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THERMAL ANALYSIS OF PIGMENTS BASED ON Bi_2O_3

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The synthesis of new pigments based on Bi_2O_3 is investigated because they give interesting orange hues and can substitute the pigments problematic from the environmental point of view. Chemical compounds of the $Bi_{2-x}Zr_{3x/4}O_3$ type were synthesized. The host lattice of these pigments is Bi_2O_3 that is doped by Zr^{4+} ions. The area of ZrO_2 solubility in Bi_2O_3 at 800°C forming solid solution of both oxides was studied. The incorporation of doped ions provides interesting colours and contributes to a growth of the thermal stability of these compounds. The simultaneous TG-DTA measurements were used for determination of the temperature region of the pigment formation and thermal stability of pigments.

Keywords: *bismuth-rare earth mixed oxides, colour properties, ecological pigments, inorganic pigments, thermal analysis*

Introduction

Historically, cadmium pigments and chromate pigments have been very important, as they provide a range of clean, bright hues of yellow, orange, red and maroon colours. Their importance, however, decreases continually because of the environmental issues associated with the production and the use of Cd, Cr(6+), Se and compounds containing Hg. At this time, most users are looking for safer replacements of the mentioned pigments and only a few pigment producers continue their production. Originally, these pigments were produced for artistic paints.

While many arguments have been presented about the low toxicity of cadmium pigments, ecological consequences of their production, use, and disposal will limit their future applications to only the most demanding colouring jobs. Their future is certainly not very bright and the developmental efforts of many laboratories have been directed towards finding suitable replacements.

Chrome yellows, oranges and molybdate oranges are used in a large number of different paint systems, which are restricted mostly to maintenance and industrial finishes, because of their toxicity and potential carcinogenic nature. Traditional use of these pigments in traffic paint formulations has been decreasing as a result of environmental regulations. Less toxic, inorganic metal-oxide yellow pigments, such as titanium-nickel yellow, bismuth vanadate and their combinations with organic pigments, are being used increasingly as a replacement for lead chromate pigments [1].

For this reason, possibilities of preparation of new inorganic pigments based on bismuth oxide are considered. This oxide of very light yellow colour can be doped for instance by zirconium or rare earth elements [2] what affects significantly the resulting colour hue. The compounds prepared by this method not only fulfil the desired assortment of colour hues from bright yellow to orange, but they are fully hygienical- and environmental-friendly.

The main attention was focused on the pigment synthesis based on Bi_2O_3 doped by zirconium ($Bi_{2-x}Zr_{3x/4}O_3$). The object was to suggest and elaborate synthesis conditions of these compounds, investigate their colour possibilities and verify their applicability.

Experimental

Materials

As starting materials for the preparation of $Bi_{2-x}Zr_{3x/4}O_3$ pigments (where x=0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6 and 1.8) we used Bi_2O_3 of 99% purity (Merck, Germany) and ZrO_2 95% purity (Indian Rare Earths Ltd., India). The starting mixtures containing the both basic oxides (Bi_2O_3 and ZrO_2) were homogenised in an agate mortar. The mixtures were then calcinated in corundum crucibles in an electric resistance furnace with the heating rate of 10°C min^{-1}. The calcination temperature was 800°C and its duration was one hour. The pigments prepared were applied to organic matrix (Balakom, a.s., Czech Republic) in mass tone.

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The final applications were evaluated with regard to their colour hues by measurements of spectral reflectance in the visible region (400–700 nm) using a MiniScan (HunterLab, USA). The measurement conditions were following: an illuminant D65, 10° complementary observer and measuring geometry d/8°.

The colour was described in terms of CIE $L^*a^*b^*$ and CIE L^*CH° system. The values a^* (the axis red – green) and b^* (the axis yellow – blue) indicate the colour hue. The value L^* represents the lightness or darkness of the colour as related to a neutral gray scale. In the $L^*a^*b^*$ system it is described by numbers from zero (black) to hundred (white). The value C (chroma) represents saturation of the colour. The hue angle H° is defined by an angular position in the cylindrical colour space (for the red is H°=0°–35°, for the orange H°=35°–70°, for the yellow H°= 70°–105°).

Methods

The formation of the pigments was followed by thermal analysis using STA 449C Jupiter (Netzsch, Germany) which allows the simultaneous registration of the thermoanalytical curves TG and DTA. The starting raw material and the prepared starting mixtures were studied by thermal analysis in corundum crucible in air in temperature region from 100 to 1000°C. The heating rate was 10°C min^{-1}, α-Al_2O_3 was used as a reference material [3].

The powder pigments were studied by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained using a vertical X-ray diffractometer HZG-4B (Freiberger Präzisionsmechanik, Germany) equipped with a goniometer of 25 cm diameter in the range of 2Θ from 20 to 60°. CuK_λ (λ=0.154178 nm) radiation was used [4].

The particle size distribution was measured by a Mastersizer 2000/MU (Malvern Instruments, GB). It is the highly integrated laser measuring system (He-Ne laser, λ=633 nm) for the analysis of particle size distribution. The equipment uses scattering of the incident light on particles. The signal is evaluated on the basis of Mie theory or Fraunhofer bending.

