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New green pigments; ZnO–CoO

Petra Šulcová, Miroslav Trojan *

Department of Inorganic Technology, Faculty of Chemical Technology, University of Pardubice, Legions Sq. 565, 532 10 Pardubice
Czech Republic

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Abstract

A zinc oxide pigment with an admixture of cobalt oxide has been prepared as a new green pigment for colouri plastics and paints. The effect of the CoO content in the starting mixture on the colour hue of the pigment has be evaluated and calcination conditions of the pigment synthesis have been established. The optimum conditions for t synthesis of pigments and the properties of the products (colour hue and structure) have been estimated. © 19 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Zinc oxide is the most common and one of the longest known and widely used white inorganic pigments. New compounds are based on the wurtzite structure of zinc oxide with an admixture of cobalt and such compounds have an interesting and intensive colour, and can be used as medium temperature pigments.

Pigments based on zinc oxide in new green hues have been synthesized in our laboratory [1]. A pigment of the ZnO–CoO system was found to give intensive green hues and also had a relatively low cobalt content. This type of pigment was prepared from commercially available zinc white as starting raw material and the pigments are of interest because of their colour hues and their formation which is based on the mutual supressi of the nonstoichiometry of the crystal lattices ZnO and CoO.

2. Experimental

As starting material for the preparation of t $Zn_{1-x}Co_xO$ pigments we used commercial zi white of 'silver seal' type (99.2% ZnO) from t Slovlak Košeca company (Slovakia) and coba hydroxide–carbonate from Lachema Brno (Czec Republic). The starting mixtures containing t required content of CoO admixtures were calcinat in porcelain crucibles in an electric resistance fu nace LM 112.10 (VEB Electrobad Frankenhause Germany) for 2 h. The increase of temperatu was 10°C/min and the pigments were calcinat at 1000°C.

The colour properties of all the pigments prepar and pigments applied in an acrylate copolymer we

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* Corresponding author. Fax: +420-40-6037068; e-mail: miroslav.trojan@upce.cz

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evaluated by using the L^*, a^*, b^* coordinates in the CIE $L^*a^*b^*$ system. The values of these coordinates were obtained with regard to the colour hues of the pigments by measurements of spectral reflectance in the visible region using a MiniScan (HunterLab, USA).

The pigments were also studied by X-ray diffraction analysis. X-ray diffractograms of the samples were obtained using a vertical X-ray diffractometer HZG-4B (Freiberger Präzisionsmechanik, Germany) equipped with a gonlometer of 25 cm diameter in the range of 5 to 90°2ϑ; Cu $K_{\alpha'}$ ($\lambda = 0.154178$ nm) radiation was used for the angular range of $2\lambda < 35°$ and $K_{\alpha'}$ ($\lambda = 0.154051$ nm) for the range of $2\lambda > 35°$, employing a nickel filter for attenuation of the K_β radiation. A proportional detector was used. Powder silicon ($a = 0.543055$ nm) served as an internal standard.

3. Results and discussion

The influence of increasing amounts of cobalt oxide on the colour of the ZnO–CoO pigments was initially studied. The starting mixtures containing an increasing content of cobalt(II) oxide were homogenized by a wet process. The prepared mixtures were calcinated at 1000°C for 2 h. The prepared pigments were applied to acrylate copolymer and the colour hues of the final paints, express by spectral reflectance in the visible region, a shown in Fig. 1.

On the basis of the L^*, a^*, b^* values (Table 1), pigment was chosen having sufficient deep gre colour without any additional grey or black hu This hue deteriorates the colour properties of t pigment, as it causes an undesirable opacity. very good green hue was achieved for the pigme containing 10 mol% CoO, as was observed for t powder pigment ($L^* = 51.26$, $a^* = -16.41$, $b^* = 7.7$ and for the pigment also used in the acrylate cop lymer ($L^* = 37.01$, $a^* = -20.72$, $b^* = 6.11$). A low content of cobalt oxide gives a grey hue to the gre colour of the pigment. A higher content of coba oxide in the mixture results in a shift of colour fro dark green hues to black–green hues (as the cent of the axis cross of the colour coordinates L^*, a^*, is shifted). The effect of the increasing content the starting mixtures on the colour hue of the pigments is demonstrated in Fig. 2.

Pigments of the ZnO–CoO system are cha acterized by an intense green colour, and whi therefore could be possible substitutes for gre pigments based on chromium in the 3+ oxidati state, i.e. chromium oxide and hydrated chromiu oxide with thermal stability up to 160°C.

