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STUDY OF CeO_2-PrO_2-Y_2O_3 CERAMIC PIGMENTS

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The synthesis of new colourants based on CeO_2 has been investigated, the focus of which was the preparation of pigments for colouring ceramic glazes. The synthesis of these colourants involved high-temperature calcination of starting oxides, and the optimum conditions for their synthesis were determined. The pigments were evaluated from the standpoint of their structure, hue and ability to colour ceramic glazes.

Introduction

The pigments for colouring ceramics, usually inorganic products composed of metal oxides or compounds capable to form metal oxides, must possess thermal and chemical stability at high temperature and must be inert to the chemical action of the molten glaze [1]. These demanding requirements restrict the range of ceramic pigments and only a very small number of refractory compounds that are relatively inert to the medium in which they are dispersed can be used. New pigment compounds have been dominating the research and development of recent years.

The research activities of our laboratory are focused on investigation of special inorganic pigments, mainly on ceramic pigments. Many pigments used just now are questionable from the hygienic point of view. The fact that most of the pigments contains problematic elements opens the necessity for substitution of pigments containing toxic metals (lead, chromium). Yellow ceramic pigments commonly used, such as $Pb_2Sb_2O_7$ and CdS, are now withdrawn from the market because of their toxicity [1]. For this reason the main attention has been directed to the synthesis of new inorganic compounds mainly with yellow, orange and red colour hues which can be used as pigments for colouring of glaze, plastics, paints or building materials.

Ecological pressure opens a new way to the pigment research. Compounds unacceptable in the past because of high prices become interesting. These compounds contain elements of the rare earths. Such pigments are compounds of oxide or sulphide of lanthanide compounds or compounds created by the host crystal structure (ZrO_2, Al_2O_3). Ions of lanthanides act as chromophores there [2]. In harmony with this postulate the pigments based on CeO_2 represent new special inorganic pigments with high-temperature stability [3]. Pigments with supporting structures of the fluorite lattice CeO_2 and ions of praseodymium which act as a chromophore seem to be promising. The pigment is formed by the solid solution of cerium oxide and praseodymium $Ce_{1-x}Pr_xO_2$ and is produced during high-temperature calcination (> 1300 °C), i.e. when the praseodymium oxide is dissolved in CeO_2. The colour pigment hue depends on the praseodymium content. The colour range begins at pink-orange, continues to red-brown and ends at brown [4]. In the present study, the formula $Ce_{1-(x+y)}Pr_xY_yO_{2-y/2}$ of new pigments was studied. The aim was to develop conditions for the synthesis of this type of pigments and to determine the influence of yttrium on the colouring effects of $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ pigments. Yttrium oxide (Y_2O_3) and praseodymium dioxide (PrO_2) are dissolved in the cerium dioxide at 1300 °C forming a solid solution of the mentioned oxides. This work is meaningful because these pigments give interesting hues into ceramic glazes, are heat-resistant and represent potential alternative inorganic pigments, being more environmentally friendly. The commercial significance of compounds based on CeO_2 is in thermal, chemical and light stability combined with their low toxicity.

Experimental

The starting materials for the preparation of the $Ce_{1-(x+y)}Pr_xY_yO_{2-y/2}$ pigments were CeO_2 of 95 % purity (2 % La_2O_3, 0.5 % Tb_4O_7, 0.25 % Ho_2O_3, 0.25 % Yb_2O_3, 1 % Gd_2O_3 and 1 % Sm_2O_3), Pr_6O_{11} of 90 % purity (1 % CeO_2, 1.5 % Nd_2O_3, 0.5 % La_2O_3, 6.5 % Eu_2O_3 and 0.5 % Dy_2O_3), Y_2O_3 of 99 % (Indian Rare Earths Ltd.).

