

STUDIES ON OBTAINING OF ZINC PHOSPHATE NANOMATERIALS

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Abstract. Among the phosphate pigments, zinc phosphate found the widest application in paints, since it provides excellent corrosion resistance and is non-toxic. The two methods of preparation of zinc phosphate with the average crystallite size of 30-40 nm have been developed. Nanocrystalline zinc phosphate tetrahydrate was formed in the three-stage process: the synthesis of $Zn_3(PO_4)_2 \cdot 4H_2O$ from diammonium phosphate and zinc nitrate, low-temperature calcination of precipitated phosphate, and the hydration of the intermediate. Whereas the anhydrous zinc phosphate was obtained in the two-stage process of calcination (initially at low temperature, subsequently at higher temperature) of the gel formed as a result of treatment of aqueous solution containing $Zn(NO_3)_2$, $(NH_4)_2HPO_4$, and citric acid.

1. INTRODUCTION

The primary objective of the application of paint and coating products is an effective protection of the metallic surfaces against an aggressive influence of the environment. The paints are mixtures composed of binder, pigment, solvent, and additives. Until recently, the most frequently used pigments, possessing very good anticorrosive properties, included red lead and zinc chromate. However, both pigments belong to very hazardous and highly toxic substances. With regard to the ecological reasons, these pigments are withdrawn from the paint composition and they are replaced by the environmental friendly pigments. Such pigments include, among others, the phosphates, among which the zinc phosphate found the widest application. This compound is non-toxic, it possesses excellent anticorrosive properties and can be used

in numerous binders. Zinc phosphate is produced on a commercial scale either from zinc oxide and phosphoric acid or zinc salt and phosphates. The anticorrosive properties of zinc phosphate depends, in a large degree, on the distribution of the particle size. Hence, it is aimed to obtain the pigments with the appropriate size already in the technological process or they are subjected to micronization. It would be the most advantageous to prepare the single particle with the size which does not exceed 100 nm, that is being characteristic for the nanoparticles [1].

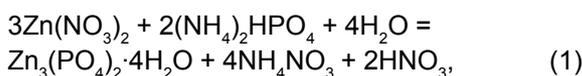
Several methods of zinc phosphate synthesis on the base of different raw materials have been developed. However, the products obtained within this approach can hardly be classified as nanomaterials [2-5].

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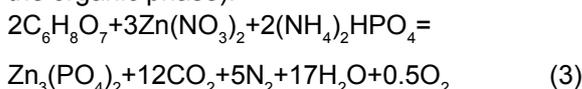
The objective of these studies was to elaborate a new method of preparation of zinc phosphate with the crystallite size as small as possible with the utilization of the inorganic compounds as the precursors.

2. EXPERIMENTAL

The reagents of analytical grades were used in these studies. Zinc phosphate was prepared as a result of the reaction of zinc nitrate with diammonium phosphate in an aqueous solution without or in the presence of the complexing agent (citric acid). In the first case, the process was conducted in three stages: precipitation of $Zn_3(PO_4)_2 \cdot 4H_2O$ (hopeite) at temperature from 273 to 363K, low temperature calcination (473-523K) to $Zn_3(PO_4)_2$ for a time of 1-2 h, and a repeated hydration to hopeite (temperature 293K, 0.5h, the liquid phase to the solid phase ratio of 4:1):



Whereas in the second case, the reaction mixture containing zinc nitrate, diammonium phosphate, and citric acid was concentrated to achieve a thick foam, that was subjected to a two stage thermal treatment. The concentration was carried out in an ultrathermostate (MLW, type U15^c) at temperatures of 348-353K for about 3 h. The first stage of calcination proceeded at temperature 453K for 5–120 min (spontaneous ignition and swelling of the material), and the second one at temperatures of 873-1023K for a time of 30-120 min (oxidation of the organic phase):



The calcination was carried out in a muffle furnace (LINN HIGH THERM GMBH of type LM 412.24 with a electronically programmed controller SE 40LI). The obtained products were examined by X-ray diffraction analysis. The studies were performed on a X'Pert PRO (Philips) diffractometer using the X-ray tube with a cobalt anode. The phase composition and the average of crystallite size of obtained compounds were determined. The changes of crystallites average size were determined using Scherrer's equation [6]. The average size of crystallites was calculated from the (460) reflection of $Zn_3(PO_4)_2 \cdot 4H_2O$ (JCPDS 33-1474) and the (611) reflection of $Zn_3(PO_4)_2$ (JCPDS 29-1390). The width of the peak at half maximum value was

calculated taking into account the so-called apparatus broadening. This parameter was determined on the basis of the sample of coarse crystalline silicon.

3. RESULTS AND DISCUSSION

Several experiments were performed during the studies on the preparation of nanocrystalline zinc phosphate tetrahydrate (method I), in which the following parameters were changed: the molar ratio of $Zn:PO_4^{3-}$ (in the range of 1.2-1.5:1), the concentrations of the reagents in used solutions (15-50 wt.% of $Zn(NO_3)_2$, 7-50 wt.% of $(NH_4)_2HPO_4$). Depending on the assumed process parameters, the following compounds were identified in the reaction products: $Zn_3(PO_4)_2 \cdot 4H_2O$, $Zn_3(PO_4)_2 \cdot 2H_2O$ or $Zn_3(PO_4)_2 \cdot 2H_2O$, and a small amount of $Zn_3(PO_4)_2 \cdot 4H_2O$. As a result of dehydration of these products $Zn_3(PO_4)_2$ or a mixture of $Zn_3(PO_4)_2$ and $Zn_3(PO_4)_2 \cdot 2H_2O$ was obtained. A repeated hydration of mentioned phosphates leads to the preparation of pure hopeite or a mixture of hopeite and $Zn_3(PO_4)_2$.