Results and discussion

Prepared pigments of $Bi_{2-x}Zr_{3x/4}O_3$ type were tested in order to determine their colour properties. The best result was obtained for the pigment with the lowest Zr content (x=0.2) which indicates the highest colour values a^* (red) and the lowest hue value H°=65.14, which corresponds to the rich orange colour. Increasing content of Zr (x=0.4 to 0.6) brings a slight decrease of the colour value a^* (red), hues of these pigments are orange, too. Further increase of the Zr content (x=0.8 to 1.2) brings about a decrease of the colour value a^* (red); however, the value b^* (yellow) indicates a slight growth and at the same time the value L^* indicates bleaching of the final yellow-orange colour. The pigments with x=1.4 and 1.6 present another decrease of the colour value a^* (red), another decrease is seen also at the value b^* (yellow), on the other hand the value of brightness L^* grows. Such pigments give slight yellow-ochre colours. The pigment with the highest Zr content (x=1.8) indicates the lowest value a^*, b^* and chroma C, but also demonstrates the highest value of brightness L^*, which makes slight beige colour (Table 1).

The particle sizes and particle size distribution can markedly affect the colour properties of inorganic pigments so that the pigment grain sizes (particle sizes) of the prepared compounds were also tested. The mean particle sizes (d_{50}) of pigments used for colouring of ceramic glazes or bodies lie in region from 5 to 15 μm.

The measurement of particle size distribution was determined for unmilled pigments. The values of pigment particles are in range from 2 μm (d_{10}) to 26 μm (d_{90}). The mean particle sizes (d_{50}) of the prepared pigments with x=0.2 and 0.4 is about 10 μm. These pigments with small particles are characterized by intense orange colour. The values of particle sizes

Table 1 Colour properties of the $Bi_{2-x}Zr_{3x/4}O_3$ pigments applied into organic matrix

x	L^*	a^*	b^*	C	H°
0.2	58.22	24.32	52.49	57.85	65.14
0.4	58.34	21.80	52.74	57.07	67.54
0.6	61.16	21.27	52.99	57.10	68.13
0.8	64.72	19.39	54.97	58.29	70.57
1.0	66.69	17.84	58.89	61.53	73.15
1.2	67.77	15.68	57.54	59.64	74.76
1.4	69.09	12.65	52.35	53.86	76.42
1.6	75.20	9.14	48.46	49.31	79.32
1.8	77.84	8.03	29.09	30.18	74.57

Table 2 Particle sizes of the $Bi_{2-x}Zr_{3x/4}O_3$ pigments

x	d_{10}/μm	d_{50}/μm	d_{90}/μm
0.2	1.99	9.63	22.02
0.4	2.08	9.87	22.10
0.6	2.09	11.01	23.15
0.8	2.21	12.28	23.67
1.0	2.25	12.47	24.89
1.2	2.85	12.92	24.97
1.4	2.91	13.07	25.27
1.6	2.97	13.47	25.89
1.8	2.98	13.65	26.12

Table 3 Lattice parameters of the $Bi_{2-x}Zr_{3x/4}O_3$ pigments and β-Bi_2O_3

x	a/nm	c/nm	c/a	V/nm^3
0	1.09497	0.56334	0.51448	0.67542
0.2	0.77182	0.56322	0.72973	0.33542
0.4	0.77103	0.56321	0.73046	0.33471

are shown in Table 2. The samples with higher zirconium content have a little higher values d_{50} that lie in range from 11 to 14 μm. Their colour seems lighter.

All prepared compounds were studied by X-ray diffraction analysis. Series of samples of the $Bi_{2-x}Zr_{3x/4}O_3$ system fired at temperature 800°C were tested. The test revealed that investigated samples with x=0.2 and 0.4 were single-phased systems since the diffractograms indicated only lines corresponding to Bi_2O_3. On the base of literature data on the stability of individual modifications of Bi_2O_3, it would be possible to expect a formation of stable cubic modification δ-Bi_2O_3 at the mentioned temperature [5]. However, the experiments confirmed tetragonal modification β-Bi_2O_3. Lattice parameters of Bi_2O_3 for both samples are given in Table 3. Considering these values for Bi_2O_3–ZrO_2 system, it is seen a decrease of lattice parameters a and c. Volume of the elementary cell of the crystal lattice of Bi_2O_3 decreases in comparison with the lattice parameters of tetragonal modification β-Bi_2O_3. The decrease observed obviously results from different sizes of bismuth and zirconium ions (r(Bi^{3+})=0.120 nm, r(Zr^{4+})=0.080 nm). For the sample with x=0.6, the diffractogram exhibited a visible indication of the most intense line of ZrO_2 situated at 2θ app. 31° and 49°. This indicates that the sample is double-phased. Other lines associated with ZrO_2 are seen for the samples with a higher zirconium content. On the base of results of X-ray diffraction analysis it can be concluded that the samples of $Bi_{2-x}Zr_{3x/4}O_3$ system are single-phased for x=0.2 and 0.4. These samples are characterized by intense orange hues (the value H° is about 66°). The higher

