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

PREPARATION AND COLOUR PROPERTIES OF $Ce_{1-x}Tb_xO_2$ PIGMENTS

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Received September 27, 2007

New inorganic pigments based on CeO_2 were synthesized as high-temperature environment-friendly inorganic pigments. This work is focused on mixed oxides based on ceria which are doped with rare earth elements. The pigments were prepared in the series with increasing content of terbium. Their colour properties were investigated depending on content of terbium and temperature of calcination. The pigments of $Ce_{1-x}Tb_xO_2$ were applied into organic matrix and ceramic glaze. The pigments were evaluated from the standpoint of their structure, colour and particle sizes.

Introduction

Inorganic pigments have been applied in various areas such as paints, ceramics, plastics, enamels and glazes [1]. However, most of conventional inorganic pigments applicable for these purposes contain the toxic metals such as Cd, Co,

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Cr, Hg, Pb and Sb that can adversely affect the environment and human health. Therefore, development of safe inorganic pigments has been required in order to replace the toxic inorganic pigments by environment-friendly pigments or less toxic substances [2].

The research activities of our laboratory are focused on investigation of special inorganic pigments, mainly on ceramic pigments [3]. Growing demands for thermal stability and ecological purity of pigments make it difficult to compile a colour range of available pigments and their colour hues. The most demanded hues are yellow, pink, orange and red. Their presence in the ceramic field is deficient. Nowadays, pigments which are doped with lanthanides (oxide or sulphide compounds) are studied. These pigments are formed by the host crystal structure where ions of lanthanides represent chromophores.

In recent years, the pigments based on fluorite type CeO_2 are of great interest due to their high temperature stability [4]. These pigments give various brown (after application into organic matrix) and orange (pigments which are applied into glaze) hues and are based on incorporation of terbium ions into the host lattice of fluorite type cerium dioxide. Systems of CeO_2-Tb_4O_7 pigments are usually prepared by solid-state reactions. The raw material for the preparation of the $Ce_{1-x}Tb_xO_2$ pigment was mixed oxide Tb_4O_7. Terbium ions are available in two oxidation states in this mixed oxide Tb_4O_7, i.e. $2TbO_2.Tb_2O_3$. During the high-temperature calcination (1300-1600 °C) terbium ions enter the CeO_2 and form $Ce_{1-x}Tb_xO_2$ solid solution. The colour of pigment depends on the terbium content, temperature of calcination and on the way of application, too. This research is very significant because these pigments giving interesting hues in ceramic glaze are heat-resistant and represent possible alternative inorganic pigments, being more ecological. The commercial significance of compounds based on CeO_2 is in thermal, chemical and light stability combined with their low toxicity [3].

Experimental

The $Ce_{1-x}Tb_xO_2$ pigments were prepared by the classical dry process i.e. solid state reaction. Cerium dioxide of 99.5 % purity and terbium oxide of 99 % purity were used as starting compounds (Trading Bochemie, a.s., CZ). The starting mixtures containing both basic oxides (CeO_2, Tb_4O_7) with increasing content of terbium (x = 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9) were homogenised in a porcelain mortar. Each of the mixtures was submitted to calcination in corundum crucibles in an electric resistance furnace with the heating rate of 7 °C min^{-1}. The calcination temperatures of 1300, 1400, 1500 or 1600 °C were maintained for 1 hour. In this manner prepared pigments were applied into organic matrix (Balakom, a.s., CZ) in a mass tone and into the ceramic glaze G 05091 (Glazura, s.r.o. Roudnice nad Labem, CZ). The mixture of pigment in amounts of 10 % w/w and glaze was glazed at 1000 °C and the temperature was held for 15 min.

The colour of pigments was measured in the visible region of light (400-700 nm) using ColorQuest 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). In this system, L^* is a degree of lightness and darkness of colour in relation to scale extending from white ($L^* = 100$) to black ($L^* = 0$), the values a^* [the green ($-a^*$) to red ($+a^*$) axis] and b^* [the blue ($-b^*$) to yellow ($+b^*$) axis] indicate the colour hue. The value C (chroma) represents saturation of the colour and is calculated according to the formula: $C = (a^{*2} + b^{*2})^{1/2}$. The colour of pigments is also expressed by the hue angle $H°$ defined by an angular position in the cylindrical colour space (for the red is $H° = 0\text{-}35°$, for the orange $H° = 35\text{-}70°$, for the yellow $H° = 70\text{-}105°$). The equation for calculation of the hue angle is $H° = \text{arc tg}\,(b^*/a^*)$ [5].

