

SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
13 (2007)

**SYNTHESIS AND COLOUR PROPERTIES
OF $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ PIGMENTS**

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Received September 2, 2007

$(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ solid solutions were synthesized as new inorganic yellow and orange pigments and their colour properties have been investigated as possible ecological materials. The pigments were prepared by the solid state reaction of mixed oxides $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ with nominal compositions: $x = 0.1-0.9$. All the synthesized pigment samples were found to have colour coordinates, low a^ and high b^* and exhibit the colour from pale yellow to orange. Characterization of the $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ solid solutions suggests that they have a potential to be alternative yellow colorants for paints, inks, plastics, and ceramics.*

Introduction

The pigments for colouring ceramics, usually inorganic products composed of metal oxides or compounds formed from metal oxides, must possess thermal and chemical stability at high temperature and must be inert to the chemical action of

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the molten glaze [1]. Inorganic pigments are widely used in various applications such as paints, inks, plastics, rubbers, ceramics, enamels and glasses. Unfortunately, the majority of inorganic pigments for the above applications currently employed are toxic metals such as cadmium, lead, chromium or cobalt. Thus, a serious need arises to search for materials of environmentally friendly and economically viable materials for the replacement of toxic inorganic pigments.

Bismuth trioxide has four polymorphs: monoclinic (or pseudo-orthorhombic) α -form, face-centred cubic (*fcc*) δ -form, tetragonal β -form and body-centred cubic (*bcc*) γ -form. Only α - Bi_2O_3 is a stable phase of pure Bi_2O_3 at room temperature from among these polymorphs. When pure α phase is heated to about 730 °C, transition to the δ - Bi_2O_3 occurs and this phase is stable only between 730 °C and its melting point of 825 °C. Large thermal hysteresis effects are present upon cooling, and δ phase transforms to one of the two intermediate phases which are β -form (formed at 650 °C) and γ -form (formed at 639 °C). The γ -phase can be obtained by controlled cooling of β - Bi_2O_3 . The last two phases are metastable and they usually transform to the α phase in the temperature range of 650-500 °C [2].

The high temperature phase of bismuth sesquioxides Bi_2O_3 , which is stable in the 730-825 °C temperature range, has been intensively studied because of its high oxygen conductivity [3]. The structure of the δ -phase is based on a face-centered cubic cation sublattice and can be described as a defective fluorite structure where $\frac{1}{4}$ of the anion sites are vacant [4]. This high oxygen vacancy concentration gives rise to high oxygen-ion mobility. The δ -phase may be stabilized below room temperature by partial cationic substitution of Bi^{3+} . The use of rare-earth cations has appeared as effective path for the preparation of different crystal phases. Effectiveness depends on the kind and the amount of rare-earth cation used and the synthesis conditions employed [3]. In the present study, the new pigments having the formula $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ with various rare earth concentration levels have been prepared and their colour properties, as possible ecological inorganic pigments have been investigated.

Experimental

Mixed oxides $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ with nominal compositions $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9 have been prepared. Starting materials for the preparation of the $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ pigments were Bi_2O_3 (Lachema Brno, the Czech Republic) and Gd_2O_3 (Bochemie Bohumín, the Czech Republic). The starting mixtures containing both oxides were then homogenized in an agate mortar. The mixtures were calcinated in porcelain crucibles in an electric resistance furnace, with heating rate 10 °C min^{-1} . The calcination temperatures of 700, 750, 800 and

850 °C were maintained for two hours. Further, the pigment with best orange colour was prepared with an agent of mineralization. The agents of mineralization used in this study were NaF, CaF₂, MgF₂, Na₃AlF₆, Na₂SiF₆, AlF₃, KCl. The agent of mineralization was used in a quantity of 5 %. The prepared mixtures were calcinated at 700, 750, 800 and 850 °C for 2h.

The calcinated pigments were applied to an organic matrix in mass tone and in reduced tints in weight ratios of 1:1 (RG – 15, Precheza a.s., Přešov, the Czech Republic). The final paints were evaluated for colour change by measuring spectral reflectance in the visible region of light (400-700 nm) using a Color Quest XE (HunterLab, USA). The measurement conditions were as follows: an illuminant D65, 10° complementary observer and measuring geometry d/8°.

The colour properties are described in terms of CIE $L^*a^*b^*$ system (1976). The value a^* (the red-green axis) and b^* (the yellow-blue axis) indicate the colour hue. The value L^* represents the lightness or darkness of the colour as related to the natural grey 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 and is calculated according the formula: $C = (a^{*2} + b^{*2})^{1/2}$. The total colour difference ΔE^*_{CIE} in the CIE $L^*a^*b^*$ diagram, which indicates the degree of colour difference between the two samples, is defined by the following equation: $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$, where ΔL^* , Δa^* , Δb^* are difference in L^* , a^* , and b^* values between the sample colour and the standard colour. It is possible to express the colour of pigment as a hue angle ($H^\circ = \arctg(b^*/a^*)$), too [5].

