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New Yellow Pigments: $ZnO–Bi_2O_3$

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ABSTRACT

A zinc oxide pigment with an admixture of bismuth oxide has been prepared as a new yellow pigment for colouring plastics and paints. The effect of the Bi_2O_3 content in the starting mixture on the colour hue of the pigment and the temperature conditions for the pigment synthesis have been evaluated. The optimum conditions for the synthesis of the pigments have been estimated, and also the properties of the product (colour hue and structure) established. © *1998 Elsevier Science Ltd*

Keywords: polycrystalline $ZnO–Bi_2O_3$ samples, solid solutions ZnO–CoO, lattice parameters, point defects, optical properties.

INTRODUCTION

Zinc oxide is one of the longest known white inorganic pigments and has been extensively used in this respect. New coloured compounds have now been prepared using, as base, zinc oxide, and these can be used as new colour pigments for colouring plastics and paints. Their structure and properties show that these compounds are environmentally friendly. This type of pigment can therefore be used as substitute for some more problematic pigments from an environmental point of view, especially, compounds of chromium.

The pigments based on zinc oxide in admixture with bismuth oxide give an intensive yellow colour. The pigments of the $ZnO–Bi_2O_3$ system are formed by the Bi_2O_3 phase on the surface of ZnO by decomposition of $Bi(NO_3)_3 \cdot 5H_2O$ at temperatures of about 550°C. The pigment synthesis is described in this present report.

EXPERIMENTAL

As starting materials for the preparation of the $(1-x)ZnO \cdot xBi_2O_3$ pigments, we used commercial zinc white 99.2% ZnO (Slovlak Košeca, Slovakia) and $Bi(NO_3)3.5H_2O$ p.a. (Lachema Brno, Czech Republic).

The $ZnO–Bi_2O_3$ samples were prepared in the following way. ZnO was suspended in an aqueous solution of $Bi(NO_3)_3$ in the required ratio. This suspension was thoroughly homogenized and then dried by careful evaporation. The dry product was homogenized in an agate mortar. The mixtures were then calcinated at 600°C in porcelain crucibles in an electric resistance furnace (the increase of the temperature was 10°C min^{-1}) for a period of two hours.

The calcinated pigments were applied to an acrylate copolymer. The final paints were evaluated with regard to their colour hues by measurements of spectral reflectance in the visible region using a MiniScan (HunterLab, USA).

The temperature region of the formation of this type of pigment was followed by thermal analysis using a Derivatograph-C (MOM Budapest, system of J. Paulik, F. Paulik and L. Erdey; the rate of temperature increase was 5°C min^{-1}; α-Al_2O_3 was used as standard; the atmosphere was air and a corundum crucible was used).

The powder pigments were studied by X-ray diffraction using an X-ray diffractometer HZG4B (Freiberger Pracisionsmechanic, Germany).

RESULTS AND DISCUSSION

The starting mixtures containing increasing content of bismuth oxide (3, 5, 8, 10, 13, 15, 18, 20 and 22 mol% Bi_2O_3) were homogenized by a wet process. The prepared mixtures were calcinated at 600°C for 2 h. This calcination temperature was determined on the basis of results of the thermal analysis of the bismuth nitrate used as start material for the preparation of the $(1-x)ZnO \cdot xBi_2O_3$ pigments.

The thermal analysis provided initial information about the temperature region of the formation of this type of pigment. 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.

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

$$300°C : Bi(NO_3)_3 \rightarrow BiO_{0.5}(NO_3)_3 + \frac{1}{2}N_2O_5$$

$$400°C : BiO_{0.5}(NO_3)_3 \rightarrow BiONO_3 + \frac{1}{2}N_2O_5$$

$$500°C : BiONO_3 \rightarrow \frac{1}{2}Bi_2O_3 + \frac{1}{2}N_2O_2$$

On the basis of the thermal analysis results (Fig. 1) it follows that bismuth nitrate partially decomposes into reactive intermediates. The decomposition of bismuth nitrate to bismuth oxide ceases at temperatures of about 550°C. This implies that a calcination temperature of 600°C is sufficient for the preparation of the $(1-x)ZnO \cdot xBi_2O_3$ pigments. This temperature of 600°C is also in agreement with the results of the thermal analysis of the starting mixture containing 18 mol% Bi_2O_3 (Fig. 2).

Initially studied was the effect of the Bi_2O_3 content in the starting mixtures on the colour hue of the pigment. The prepared pigments were applied to acrylate copolymer. The colour hues of the final paints, as expressed by spectral reflectance in the visible region, are shown in Fig. 3.