From the measured L^*, a^*, b^* values of t ZnO–CoO pigments, it follows that the pigme

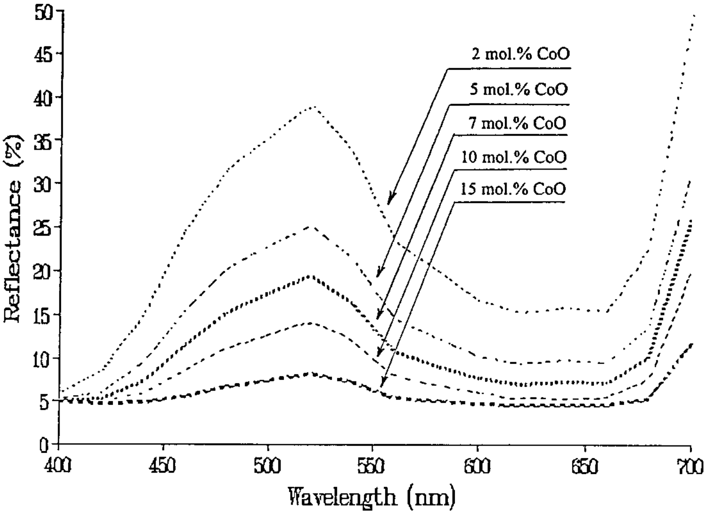

Fig. 1. The effect of increasing content of cobalt oxide on the colour hue of $Zn_{1-x}Co_xO$ pigments.

containing 10 mol% of CoO corresponds to hydrated chromium oxide. This pigment (for which zinc white of 'silver seal' type from Slovlak Košeca company was used, and cobalt hydroxide–carbonate from Lachema Brno as a starting cobalt compoun
has a deep green colour ($L^* = 33.68$, $a^* = -16.0$
$b^* = 5.48$) and is close to 'Chromium-hydrat
green ($L^* = 33.65$, $a^* = -16.02$, $b^* = 4.73$). This w
confirmed by calculation of the total colour d
ference ΔE between these two pigments. The val
ΔE is a measure of the perceptive colour differen
between a sample and a standard. The calculat
value of 0.75 is very low, and virtually imperce
tible. From the colour difference values, this pi
ment, in comparison with the 'Chromium-hydrat

Table 1
The effect of increasing content of cobalt oxide on the colour hue of the Zn$_{-x}$Co$_x$O pigments (L^*, a^*, b^+ coordinates)

x (mol% CoO)	L^*	a^*	b^*
0.5	73.62	−26.36	11.05
1	67.72	−30.86	12.11
2	58.81	−30.03	10.63
3	54.62	−31.38	10.85
4	51.04	−29.22	9.65
5	48.16	−26.62	8.69
6	44.45	−25.88	8.15
7	42.44	−24.72	7.71
8	38.87	−22.28	6.42
9	37.39	−21.47	6.16
10	37.01	−20.72	6.11
11	31.56	−13.52	3.97
12	30.23	−11.27	3.11
13	29.75	−10.58	2.88
15	28.09	−8.93	1.97
20	27.42	−5.24	0.61
25	26.71	−3.12	0.34

Table 2
Lattice parameters of samples of the Zn$_{1-x}$Co$_x$O pigments

x (mol% CoO)	a (nm)	c (nm)	c/a	V (nm
0	0.32495	0.52054	1.6021	0.0475
2	0.32498	0.52056	1.6019	0.0476
5	0.32499	0.52051	1.6016	0.0476
8	0.32503	0.52044	1.6015	0.0476
10	0.32512	0.52041	1.6007	0.0476
12	0.32515	0.52037	1.6004	0.0476
15	0.32521	0.52035	1.6001	0.0476
20	0.32529	0.52031	1.5995	0.0476
25	0.32531	0.52025	1.5993	0.0476