Physical-chemical analysis (particle size distribution, specific weight, oil number, and CPVC) were also determined. In order to obtain the pigments with optimum particle sizes, the pigments were wet ground with ethanol and zircon corpuscles (1.8 mm in diameter) in planetary mill Pulverisette 5 (Fritsch, GmbH Germany). The milling times were 15, 30, 45 and 60 minutes. The distribution of particle sizes of the calcinated powders was obtained by laser scattering using Mastersizer 2000 MU (Malvern Instruments, GB). It is a highly integrated laser measuring system (He-Ne laser, $\lambda = 633$ nm) for the analysis of particle size distribution.

Specific weight is one of the basic physical-chemical parameters which characterize the powder substance. For the pigments prepared, its value was determined by pycnometric method [6]. Oil number was determined by standard method "mortar-pestle" [7]. Linseed oil was used as a binder. The values of CPVC (Critical Pigment Volume Concentration) [7] were calculated from the specific weight and the oil number. CPVC characterizes a state when the space between the particles of a pigment is only filled with the binder.

Results and Discussion

The aim of the present work is to investigate the influence of growing gadolinium content on the colouring effect of the $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ with $x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9 . The mixtures were calcinated at $700, 750, 800$ and 850 °C.

At first, the effect of the Gd content in the starting mixtures and calcination temperature on the colour hue of the pigment was studied. The prepared pigments were applied to an organic matrix. Based on values a^* and b^* of powder pigments (Table I), it can be seen that the increasing gadolinium content increases the colour value a^* (red hue) up to $x = 0.4$ for three temperatures $750, 800$ and 850 °C. The increase of Gd content did not markedly affect the colour value b^* (yellow hue). The highest value of this colour coordinate is exhibited by the pigment $(\text{Bi}_2\text{O}_3)_{0.7}(\text{Gd}_2\text{O}_3)_{0.3}$ calcinated at 800 °C. The growth of gadolinium content above the level $x = 0.7$ results in a marked decrease in a^* and b^* values. The pigments applied to organic matrix in reduced tints have a similar trend for the colour coordinates. The highest value a^* (red hue) was exhibited by the pigment $(\text{Bi}_2\text{O}_3)_{0.6}(\text{Gd}_2\text{O}_3)_{0.4}$ at all calcination temperatures. Pigments with nominal composition $x = 0.1$ and 0.4 to 0.6 produce an orange colour. The samples with $x = 0.2, 0.3$ and 0.7 have a yellow-orange colour, which at the highest gadolinium contents ($x = 0.8$ and 0.9) is shifted to light yellow.

Table I The effect of Gd content and temperature on the colour co-ordinates a^* and b^* of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ (an application into organic matrix in mass tone)

x	Temperature, °C							
	700		750		800		850	
	a^*	b^*	a^*	b^*	a^*	b^*	a^*	b^*
0.1	8.56	58.72	13.47	57.05	12.07	56.67	-	-
0.2	3.64	60.33	3.94	55.67	1.09	56.79	3.37	45.69
0.3	3.46	59.26	2.96	60.79	3.72	62.52	5.43	58.54
0.4	9.28	58.88	13.16	57.51	14.80	57.60	14.31	56.17
0.5	9.30	62.12	12.54	58.32	12.70	57.12	11.50	56.56
0.6	7.48	56.15	7.41	55.41	7.13	56.95	6.08	57.07
0.7	1.74	56.26	0.43	55.88	-0.12	53.08	-3.59	53.10
0.8	-2.03	48.77	-5.21	48.36	-7.77	43.58	-5.20	33.92
0.9	-6.92	36.37	-6.63	33.28	-5.70	26.69	-1.60	17.22

For other studies we used the pigment $\text{Bi}_{1.2}\text{Gd}_{0.8}\text{O}_3$ because it should possess the most intense orange colour. This pigment was studied to determine the effects of milling and agent of mineralization on colour hue. The particle sizes and particle size distributions can markedly affect the colour properties of inorganic pigments. That is why the prepared samples were tested from this point of view. The main aim was to decrease the particle sizes and monitor the influence of particle sizes on the colour properties of the pigment. The reduction of particle sizes influenced the colour properties of the pigment. Table II shows that the L^* value increases with growing milling time, but the chroma changes only a little. Grinding has a marked effect on the ΔE^* values. The colour coordinates b^* of the pigment change only a little, but colour coordinates a^* decrease (Fig. 1). The hue of the pigment is shifted from orange to a light yellow-orange colour with increasing milling time. The optimum milling time is 15 minutes for colour properties, because there is no change in the colour hue of the pigment ($H^\circ = 75.96$ for unmilled pigment and $H^\circ = 77.65$ for milled pigment). The optimum grinding time is 60 minutes for the particle size of the pigment, the particle size decreased from $3.86 \mu\text{m}$ to $0.96 \mu\text{m}$. Wet grinding in the planetary mill Pulverisette 5 in ethanol medium leads to decreasing of the particle size of the pigment $(\text{Bi}_2\text{O}_3)_{0.6}$