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.

The structure of the prepared pigments was also investigated. The prepared pigments were studied by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained using a Diffractometer D8 (Bruker, GB), CuK_α radiation with scintillation detector.

Results and Discussion

The aim of the present work was to investigate the influence of growing content of terbium on the colouring effect of the $Ce_{1-x}Tb_xO_2$ with $x = 0.05$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9.

The colour hue of pigments applied into organic matrix is practically independent of the calcination temperature. On the other hand, the colour hue changes with increasing amount of terbium in the pigment and the colour shifts from light brown to brown-black, except pigment with $x = 0.05$ producing brick colour at the temperature of 1600 °C. Based on values a^* and b^* of powder pigments (Table I) it can be seen that the increasing Tb content decreases the colour values a^* (red hue) and b^* (yellow hue). The growing amount of terbium subsequently lowers the quality of colour properties of prepared compounds. This trend is also demonstrated by decreasing coordinates L^* (brightness), C (chroma) and $H°$ (hue angle).

The change in a colour hue is also apparent for the pigments applied into the ceramic glaze, especially after calcination at the temperature of 1500 and 1600 °C (Table I). The colour properties of pigments after application into glaze are also influenced by the amount of Tb in the pigment composition. This influence is showed in Fig. 1 (the arrow only indicates the increasing of Tb content in samples without statistic evaluation). The samples with lower content of terbium (x = 0.05, 0.1, 0.2 and 0.3) have high levels of value a^* and provide saturated dark-orange colour. On the other hand, the hue of compounds with higher values of coordinate b^* (x = 0.5-0.9) is shifted to orange-yellow. It means that the increasing content of Tb rises value L^* and the pigment becomes lighter (Table I). From the values of $H°$ it follows that range of calculated dates is between 50 and 86 degrees which corresponds with colour transition from dark orange to yellow. The chroma C decreases from x = 0.05 to x = 0.2; then value C a little increases to x = 0.5 (C = 43.38) and finally decreases to the level *of* C = 31.26 (x = 0.9).

Table I The effect of increasing Tb content on the colour properties of the $Ce_{1-x}Tb_xO_2$ pigments applied into organic matrix and into ceramic glaze (1600 °C)

x	Organic matrix					Ceramic glaze				
	L^*	a^*	b^*	C	$H°$	L^*	a^*	b^*	C	$H°$
0.05	48.20	21.68	21.38	30.45	44.60	56.78	24.85	30.03	38.98	50.39
0.1	34.77	13.88	9.65	16.90	34.81	50.92	26.16	27.36	37.85	46.28
0.2	28.41	5.83	2.30	6.27	21.53	52.12	23.06	24.40	33.57	46.62
0.3	26.67	4.72	1.49	4.95	17.52	58.03	23.28	30.47	38.35	52.62
0.4	28.54	4.21	0.85	4.29	11.41	62.61	22.90	35.40	42.16	57.10
0.5	25.07	4.57	1.48	4.80	17.94	65.15	21.37	37.75	43.38	60.49
0.6	24.98	4.65	1.42	4.86	16.98	66.19	19.64	37.15	42.02	62.14
0.7	27.66	3.85	0.80	3.93	11.74	67.22	17.11	37.19	40.94	65.29
0.8	25.89	4.01	0.87	4.10	12.24	70.59	10.49	36.85	38.31	74.11
0.9	27.99	3.30	0.15	3.30	2.60	78.21	2.56	31.15	31.26	85.30

The colour difference between ceramic glaze application and powder pigments is very well evident from Fig. 2. This picture shows the chosen pigment $Ce_{0.9}Tb_{0.1}O_2$ applied into ceramic glaze with the same composition after application into organic matrix and calcinated at the temperatures of 1300, 1400, 1500 or 1600 °C. Powder pigments have a very close interval of a^* and b^* values, which is shifting from 9.52 to 13.88 for colour coordinate a^* and from 9.02 to 10.22 for coordinate b^*. These values correspond to brown and black brown tinge. Pigments applied into glaze have higher levels of values a^* at the temperatures of 1500 and 1600 °C (Table II) which make dark orange colour. Samples that were prepared by calcination at the temperatures of 1300 and 1400 °C provide hues of cream.

