

## **THERMAL SYNTHESIS OF THE $Zn_{1-x}Co_xO$ PIGMENTS**

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### **Abstract**

In our laboratory, the synthesis of new inorganic pigments is followed by thermal analysis using a derivatograph apparatus. First information about the temperature region of the formation of the pigments investigated is provided by thermal analysis. The attention was directed to the preparation of the pigments based on zinc oxide in new green hues which can be used as medium colour pigments.

**Keywords:** lattice parameters, point defects, solid solutions ZnO–CoO

### **Introduction**

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

The pigments based on zinc oxide in new green hues have been synthesized in our laboratory. The pigments of the ZnO–CoO system give intensive green hues and at the same time being of the low content of cobalt. This type of pigments were prepared from commercially available zinc white as a starting raw material of zinc. These pigments seem to be interesting because of their colour hues and their formation that are based on the mutual suppressing of nonstoichiometry of crystal lattices of ZnO and CoO.

### **Experimental**

As a starting material for the preparation of the  $Zn_{1-x}Co_xO$  pigments we used commercial zinc white of 'silver seal' type (99.2% ZnO) from Slovlak Košeca company (Slovakia) and cobalt hydroxide-carbonate from Lachema Brno (Czech Republic) as a starting cobalt compound.

The starting mixtures containing the required content of admixture CoO were calcinated in porcelain crucibles in an electric resistance furnace LM 112.10 (VEB Electrobad Frankenhausen, Germany) for 2 h. The increase of the temperature was  $10^\circ\text{C min}^{-1}$ . The pigments of the ZnO–CoO type were calcinated at a temperature of  $1000^\circ\text{C}$ .

The temperature region of the formation of these types of pigments was followed by thermal analysis using a Derivatograph-C apparatus (MOM Budapest, Hungary; system of Paulik, Paulik and Erdey) which allows the evaluation of data and simultaneous registration of the thermoanalytical curves TG, DTG and DTA. The starting raw cobalt material and some starting mixtures prepared were studied by thermal analysis in ceramic crucible in the air. The increase of temperature was  $5^{\circ}\text{C min}^{-1}$ . As a heat-resistance standard  $\alpha\text{-Al}_2\text{O}_3$  was used.

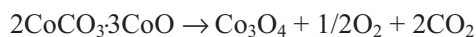
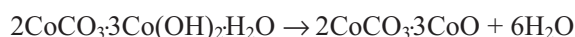
The powder pigments were studied by X-ray diffraction analysis. The X-ray diffractograms of the samples were obtained using a vertical X-ray diffractometer HZG-4B (Freiberger Präzisionsmechanik, Germany) equipped with a goniometer of 25 cm diameter in the range of  $5$  to  $90^{\circ} 2\theta$ . A proportional detector was used. Powder silicon ( $a=0.543055$  nm) served as an internal standard.

## Results and discussion

The influence of the increasing amount of cobalt oxide on colouring of the ZnO–CoO pigments was studied. The starting mixtures containing the increasing content of CoO were homogenized by wet process. The prepared mixtures were calcinated at a temperature of  $1000^{\circ}\text{C}$  for 2 h. The prepared powder pigments were applied to acrylate copolymer. The colour hues of the final paints, which were expressed by spectral reflectance in visible region of light.

On the basis of the  $L^*$ ,  $a^*$ ,  $b^*$  values measured of the colour coordinates of the CIE  $L^*a^*b^*$  system, a pigment having sufficient deep green colour without any additional gray or black hue was chosen. Very good hue of the green colour was achieved for pigment containing 10 mol% CoO [1]. Lower content of cobalt oxide causes gray hue in green colour of the pigment. Higher content of cobalt oxide in the mixture increases shift of colour from dark green hues to black-green hues.

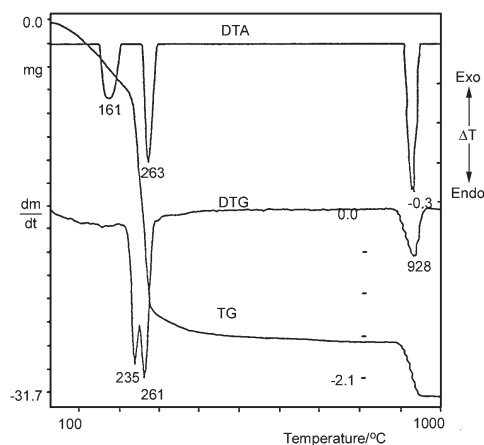
Thermal analysis provided the first information about the temperature region of the formation of this type of pigments. Cobalt hydroxide-carbonate from Lachema Brno as a starting cobalt compound was used for synthesis of the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  pigments. From the thermoanalytical curves TG, DTG and DTA it follows that cobalt hydroxide-carbonate decomposes in several steps. The supposed decomposition of this compound can be represented schematically by the following reactions.



On the base of results of thermal analysis it follows that the loss of the water content of the sample takes place in the temperature interval from  $20$  to  $210^{\circ}\text{C}$  (mass loss 5.98 mg). The TG curve shows (in the temperature interval from  $210$  to  $310^{\circ}\text{C}$ ) the intense decrease of mass (20.67 mg) which attends the formation of the oxide  $\text{Co}_3\text{O}_4$  from  $2\text{CoCO}_3 \cdot 3\text{CoO}$ . The decomposition of  $2\text{CoCO}_3 \cdot 3\text{CoO}$  begins near  $250^{\circ}\text{C}$

where there is a break on the TG curve. The conversion of  $\text{Co}_3\text{O}_4$  into  $\text{CoO}$  begins around 885 and is completed at 950°C. The loss of mass reveals the change into  $\text{CoO}$ .