The effect of the increasing content in the starting mixtures on the colour hue of these pigments is demonstrated in Fig. 4. Table 1 shows that the L^*

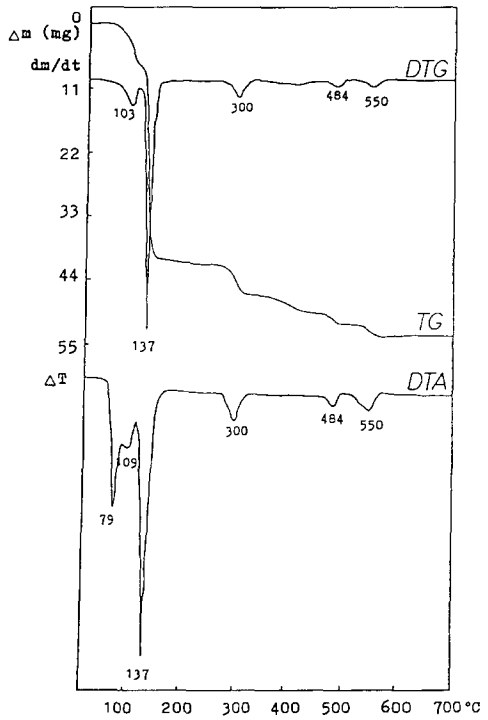

Fig. 1. Thermoanalytical curves of $Bi(NO_3)_3 \cdot 5H_2O$ for the synthesis of the $(1-x)ZnO \cdot xBi_2O_3$ pigments.

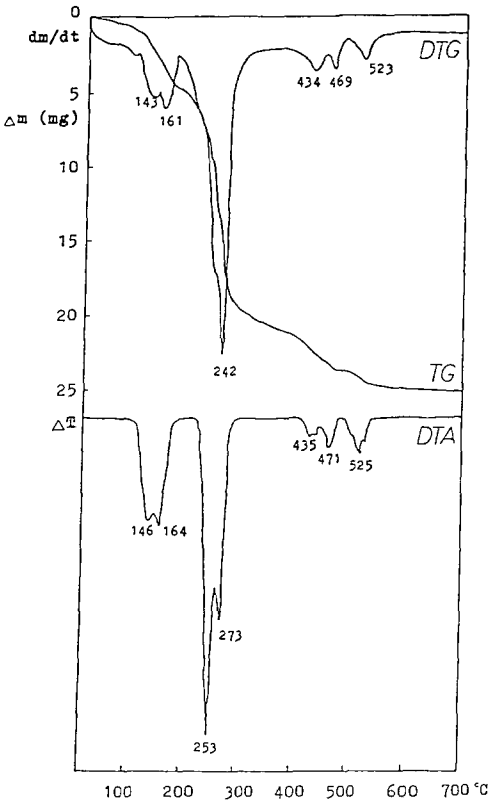

Fig. 2. Thermoanalytical curves of the starting mixture for the synthesis of the $Zn_{0.70}Bi_{0.30}O_{1.15}$ pigment.

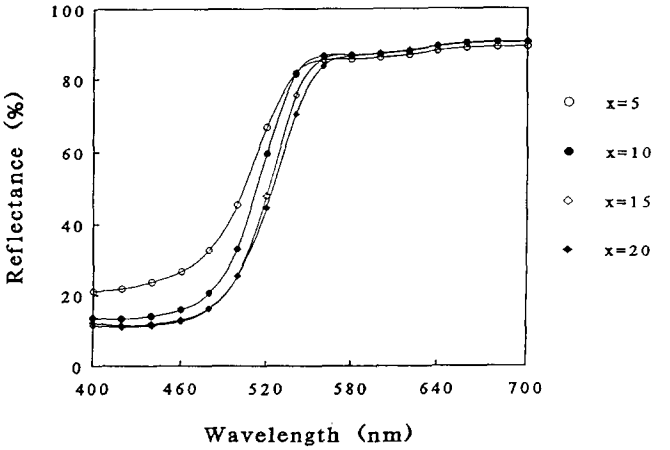

Fig. 3. The effect of the increasing content of bismuth on the colour hue of the $(1-x)ZnO{\cdot}xBi_2O_3$ pigments.

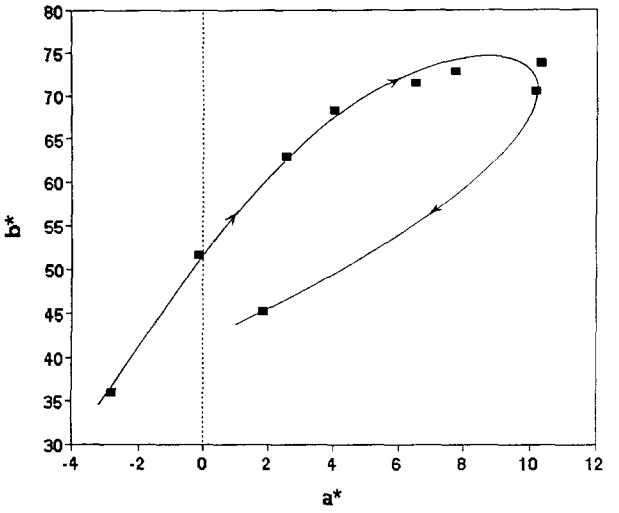

Fig. 4. The effect of the increasing content of bismuth on the colour hue of the $(1-x)ZnO{\cdot}xBi_2O_3$ pigments in a^*, b^* coordinates.