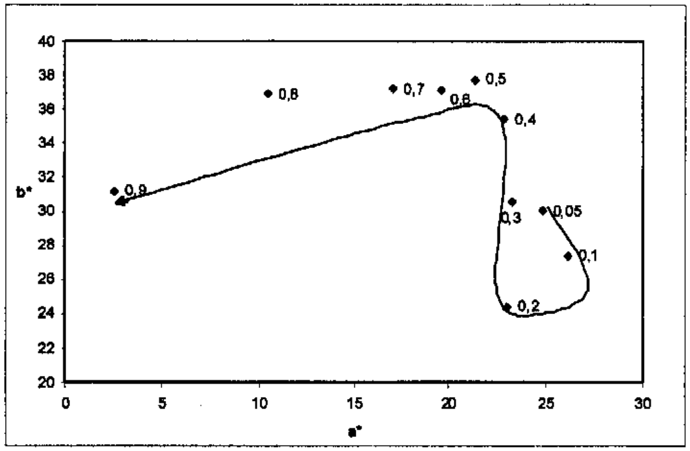

Fig. 1 The effect of Tb content on the colour co-ordinates a^* and b^* of $Ce_{1-x}Tb_xO_2$ pigments applied into ceramic glaze (1600 °C)

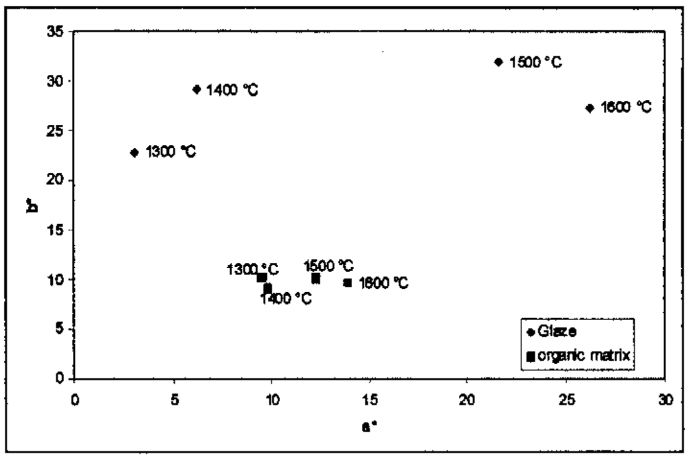

Fig. 2 The influence of calcination temperature on the colour properties of pigment $Ce_{0.9}Tb_{0.1}O_2$ applied into organic matrix and ceramic glaze

Table II The effect of calcination temperature on colour properties of the $Ce_{0.9}Tb_{0.1}O_2$ pigment applied into ceramic glaze

T, °C	*L**	*a**	*b**	*C*	*H*°
1300	84.50	3.05	22.80	23.00	82.38
1400	81.60	6.20	29.23	29.88	78.02
1500	64.88	21.61	31.92	38.55	55.90
1600	50.92	26.16	27.36	37.85	46.28

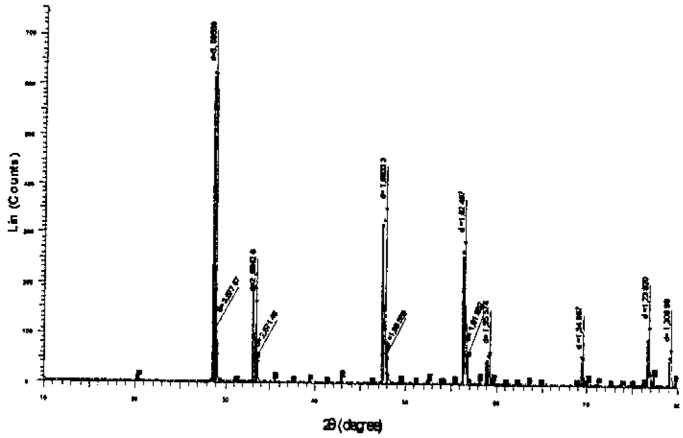

Fig. 3 Powder X-ray diffraction pattern of $Ce_{0.9}Tb_{0.1}O_2$ pigment obtained by calcination at 1300 °C