The starting mixtures containing both basic oxides (CeO_2 and Pr_6O_{11}) with the required content of Y (y = 0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75, 0.85) were homogenised in an agate mortar. The mixtures were then calcinated in corundum crucibles in an electric resistance furnace, increasing the temperature at a rate of 10 °C min^{-1}. The calcination temperature of 1350 °C was maintained for 1 h. The pigments (10 % w/w) were added to a middle-temperature borate-silicate (transparent leadless) glaze at 1000 °C and the temperature was held for 15 min. The final glazes were evaluated for colour change by measuring spectral reflectance in the visible region of light (400-700 nm) using a MiniScan instrument (HunterLab, USA). The measurement conditions were following: an illuminant *D*65, 10° complementary observer and measuring geometry *d*/8°.

The colour properties are described in terms of CIE $L^*a^*b^*$ system (1976). The values 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 neutral 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 to the formula: $C = (a^{*2} + b^{*2})^{1/2}$.

The X-ray diffractograms of pigment powders were obtained using a vertical X-ray diffractometer HZG-4B (Freiberger Präzisionsmechanik, Germany) equipped with a 25 cm diameter goniometer. Cu K_α radiation was used, employing a nickel filter for attenuation of the K_β radiation. A proportional detector was used.

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, λ = 633 nm) for the analysis of particle size distribution.

Results and Discussion

The aim of the present work is to investigate the influence of growing yttrium content on the colouring effect of the $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-2/y}$ with y = 0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75 and 0.85.

Based on values a^* and b^* of powder pigments (Table I) it can be seen that increasing Y content increases the colour value a^* (red hue) up to y = 0.55. Higher Y content then makes consequential decrease of this value (Fig. 1). Increasing Y content also increases the colour value b^* (yellow hue). Nevertheless, the highest value is exhibited by the pigment with y = 0.75. The highest Y content (y = 0.85) indicates a slight decrease. Pigments with y = 0.05 to 0.25 produce brown-red colour. Increasing Y content shifts their colour into red-brown (y = 0.35 to 0.65). The sample with y = 0.75 has orange-brown colour which at the highest Y content (y = 0.85) is shifted to brown-yellow. Growing Y content increases brightness at the value L^* and the final colour of pigments becomes gradually lighter (Table I).

After application into the glaze pigments with y = 0.05 obtain intense pink-

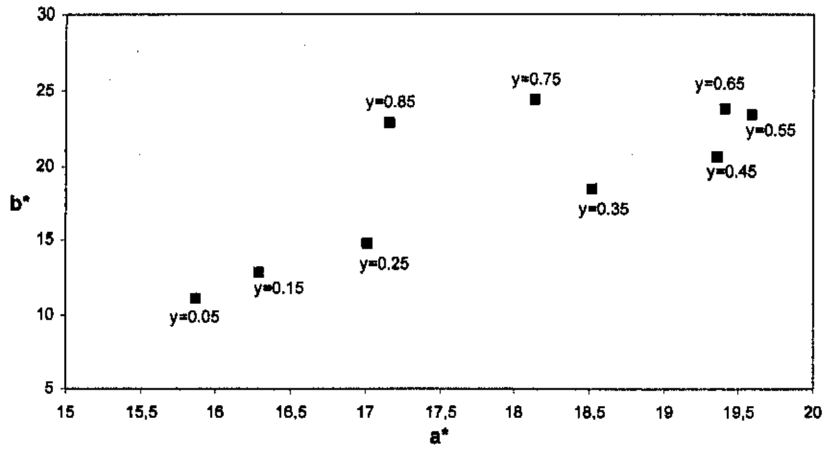

Fig. 1 The effect of Y content on the colour co-ordinates a^* and b^* of $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ pigment powders

Table I The effect of Y content on the colour properties of $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ pigments

