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THE THERMAL SYNTHESIS OF THE $ZnO–Bi_2O_3$ PIGMENTS

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Abstract

A zinc oxide pigment with an admixture of bismut oxide has been prepared as new yellow pigment for colouring of plastics and paints. The effect of the Bi_2O_3 in the starting mixture on the colour hue of the pigment has been evaluated. The calcination conditions of the pigment synthesis have been established. The synthesis of these pigments was followed by thermal analysis using a derivatograph apparatus in our laboratory. The optimum conditions for the synthesis of pigments and the properties of the products have been estimated.

Keywords: lattice parameters, point defects, solid solutions $ZnO–Bi_2O_3$

Introduction

The increasing need of pigments for and the fact that the most of the pigments, especially in yellow hues, contains elements (lead, chromium, antimony, cadmium, selenium), which are questionable from the hygienic point of view, opens the great necessity for development and investigation of new ecological pigments. For this reason the main attention has been directed to the preparation of new compounds of oxide type which would be found useful as colour pigments.

The pigments based on zinc oxide in new yellow hues have been synthesized in our laboratory. The pigments of the $ZnO–Bi_2O_3$ system give intensive yellow hues. This type of pigments has been prepared from commercially available zinc white as a starting raw material of zinc. These pigments seem to be interesting because of their colour hues and their formation which is based on the mutual suppressing of non-stoichiometry of crystal lattices of ZnO and Bi_2O_3.

This pigment is formed by zinc oxide grains on surface of which is a layer of bismuth oxide formed by thermal decomposition of bismuth nitrate at temperature of about 500°C. An idea of interaction of zinc oxide with bismuth oxide is based on the fact that zinc oxide (*n*-type electrical semiconductor) has a deficiency of oxygen which is characterized by vacancies of oxygen in crystal lattice or Zn-interstitials. Bismuth oxide is a *p*-type electrical semiconductor which has overstoichiometry of oxygen. An interaction of both oxides can be based on a transportation of overstoichiometric oxygen atoms from Bi_2O_3 towards the contact regions between both

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phases, where these atoms occupy oxygen vacancies on the surface of the zinc oxide grains. Diffusion of oxygen into the crystal lattice of ZnO, where can occupy oxygen vacancies as another type of the interaction of oxides ZnO and Bi_2O_3, is also accepted.

Experimental

The starting mixtures containing the required content of admixtures were calcinated in porcelain crucibles in an electric resistance furnace LM 112.10 (VEB Electrobad Frankenhausen, Germany) for two h. The increase of the temperature was 10°C min^{-1}. The pigments of the $ZnO–Bi_2O_3$ type were calcinated at temperature of 600°C.

The temperature region of the formation of these types of pigments was followed by thermal analysis using a Derivatograph-C apparatus (MOM Budapest, Hungary; system of Paulik, Paulik and Erdey) which allows the evaluation of data and simultaneous registration of the thermoanalytical curves TG, DTG and DTA. The starting raw bismuth material and some starting mixtures prepared were studied by thermal analysis in ceramic crucible in air. The increase of temperature was 5°C min^{-1}. As a heat-resistance standard was used α-Al_2O_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).

Results and discussion

The main aim was to propose, verify and analyse conditions of the synthesis of this type of pigments based on the wurtzite structure of zinc oxide with an admixture of bismuth oxide. Our attention was focused on finding such pigments which would give the most intensive colour.

The starting mixtures containing the increasing content of bismuth oxide (3, 5, 8, 10, 13, 15, 18, 20 and 25 mol% Bi_2O_3) were homogenized by wet process. The prepared mixtures were calcinated at the temperature of 600°C for 2 h. This calcination temperature was determined on the base of results of thermal analysis of bismuth nitrate which was used as starting material of bismuth for the preparation of the $(1–x)ZnO{\cdot}Bi_2O_3$ pigments.

The thermal analysis provided the first information about the temperature region of the formation of this type of pigments. From the thermoanalytical curves TG, DTG and DTA it follows that bismuth nitrate decomposes in several steps. The supposed decomposition of bismuth nitrate can be represented schematically by the following reactions.

100–150°C: $Bi(NO_3)_3{\cdot}5H_2O \rightarrow Bi(NO_3)_3+5H_2O$

250°C: $Bi(NO_3)_3 \rightarrow BiO_{0.5}(NO_3)_2+1/2N_2O_5$

440–500°C: $BiO_{0.5}(NO_3)_2 \rightarrow BiONO_3+1/2N_2O_5$

560°C: $BiONO_3 \rightarrow 1/2Bi_2O_3+1/2N_2O_5$

On the base of results of thermal analysis (Fig. 1) it follows that bismuth nitrate partially decomposes into reactive intermediates. The decomposition of bismuth nitrate to bismuth oxide is ended at the temperatures of about 560°C (forming bismuth oxide). This process represents the formation of the monoclinic modification of Bi_2O_3 oxide (the temperature maximum T_{max} of this endothermic effect on the DTA curve is 563°C). This result is in an agreement with the published data [1] about the stability of individual modifications of Bi_2O_3. The DTA curve shows the endothermic effect with the temperature maximum T_{max} at the temperature of 632°C. At this temperature the cubic modification of Bi_2O_3 starts to appear. This modification is characterized by the lattice constant a=1.0223 nm.