It was found that zinc phosphate tetrahydrate with the average crystallite size of about 180 nm can be obtained as a results of a rapid mixing of a 20 wt.% solution of zinc nitrate with 40 wt.% solution of diammonium phosphate at temperature of 346K. The diffraction pattern of this product was presented in Fig. 1. When the calcination of precipitated phosphate was performed at temperature of 524K for 1h, an anhydrous zinc phosphate was obtained, from which, after the hydration, zinc phosphate tetrahydrate was again obtained (Fig. 1). The average crystallite size of the final product amounted to about 30 nm and it was six times smaller than $Zn_3(PO_4)_2 \cdot 4H_2O$ obtained after the first stage of process. This effect was achieved as a result of double recrystallization of the phosphates crystallizing in the various crystallographic systems with a different size of the unit cell. $Zn_3(PO_4)_2 \cdot 4H_2O$ crystallizes in the orthorhombic system, whereas $Zn_3(PO_4)_2$ in the monoclinic system. The volume of the unit cell of these compounds amounts, respectively 0.978 nm³ and 0.668 nm³.

In the second series of experiments, the method of zinc phosphate preparation was changed. The process was carried out in the presence of citric acid complexing the zinc ions in the reaction of precipitation of zinc phosphate and causing the formation of gel during a stage of the concentration of post-reactive mixture. The final stage of the process was a high-temperature crystallization of zinc phosphate.

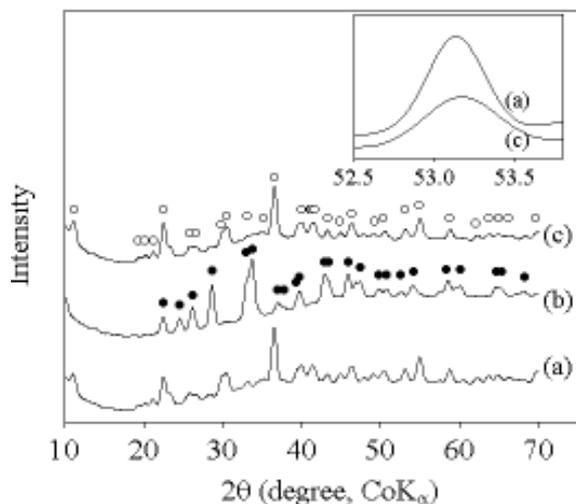


Fig. 1. The diffraction pattern of products: (a) – $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ obtained as a result of the reaction of zinc nitrate with diammonium phosphate; (b) – $\text{Zn}_3(\text{PO}_4)_2$ after the calcination process and (c) – $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ after hydration. o – $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, • – $\text{Zn}_3(\text{PO}_4)_2$.

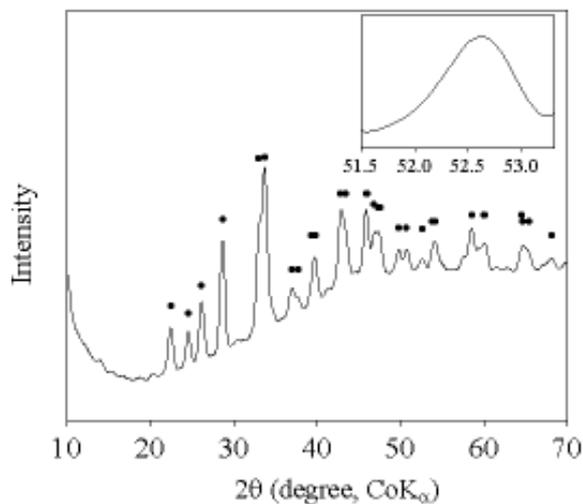


Fig. 2. The diffraction pattern of zinc phosphate. • – $\text{Zn}_3(\text{PO}_4)_2$.

In the subsequent studies, the following parameters were changed: the molar ratio of the reagents ($\text{Zn}(\text{NO}_3)_2 : (\text{NH}_4)_2\text{HPO}_4 : \text{C}_6\text{H}_8\text{O}_7 = (1.5-1.8):1:(0.8-2.3)$), calcination time, and temperature of the second stage of calcination. A solid citric acid was added to a solution of zinc nitrate (39-82 wt.%) and subsequently a solid diammonium phosphate or its solution (30-57 wt.%).

As a result of performed experiments, a pure zinc phosphate or this compound with a small fraction of zinc pyrophosphate was obtained depending on the process parameters. The average size of $\text{Zn}_3(\text{PO}_4)_2$ crystallites was varied and amounted to 43-130 nm.

On the basis of performed studies it was found, that at the appropriate molar ratio of reagents and the salt concentration in the reaction mixture, the calcination of intermediate, initially at temperature 453K for 5 min, and subsequently at 973K for 60 min, a pure zinc phosphate with the average crystallite size of about 43 nm can be obtained. The diffraction pattern of this product was presented in Fig. 2.

2. CONCLUSIONS

It was found that a nanocrystalline zinc phosphate tetrahydrate (about 30 nm) can be obtained in the

following processes: the synthesis of $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ from diammonium phosphate and zinc nitrate, a low-temperature calcination of precipitated phosphate and the hydration of intermediate. Whereas an anhydrous zinc phosphate with the average crystallite size of about 40 nm can be obtained in the process of a two-stage calcination (initially at a low temperature, and subsequently at a higher temperature) of the gel obtained as a result of the treatment of aqueous solution containing $\text{Zn}(\text{NO}_3)_2$, $(\text{NH}_4)_2\text{HPO}_4$ and citric acid.

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