Table II The effect of milling on colour properties of $(\text{Bi}_2\text{O}_3)_{0.6}(\text{Gd}_2\text{O}_3)_{0.4}$ pigment calcinated at 850°C (application into organic matrix in mass tone)

Milling time, min	L^*	a^*	b^*	C	ΔE^*	H°
0	71.44	14.34	57.34	59.11	-	75.96
15	75.78	12.38	56.54	57.88	4.83	77.65
30	76.76	11.92	57.24	58.47	5.85	78.24
45	77.65	11.03	57.07	58.13	7.04	79.06
60	78.50	10.43	57.18	58.12	8.08	79.66

Table III Particle sizes of the $(\text{Bi}_2\text{O}_3)_{0.6}(\text{Gd}_2\text{O}_3)_{0.4}$ pigment calcinated at 850°C

Milling time, min	Particle size, μm	
	Particle size range	Mean particle size
0	0.56-32.28	3.86
15	0.52-6.48	1.83
30	0.41-5.37	1.29
45	0.39-3.26	1.07
60	0.34-5.48	0.96

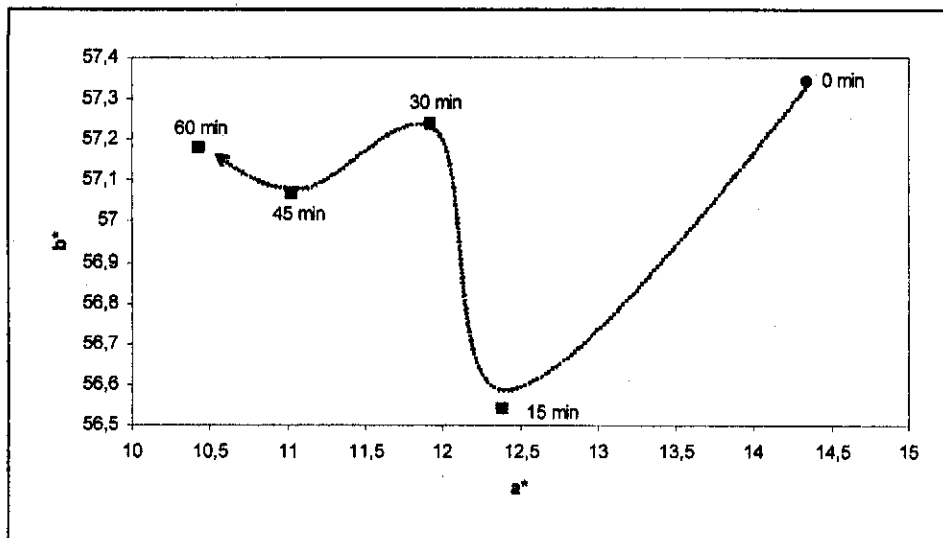


Fig. 1 The effect of milling on the colour co-ordinates a^* and b^* of $(\text{Bi}_2\text{O}_3)_{0,6}(\text{Gd}_2\text{O}_3)_{0,4}$ pigment calcinated at 850 °C (application into organic matrix in mass tone)

$(\text{Gd}_2\text{O}_3)_{0,4}$. The values of particle sizes of the samples are shown in the Table III.

The specific weight of the pigments was measured pycnometrically. The specific weight of the prepared pigment $(\text{Bi}_2\text{O}_3)_{0,6}(\text{Gd}_2\text{O}_3)_{0,4}$ is 9.60 g cm^{-3} . Invariability of the pigment production is given by oil consumption. For the pigment prepared, this parameter is 19.71 g per 100 g. The calculation of *CPVC* value is based on the knowledge of specific weight and oil consumption of a pigment. The value of *CPVC* of the prepared pigment is 32.98 %.