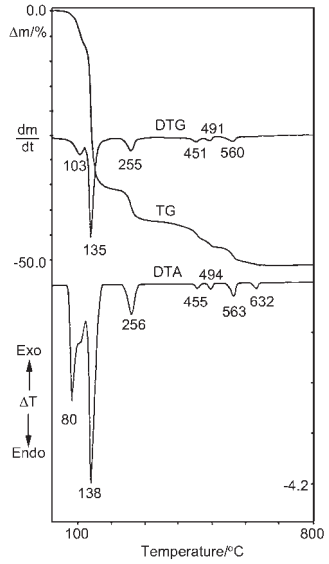

Fig. 1 Thermoanalytical curves of bismuth nitrate $Bi(NO_3)_3{\cdot}5H_2O$, Apparatus Derivatograph-C, heating rate 5°C min^{-1}, standard α-Al_2O_3, atmosphere air, ceramic crucible

From Fig. 1 it follows that bismuth nitrate partially decomposes into bismuth oxide. Its decomposition to bismuth oxide is ended at the temperatures of about 560°C. Figure 2 presents the DTA curve which indicates the endothermic process at the temperature maximum T_{max} of 533°C. This endothermic effect represents the formation of the oxide Bi_2O_3 which reacts with zinc oxide forming of the $(1–x)ZnO{\cdot}xBi_2O_3$ pigments. The endothermic effect with the temperature maximum T_{max} of 665°C represents the tendency of these pigments to sintering.

The temperature of 600°C for the pigment synthesis is also in agreement with the results of thermal analysis of the starting mixture ended at the temperature of about 520°C. The mixture had light yellow hue of Bi_2O_3. The pigment calcinated at the temperature of 600°C had the intensive yellow colour. This means that the calci-

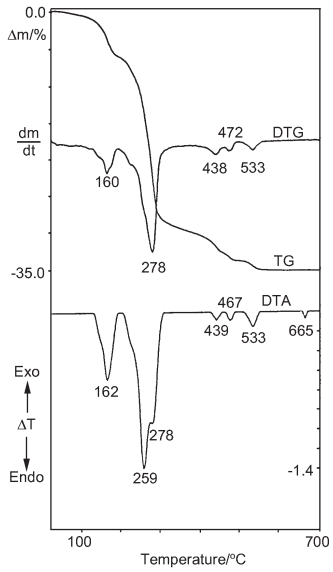

Fig. 2 Thermoanalytical curves of mixture $Zn_{0.70}Bi_{0.30}O_{1.15}$. Apparatus Derivatograph-C, heating rate 5°C min^{-1}, standard α-Al_2O_3, atmosphere air, ceramic crucible

nation temperature of 600°C is sufficiently for the preparation of the (1–*x*)ZnO·*x*Bi_2O_3 pigments.

The attention was focused on the possibilities of the production of the ZnO–Bi_2O_3 pigments as new inorganic pigments with the intensive yellow hue.

Table 1 Lattice parameters of samples of the ZnO+*x* mol% Bi_2O_3 pigments

x/mol% Bi_2O_3	*a*/nm	*c*/nm	*c*/*a*	*V*/nm^3
0	0.32499	0.52071	1.6022	0.047631
3	0.32498	0.52062	1.6019	0.047624
5	0.32499	0.52058	1.6018	0.047617
10	0.32498	0.52055	1.6017	0.047611
15	0.32493	0.52061	1.6022	0.047601
18	0.32493	0.52052	1.6019	0.047594
25	0.32494	0.52058	1.6021	0.047603

The effect of the increasing content of bismuth oxide on the colour hue of the ZnO·Bi_2O_3 pigments was followed. On the basis of the measured colour coordinates both powder pigments and pigments applied in an acrylate copolymer was selected pigment which had the highest value L^* and at the same time the lowest abundance of green tone in yellow colour of the pigment [2]. The most intensive yellow colour of the pigment was attributed to the pigment containing 18 mol% Bi_2O_3. This pigment is

described by the formula $Zn_{0.70}Bi_{0.30}O_{1.15}$. Powder pigment has coordinates L^*=93.93, a^*= –1.42, b^*=57.11. In acrylate copolymer this pigment has coordinates L^*=8.33, a^*= –2.59, b^*=79.19. At the higher content of Bi_2O_3 oxide in starting mixture the colour hue is shifted to light yellow hue.

The samples with the increasing content of Bi_2O_3 were studied by X-ray diffraction analysis [2]. Next to the observed diffraction lines corresponding with characteristic lines of wurtzite structure of ZnO our experiments have shown peaks which have been assigned to tetragonal β-modification of Bi_2O_3. All samples prepared were heterogenous. The volume of the elementary cell of zinc oxide decreases. The minimum value of the elementary cell was determined to the pigment containing 18 mol% Bi_2O_3 which is characterized by the most intensive yellow hue from all pigments prepared.

Conclusions

The pigments of the $ZnO–Bi_2O_3$ system are characterized by intensive yellow colour. They are environmentally friendly and therefore very progressive too. The yellow pigments of the $ZnO–Bi_2O_3$ system could complete the basic assortment of colour inorganic pigments and substitute some problematic pigments from the environmental point of view, especially, chrome yellows (lead chrome) which belong to the most problematic pigments at the present time.

The preparation of this pigment type was investigated within the framework of a grant project dealing with new ecological coloured inorganic pigments [3].

References

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