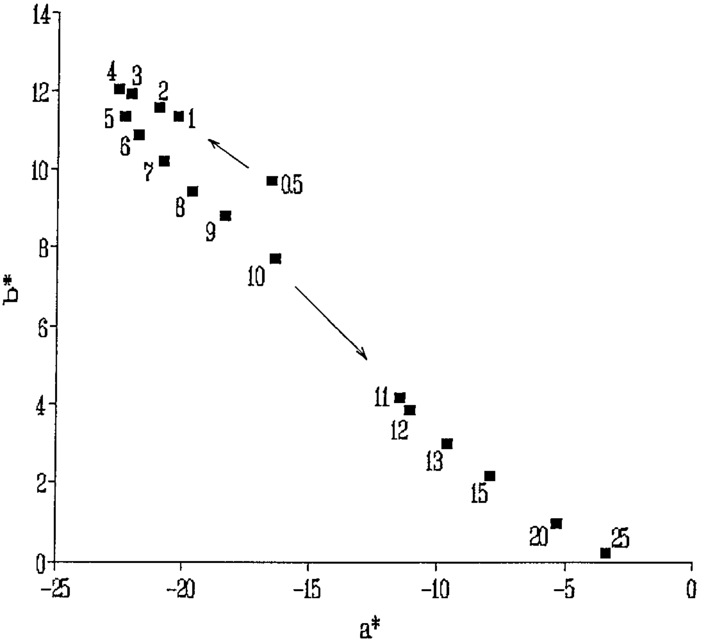

Fig. 2. The effect of increasing content of cobalt oxide (in the direction of the arrow) on the colour hue of Zn$_{1-x}$Co$_x$O pigment usi
a^* b^* coordinates.

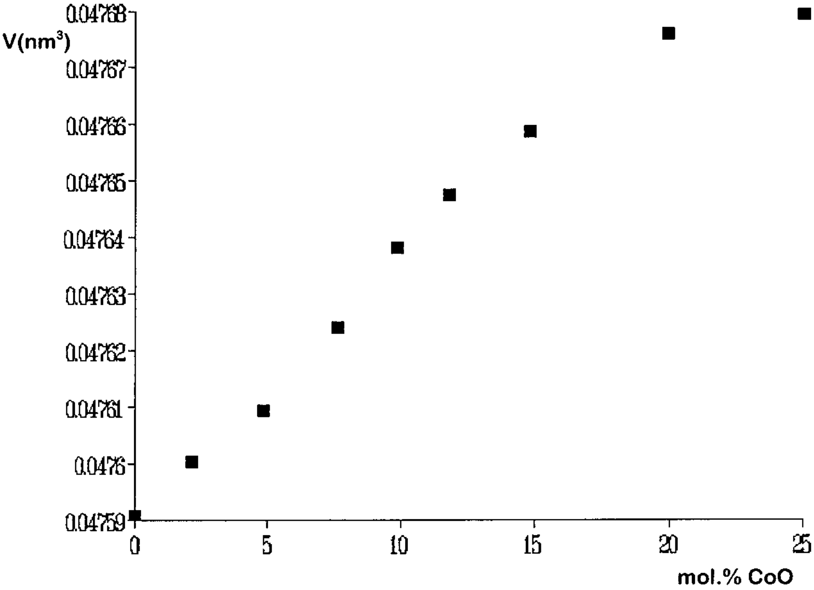

Fig. 3. Relationships between the volume of the elementary cell V and increasing content of cobalt oxide.

green, is brighter ($\Delta L > 0$), greener ($\Delta a^* > 0$) and deeper in colour ($\Delta S > 0$).

Further, pigments of the $Zn_{1-x}Co_xO$ structure were investigated. Samples with an increasing content of cobalt were studied by X-ray diffraction analysis. The observed diffraction lines corresponded to the characteristic lines of the wurtzite structure of ZnO. The sample with the highest CoO content (25 mol%) exhibited two additional peaks, which have been assigned to cobalt oxide. This implies that the sample with 25 mol% CoO heterogeneous and contains doped ZnO with CoO crystallites, probably formed at the interfaces of the ZnO grains. This result is in agreement with published data on the solubility of CoO in ZnO [2]; CoO dissolves in ZnO up to a concentration of 20 mol% forming $Zn_{1-x}Co_xO$ solid solutions. Such a solution is most probably of the substitutional type, where Co^{2+} cations are substituted in the lattice of Zn^{2+}, forming unchanged electrically neutral defects Co_{Zn}^{x}.

The values of the lattice parameters of the ZnO–CoO samples are given in Table 2 and these show that the lattice parameter c decreases with increasing content of cobalt oxide. The observed ratio c/a also decreases. The lattice parameter a and the volume of the elementary cell of zinc oxi (Fig. 3) increase with increasing content of CoO

4. Conclusion

The pigments of the ZnO–CoO system a characterized by an intense green colour. Th type of pigment could potentially be a substitu for the green pigments based on chromium in t 3+ oxidation state, i.e. chromium oxide a hydrated chromium oxide. The colour properti of the ZnO–CoO pigments, their physicochemic properties and application parameters are co parable with chromium (III) green pigments. Th also are of interest due to the low content cobalt. The preparation of this type of pigme was investigated within the framework of t grant project [1] dealing with the new ecological friendly coloured inorganic pigments.

References

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