Figure 1 presents the DTA curve whose first section indicates an endothermic process which represents the loss of water from the starting cobalt hydroxide-carbonate. The second endothermic effect represents the formation of the oxide  $\text{Co}_3\text{O}_4$  from  $2\text{CoCO}_3 \cdot 3\text{CoO}$ . The third endothermic effect on the DTA curve documents the formation of the oxide  $\text{CoO}$  from  $\text{Co}_3\text{O}_4$  by elimination of oxygen. The temperature maximum  $T_{\text{max}}$  of this endothermic effect is 928°C.



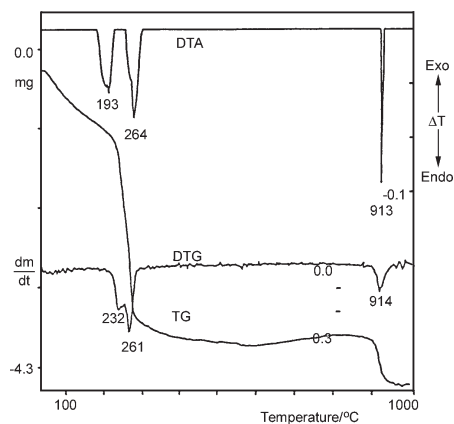
**Fig. 1** Thermoanalytical curves of cobalt hydroxide-carbonate  $2\text{CoCO}_3 \cdot 3\text{CoO}$ , Apparatus Derivatograph-C,  $T$  increase  $5^\circ\text{C min}^{-1}$ , sensitivity TG 100 mg, standard  $\alpha\text{-Al}_2\text{O}_3$  atmosphere air, ceramic crucible

The temperature of 1000°C for the pigment synthesis is also in agreement with the results of thermal analysis of the starting mixture (Fig. 2) for synthesis of the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  pigment. The third endothermic effect (the temperature maximum  $T_{\text{max}}$  is 913°C) on the DTA curve (Fig. 2) represents the formation of  $\text{CoO}$  (the reactive oxide with non-stoichiometric structure) which dissolves in  $\text{ZnO}$  forming  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  solid solutions. The formation of the pigment can be described by the following scheme:



The temperature of 1000°C for the pigment synthesis is also in agreement with the results of thermal analysis of the starting mixture ended at the temperature of about 900°C. The mixture in the crucible had black colour. The pigment calcinated at temperature of 1000°C had intensive green colour. This means that the calcination temperature of 1000°C is sufficient for the preparation of the  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  pigments.

The structure of  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  pigments was also investigated. The samples with the increasing content of cobalt were studied by X-ray diffraction analysis. The observed diffraction lines corresponded to the characteristic lines of wurtzite structure of  $\text{ZnO}$ . The sample with the highest  $\text{CoO}$  content (25 mol%) exhibited two addi-



**Fig. 2** Thermoanalytical curves of the mixture  $Zn_{0.9}Co_{0.1}O$ , Apparatus Derivatograph-C,  $T$  increase  $5^{\circ}C\ min^{-1}$ , sensitivity TG 100 mg, standard  $\alpha-Al_2O_3$  atmosphere air, ceramic crucible

tional peaks which have been assigned to cobalt oxide. It means that the sample with 25 mol% CoO is heterogeneous and contains doped ZnO with CoO crystallites formed probably at the interfaces of the ZnO grains. This result is in agreement with the published data [2] on the solubility of CoO in ZnO. CoO dissolves in ZnO up to the 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 lattice positions of  $Zn^{2+}$  forming uncharged electrically neutral defects  $Co_{Zn}^*$ .

The values of the lattice parameters of the ZnO–CoO samples are given in Table 1 and show that the lattice parameter  $c$  decreases with the increasing content of cobalt oxide. The observed ratio  $c/a$  decreases too. The lattice parameter  $a$  and the volume of the elementary cell of zinc oxide increase with the increasing content of CoO.

**Table 1** Lattice parameters of samples of the  $Zn_{1-x}Co_xO$  pigments

$X/mol\%$ CoO	$a/nm$	$c/nm$	$c/a$	$V/nm^3$
0	0.32495	0.52054	1.6021	0.04759
2	0.32498	0.52056	1.6019	0.04760
5	0.32499	0.52051	1.6016	0.04761
8	0.32503	0.52044	1.6015	0.04762
10	0.32512	0.52041	1.6007	0.04764
12	0.32515	0.52037	1.6004	0.04765
15	0.32521	0.52035	1.6001	0.04766
20	0.32529	0.52031	1.5995	0.04768
25	0.32531	0.52025	1.5993	0.04768

## Conclusions

The pigments of the ZnO–CoO system are characterized by intensive green colour. This type of pigment would be a substitute of the greens based on chromium in the 3+ oxidation state, i.e. chromium oxide and hydrated chromium oxide. The colour properties of the ZnO–CoO pigments, their physicochemical properties and application parameters are comparable with the chromium(III) green pigments. They seem to be interesting also due to the low content of cobalt.

The preparation of this pigment type was investigated within the framework of a grant project dealing with new ecological coloured inorganic pigments [3].

## References

- 1 P. Šulcová and M. Trojan, *Dyes and Pigments*, 40 (1998) 83.
- 2 C. H. Bates, W. B. White and R. Roy, *J. Inorg. Nucl. Chem.*, 28 (1966) 397.
- 3 Grant No. 104/98/P227. Grant Agency of Czech Republic.