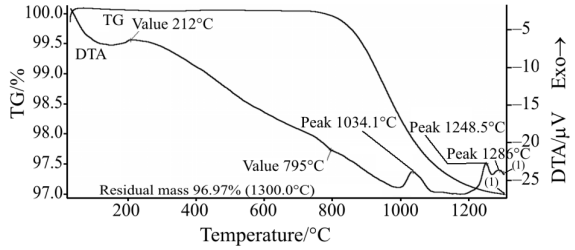

Fig. 4 DTA and TG curves of final pigment $Cu_{2.3}Mn_{2.8}Cr_{4.9}O_x$ (sample mass: 285 mg)

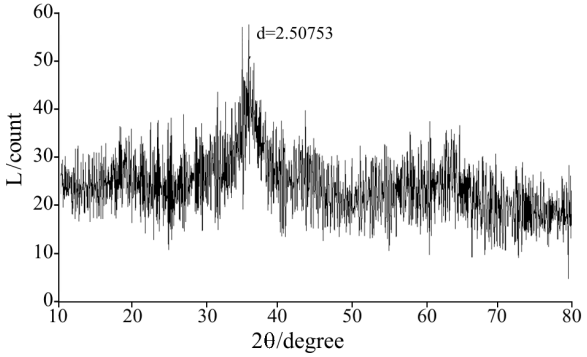

Fig. 5 X-ray diffraction pattern of reaction mixture No. 3 after first step of preparation

tion and oxidation state changes start to appear. The mass loss for final product was 3.03%.

X-ray diffraction pattern does not itemize the intensive diffraction line (Fig. 5) and sample after the first step of preparation is non-crystalline. Figure 6 shows X-ray diffraction pattern of the sample calcined at 650°C for 2 h (in second step of preparation). It is evident, that Cr_2O_3 diffraction line occurs next to spinel phase diffraction line too. Occurrence of Cr_2O_3 has negative influence of prepared pigments color properties. For one-phase system is necessary to increase the calcination temperature over 700°C (Fig. 7).

The spinel pigment $Cu_{2.3}Mn_{2.8}Cr_{4.9}O_x$ provides deep black color. The pigments were applied into organic matrix in mass tone. From color measurement (Table 1) it follows that the calcining temperature has a significant effect on the color properties. In Table 1 are stated results for reaction mixture No. 3. The most

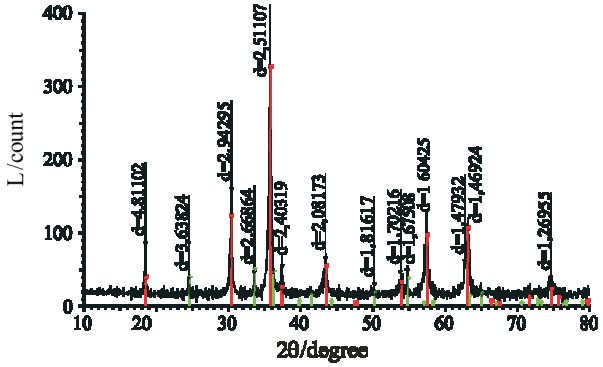

Fig. 6 X-ray diffraction pattern of pigment $Cu_{2.3}Mn_{2.9}Cr_{4.9}O_x$ calcined at 650°C

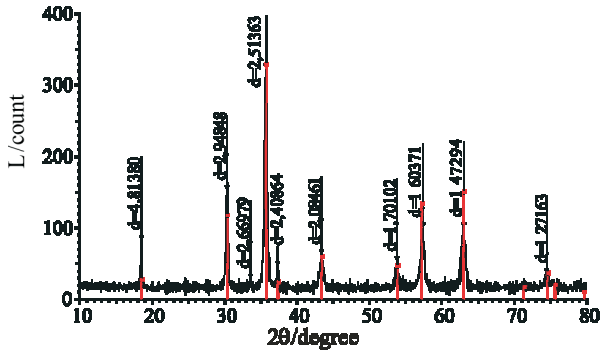

Fig. 7 X-ray diffraction pattern of pigment $Cu_{2.3}Mn_{2.9}Cr_{4.9}O_x$ calcined at 700°C

Table 1 The influence of calcining temperature on the color properties of pigment $Cu_{2.3}Mn_{2.8}Cr_{4.9}O_x$

Calcining temp./°C	L^*	a^*	b^*
600	40.48	–0.41	–2.86
650	40.95	–1.20	–3.65
700	41.62	–1.00	–4.55
750	41.79	–0.96	–4.35
800	42.37	–0.97	–4.22
850	42.77	–0.88	–4.02
900	42.83	–0.76	–3.85
950	42.90	–0.59	–3.21
1000	42.99	–0.47	–2.96

noticeable effect of temperature is on the blue hue of pigments. For black and white pigments is the tinge with blue color very important, because organic binders very often itemize tinge with yellow hue and its elimination come up easily. The optimal value for coordinates L^* and a^* is about zero. Pigments prepared in temperature interval from 700 to 900°C have color coordination b^* value up to 4. Occurrence of Cr_2O_3 at lower temperature has negative influence on color. The value of brightness (L^*) increases only slightly with growing calcining temperature. It could be de-

pended with the increase of particle size. The value of green hue (a^*) only fluctuates and decreases with calcining temperature. Pigments prepared on basis of the reaction mixtures No. 1 and 2 had the comparable color properties, but especially brightness value (L^*) was higher. This fact leads to conclusion, that sulphates as starting materials are optimal for deep black color properties.

Conclusions

The main aim of the research was to prepare spinel pigment $Cu_{2.3}Mn_{2.8}Cr_{4.9}O_x$ by two-step synthesis and evaluate synthesis process by thermal analysis. The calcining temperature up to 700°C is necessary for the best color properties of the black prepared pigment. The thermal analysis proves the crystallization and spinel lattice formation at temperature up to 400°C, but at the same time the samples contain second phase Cr_2O_3 with negative influence on color. The compound is stable up to 950°C and afterward starts the oxidation state changes which correspond with color properties degradation. As optimal precursors is possible to determine copper and manganese sulphates.

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