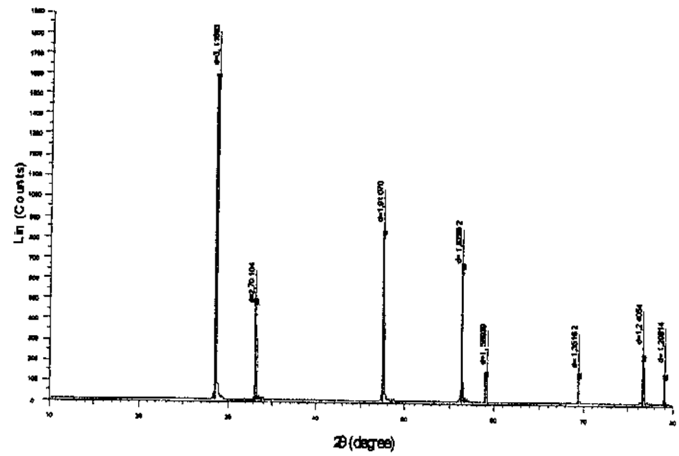

Fig. 4 Powder X-ray diffraction pattern of $Ce_{0.9}Tb_{0.1}O_2$ pigment obtained by calcination at 1400 °C

The pigment $Ce_{0.9}Tb_{0.1}O_2$ was also studied by powder X-ray diffraction analysis. It was found that the sample calcinated at the temperature of 1300 °C is heterogeneous (Fig. 3) because free Tb_2O_3 was also identified besides cubic CeO_2. The higher temperature, i.e. 1400 °C (Fig. 4) produced single-phased compound. The fluorite type CeO_2 structure of the samples with cubic symmetry with lattice parameter a = 0.5411 nm for x = 0.1 was determined. The same results were obtained for the pigments prepared at the temperatures of 1500 and 1600 °C.

The particle size and particle size distribution can markedly affect the colour properties of inorganic pigments. Therefore the synthesized samples were measured from this point of view. The test was carried out with unmilled pigments. From Table III it follows that the growing content of terbium in samples subsequently lowers the mean particle size (d_{50}) from the value 11.8 to 4.8 μm. The pigment with x = 0.3 forms an exception, because its mean particle size slightly increases to the level of 10.2 μm. The mean particle sizes of the pigment calcinated at the temperature of 1600 °C range from 5 μm to 12 μm, which means that these compounds are applicable to colouring glazes.

Table III Particle sizes of the $Ce_{0.9}Tb_{0.1}O_2$ pigments obtaining by calcination at 1600 °C

	Partilcle sizes, μm	
x	Particle size range	Mean particle size
0.05	1.9-63.8	11.8
0.1	3.3-36.6	10.7
0.2	3.2-27.1	9.7
0.3	3.4-28.8	10.2
0.4	3.4-30.4	10.1
0.5	3.1-33.2	9.8
0.6	2.8-41.2	9.1
0.7	2.6-36.5	6.9
0.8	2.3-57.6	6.4
0.9	2.1-39.3	4.8

Conclusion

Pigments based on CeO_2 are successfully prepared by adding terbium oxide. After exploration of colour properties of $Ce_{1-x}Tb_xO_2$ pigments it is possible to claim that samples calcinated at the temperatures of 1500 and 1600 °C provide a much better colour shade. Pigments with the content of Tb x = 0.1, 0.2 and 0.3 applied into ceramic glaze have the best colour qualities whose final colour is dark orange. The values of hue angle $H°$, that lie in the interval from 35 to 70, correspond with orange tinge and also confirm this conclusion.

Acknowledgements

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

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