values only slightly decrease with increasing content of bismuth oxide, but the colour coordinates a^* and b^* increase. This means that the colour hue of these pigments, with increasing content of bismuth oxide, is shifted from a white to a yellow colour. The greatest colour shift is perceptible in samples containing 3, 5, 8 and 10 mol% Bi_2O_3. The increasing content of Bi_2O_3 increases the yellow hue of these pigments.

The most intensive yellow colour of these pigments was attributed to the pigment containing 18 mol% Bi_2O_3 (Fig. 4). This pigment can be described by the formula $Zn_{0.70}Bi_{0.30}O_{1.15}$. At higher content of bismuth oxide in the starting mixture (20 mol% Bi_2O_3), the colour intensity of the pigment increases only a little, but the colour hue does not differ from the pigment containing

TABLE 1
The Effect of the Increasing Content of Bismuth on the Colour Hue of the $(1-x)ZnO{\cdot}xBi_2O_3$ Pigments in L^*, a^*, b^* Coordinates

x, mol%	L^*	a^*	b^*
3	91.51	−2.78	35.94
5	88.94	−0.14	51.61
8	87.72	2.54	62.99
10	87.11	4.03	68.29
13	86.28	6.52	71.58
15	85.83	7.77	72.94
18	84.97	10.33	73.85
20	84.99	10.16	70.55
22	86.94	1.81	45.21

TABLE 2
Lattice Parameters of Samples of the $(1-x)ZnO \cdot xBi_2O_3$ 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
20	0.32493	0.52052	1.6019	0.047594
20	0.32494	0.52058	1.6021	0.047603

18 mol% Bi_2O_3. When 22 mol% Bi_2O_3 used, the colour hue of the pigment shifted to a light yellow hue, i.e. the L^* value increases, but the colour coordinates a^* and b^* decrease, and this pigment becomes the lightest.

Further, we investigated the structure of the $(1-x)ZnO \cdot xBi_2O_3$ pigments. Samples with increasing content of Bi_2O_3 (Table 2) were studied by X-ray diffraction analysis. Next to the observed diffraction lines corresponding to the characteristic lines of the wurtzite structure of ZnO, our experiments showed peaks which have been assigned to a tetragonal β-modification of Bi_2O_3. This means that all prepared samples are heteregeneous. The values of the lattice parameters of the $ZnO-Bi_2O_3$ samples are given in Table 2 and these show that the lattice parameters a and c decrease with increasing content of bismuth oxide. The volume of the elementary cell of zinc oxide also decreases. The minimum value of the elementary cell V was determined as the pigment containing 18 mol% Bi_2O_3 (Fig. 5), which is characterized by the most intensive yellow hue of all the prepared pigments.

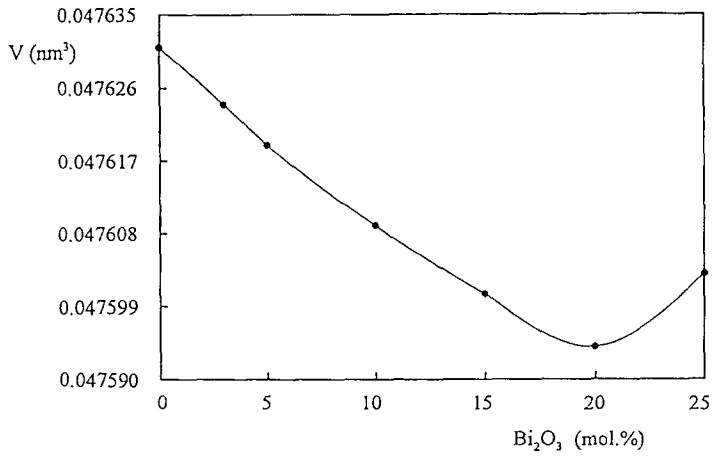

Fig. 5. The dependence of the volume of the elementary cell V on the increasing content of bismuth oxide.

CONCLUSION

Pigments of the $ZnO–Bi_2O_3$ system are characterized by an intensive yellow colour and they are environmentally friendly. The yellow pigments of this $ZnO–Bi_2O_3$ system could contribute to the basic assortment of colour parameters of inorganic pigments, and resolve the environmental problems associated with, for example, the chrome yellows (lead chrome), which are currently among the most problematic pigments.

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