Also the agent of mineralization can markedly affect the colour properties of pigments. That is why the prepared samples were also tested from this point of view. The effect of agent of mineralization on colour coordinates a^* and b^* of $(\text{Bi}_2\text{O}_3)_{0,6}(\text{Gd}_2\text{O}_3)_{0,4}$ pigment calcinated at 800 °C are shown in Fig. 2. The agents of mineralization KCl, NaF and CaF_2 do not markedly influence the colour properties of the pigment. The content of AlF_3 , Na_3AlF_6 and Na_2SiF_6 causes an increase in the colour value b^* (yellow hue). Nevertheless, the content of these agents of mineralization decreases the value a^* (red hue). The red hue in orange colour is reduced and is replaced by yellow-orange colour. The agent of mineralization MgF_2 has a marked effect on the colour properties of $(\text{Bi}_2\text{O}_3)_{0,6}(\text{Gd}_2\text{O}_3)_{0,4}$ pigment. The pigments without agents of mineralization have orange colour (the values a^* are from 8 to 13 and the values b^* are from 56 to 60). In the case of agents of mineralization, the value a^* is lower: from 0.5 to 8 and the value b^* is higher: from 64 to 69 (Table IV). With the application of agent of mineralization, the values L^* and chroma also increase.

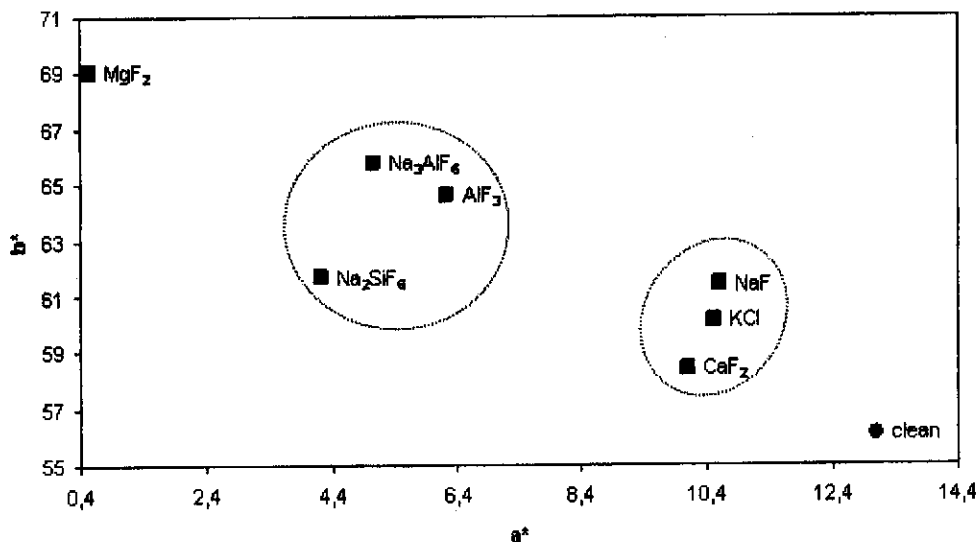


Fig. 2 The effect of agent of mineralization on colour coordinates a^* and b^* of $(\text{Bi}_2\text{O}_3)_{0,6}(\text{Gd}_2\text{O}_3)_{0,4}$ pigment calcinated at $800\text{ }^\circ\text{C}$ (application into organic matrix in mass tone)

Table IV The effect of temperature and agent of mineralization MgF_2 on colour properties of $(\text{Bi}_2\text{O}_3)_{0,6}(\text{Gd}_2\text{O}_3)_{0,4}$ pigment (application into organic matrix in mass tone)

Agent of mineralization	$T, ^\circ\text{C}$	L^*	a^*	b^*	C	H°
-	700	80.50	8.37	59.41	60.00	81.98
-	750	75.78	11.78	56.13	57.35	78.15
-	800	75.53	13.07	56.10	57.60	76.89
-	850	75.71	13.16	58.06	59.3	77.23
MgF_2	700	84.42	3.34	64.31	64.40	87.03
MgF_2	750	82.54	4.36	65.12	65.27	86.17
MgF_2	800	84.68	0.55	69.04	69.04	89.54
MgF_2	850	80.05	7.73	66.02	66.47	83.32

Conclusion

The prepared pigments provide orange colour hues shifted to light yellow over yellow colour hues. The pigment $\text{Bi}_{1,2}\text{Gd}_{0,8}\text{O}_3$ that is calcinated at $850\text{ }^\circ\text{C}$ possesses the most intensive orange colour. The optimum milling time for colour properties

of this pigment is 15 minutes. For the particle size of pigment, 60 minutes is the optimum grinding time. By using of convenient agent of mineralization, the colour hue of pigment $\text{Bi}_{1.2}\text{Gd}_{0.8}\text{O}_3$ can be changed from orange to yellow over yellow-orange. The pigments of the $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Gd}_2\text{O}_3)_x$ system are environmentally friendly. New coloured compounds could contribute to the basic assortment of orange and yellow inorganic pigments. These pigments are resistant to heat and chemical agents and represent potential alternative to inorganic pigments containing chromium and lead (chromate yellows). Thus, these pigments are potentially more environmentally friendly than those currently used.

Acknowledgements

The authors would like to thank for the financial support from the Ministry of Education, Youth and Sports of the Czech Republic (No. 0021627501).

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