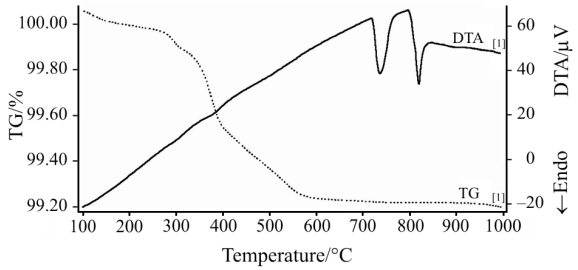

Fig. 1 TG and DTA curves of Bi_2O_3 (sample mass 256.90 mg, air, heating rate 10°C min^{-1})

Table 4 Thermal decomposition of Bi_2O_3 (Fig. 1)

Temp. range/°C	Peak temp./°C	Mass loss/%
100–270	–	0.08
270–340	308	0.10
340–400	380	0.30
400–600	–	0.30
600–1000	736 820	0.02

content of Zr in samples produces the colour change (the increase of value H°). The colour shifts from orange (x=0.6) through yellow (x=1.2) to beige (x=1.8). This fact is connected with the presence of second phase, i.e. by free ZrO_2, in these samples.

The formation of these pigments was followed by thermal analysis (TG-DTA). Thermoanalytical curves of Bi_2O_3 are given in Fig. 1. The DTA curve shows two endothermic effects. The first peak with the minimum at 736°C corresponds to the change of monoclinic modification α-Bi_2O_3 to cubic modification δ-Bi_2O_3. The peak with the minimum at 820°C is connected with melting of δ-Bi_2O_3. TG curve of Bi_2O_3 indicates the mass loss (0.78%) in the temperature range from 100 to 600°C (Fig. 1). This process is represented by the partial oxygen loss (Table 4) since Bi_2O_3 is known to possess the excess of oxygen in its crystal lattice [5]. In the DTA curve, this effect is connected only with two slight traces of peak at the temperature about 308 and 380°C.

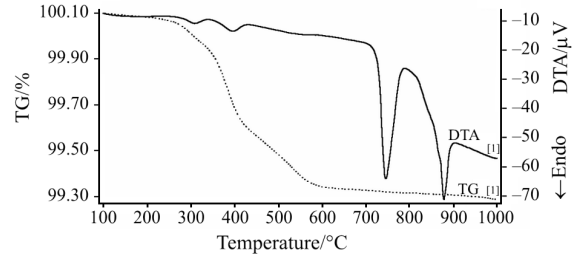

Fig. 2 TG and DTA curves of mixture for synthesis $Bi_{1.8}Zr_{0.15}O_3$ (sample mass 778.60 mg, air, heating rate 10°C min^{-1})

Table 5 Thermal decomposition of the mixture for synthesis $Bi_{1.8}Zr_{0.15}O_3$ (Fig. 2)

Temp. range/°C	Peak temp./°C	Mass loss/%
100–325	309	0.13
325–425	396	0.36
425–600	–	0.26
600–1000	746 879	0.05

Starting mixture for the pigment preparation with composition $Bi_{1.8}Zr_{0.15}O_3$ was homogenized in an agate mortar and studied by DTA (Fig. 2). The DTA curve indicates four endothermic effects, the first (with minimum at 309°C) and second effect (with minimum at 396°C) is connected with the continual oxygen loss from Bi_2O_3 (Table 5) which is detected by the mass loss in the TG curve (0.75%) at the temperature range from 100 to 600°C. This process was not so well identified in the DTA curve of starting oxide Bi_2O_3 (Fig. 1). The third endothermic effect with the minimum at 746°C corresponds to dissolution of ZrO_2 in Bi_2O_3 during the change of monoclinic modification α-Bi_2O_3 to tetragonal modification β-Bi_2O_3 forming a solid solution of both oxides, i.e. the presence of ZrO_2 supports the formation of β-Bi_2O_3. In comparison with the starting oxide Bi_2O_3 (736°C), the process moves higher by 10°C. The last peak in the DTA curve with a minimum at 879°C demonstrates the tendency of pigment to melt. This temperature also represents the stability of pigments based on Bi_2O_3. The melting temperature of pure Bi_2O_3 is only 820°C.

Conclusions

The compounds based on Bi_2O_3 were synthesized due to their ability to give interesting orange hues. Intense orange colours of these pigments are based on the incorporation of doped Zr^{4+} ions into the host lattice of Bi_2O_3. The optimum calcination temperature for pigment synthesis was determined on the base of the simultaneous TG-DTA measurements. These methods also provided the information about the temperature stability of the pigments that is about 850°C.

The compounds $Bi_{2-x}Zr_{3x/4}O_3$, where x=0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6 and 1.8, were studied. It was determined that the area of ZrO_2 solubility in Bi_2O_3 at 800°C forming solid solution of both oxides is for x=0.2 and 0.4. Higher Zr content (the presence of second phase, i.e. free ZrO_2) makes colour change from orange, yellow to beige.

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