Pigment	Powder pigments				Pigments applied into glaze			
y	L^*	a^*	b^*	C	L^*	a^*	b^*	C
0.05	34.02	15.87	11.06	19.34	62.28	19.67	26.28	32.83
0.15	36.58	16.29	12.81	20.72	66.21	19.18	24.71	31.27
0.25	37.54	17.01	14.71	22.48	67.79	17.75	24.09	29.92
0.35	37.58	18.52	18.37	26.09	69.29	15.32	23.68	28.21
0.45	38.53	19.36	20.44	28.15	70.17	13.93	23.96	27.71
0.55	39.45	19.59	23.37	30.49	70.57	13.28	24.53	27.89
0.65	40.84	19.41	23.74	30.66	74.06	13.61	26.01	29.35
0.75	41.32	18.14	24.32	30.34	74.53	14.49	28.98	32.41
0.85	42.17	17.16	22.81	28.54	78.57	9.47	36.83	38.03

orange colour. The same properties are exhibited even by the pigments with y = 0.15 and 0.25. The presence of higher Y content (y = 0.35 to 0.65) decreases of the colour values a^* (Fig. 2). The red hue in pink-orange pigment colour is reduced and it is replaced by orange-yellow. It is seen that the value b^* does not nearly change at y = 0.05 to 0.65 (Table I). Only the higher Y content (y = 0.75) produces an increase in yellow hue and the pigment is shifted to yellow-orange. All the pigments are represented by growth of brightness L^*, consequently glaze applications became lighter. The highest Y content (y = 0.85) gives yellow colour, however, the colour is light (Table I) because of the high brightness of value L^*.

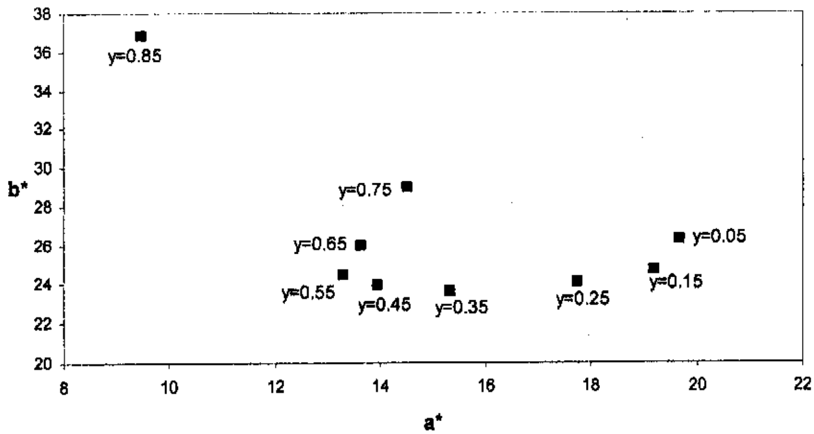

Fig. 2 The effect of Y content on the colour co-ordinates a^* and b^* of $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ pigments applied into glaze

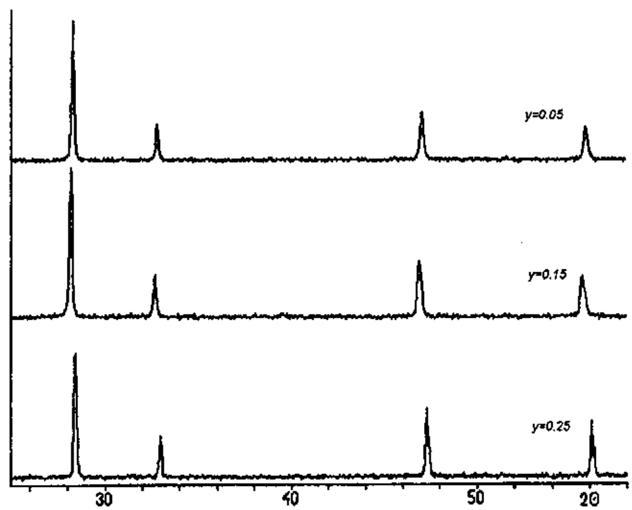

Fig. 3 Powder X-ray diffraction patterns of $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ pigments

The colour difference between glaze application and powder pigments is due to the low pigment concentration (only 10 % by weight) in the glaze. Powder pigments have dark hues of red-brown or orange-brown (the values L^* are from 34 to 42). The low content of pigment in glaze provides light hues of pink-orange or orange-yellow. In the case of glaze application, the value L^* is higher: from 62 to 79 (Table I).

Powder pigment samples $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-2/y}$ with y = 0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75 and 0.85 were studied by X-ray diffraction analysis. Diffractograms of the system samples with y = 0.05 to 0.25 are homogenous, exhibit only diffraction lines that could be assigned to CeO_2 (Fig. 3). Samples with higher Y content are heterogeneous, formed by the solid solution of $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-2/y}$ and also with free Y_2O_3. Tests of samples with higher Y content permitted to determine lattice parameter a of the cubic lattice Y_2O_3 with value 1.059 nm. The value of lattice parameter a = 1.062 nm of starting Y_2O_3 was also determined.

Table II Lattice parameters of CeO_2 and $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ pigments

Formula	a, nm	V, nm^3	$\Delta 2\upsilon$ [a]
CeO_2	0.5422	0.1594	0.002
$Ce_{0.90}Pr_{0.05}Y_{0.05}O_{1.975}$	0.5415	0.1588	0.002
$Ce_{0.90}Pr_{0.05}Y_{0.15}O_{1.925}$	0.5416	0.1589	0.001
$Ce_{0.90}Pr_{0.05}Y_{0.25}O_{1.875}$	0.5417	0.1590	0.002

[a] $\Delta 2\upsilon = N^{-1}(2\upsilon_{exp} - 2\upsilon_{calc})$, where $2\upsilon_{exp}$ is the experimental diffraction angle, $2\upsilon_{calc}$ is the angle calculated from lattice parameters, and N is the number of investigated diffraction lines

Table III Particle sizes of the $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ pigments

y	Particle sizes, μm	
	Particle size range	Mean particle size
0.05	1.5-20.1	7.5
0.15	1.5-20.2	7.6
0.25	1.9-20.5	7.9
0.35	2.2-21.2	8.2
0.45	2.5-22.7	8.3
0.55	2.9-23.2	8.5
0.65	3.4-24.6	9.1
0.75	3.9-25.8	9.4
0.85	3.9-26.2	10.1

The values of the lattice parameters of pigments are given in Table II and show that the lattice parameter a increased with increasing yttrium content. The volume of the elementary cell of CeO_2 also increased with growing Y content. Ce atoms are replaced by Pr atoms in the crystal lattice forming uncharged substitution defects Pr_{Ce}^{x} in the solid solution of $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ pigments. Incorporation of praseodymium and yttrium into the crystal lattice of CeO_2 is connected with deformation of elementary CeO_2 cell in the crystal lattice. The size of Y ions (Y^{3+} = 0.093 nm) is comparable with that of Pr ion (Ce^{4+} = 0.101 nm and Pr^{4+} = 0.092 nm).

The particle sizes and particle size distribution can markedly affect the colour properties of inorganic pigments; therefore, 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 the region from 5 to 15 μm.

The measurement of particle size distribution was carried out with unmilled pigments. The values of pigment particles are in the range from 1.5 μm to 26 μm. The average particle size of the $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ pigments after calcination obtained at 50 % cumulative mass is from 7.5 μm to 10.1 μm (Table III) and is applicable to colouring glazes.

Conclusion

The research regarding $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ with y = 0.05, 0.15, 0.25, 0.35, 0.45, 0.55, 0.65, 0.75 and 0.85 determines an area of solubility of Y_2O_3 and PrO_2 in CeO_2 at temperature 1350 °C forming the solid solution $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ with y = 0.05 to 0.25. This conclusion is proved by the evidence of colour properties of prepared compounds which provide intensive pink-orange colour hues in the area of mutual solubility of all three oxides. However, higher Y content leads to formation of Y_2O_3 (second phase) and the colour of pigments is shifted to yellow-orange (y = 0.35 up to 0.65) or light yellow (y = 0.85).

The $Ce_{0.95-y}Pr_{0.05}Y_yO_{2-y/2}$ pigments with fluorite structure are resistant to heat and chemicals, and can be used even in high temperature glazes for sanitary ceramics. These pigments have very good hiding power and intense colours in glazes.

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