



Studies on preparation of phosphate pigments for application in composite protective coatings



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ABSTRACT

Currently, the most popular methods of protection against corrosion is the application of protective coatings containing the anticorrosive pigments, such as zinc phosphate. However, with regard to the ecological reasons, this compound has been withdrawn, and new environmentally friendly compounds are being searched. The objective of studies was to obtain zinc-free phosphate pigments containing strontium, calcium and aluminum. The chemical composition, the physicochemical and anticorrosive properties of obtained materials were determined. The oil absorption number of prepared pigments was in the range of 43–88 g of oil/100 g of the product. The average particle size was 270–400 nm. The specific surface area of obtained materials was low (2–76 m²/g). The majority of these products exhibited good anticorrosive properties for steel during an electrochemical noise tests.

1. Introduction

At the present time, corrosion is one of the biggest problems of global economy. In many cases, instead of preventing this phenomenon, only its consequences are still being removed, and that makes the annual budget losses bigger and bigger in many countries. According to the latest available data (March 2016) published in the NACE International report, the estimated total costs of corrosion could reach as high as \$2.5 trillion, which is equivalent to 3.4% of the global Gross Domestic Product (GDP) in 2013 and 3.2% of the global GDP in 2017 [1]. However, the current state of the art technique can save from 15% to even 35% of these costs i.e. \$375 and \$875 billion annually [2,3].

The protection of materials against corrosion is a complex issue, which is still under investigation and the techniques related to anti-corrosion practices are constantly being improved. Taking into account the fact that corrosion is a naturally occurring phenomenon and cannot be totally eliminated, the anti-corrosion protection relies on a maximum limitation of the effects of the destruction of a material as a result of corrosion. The risk of corrosion can be reduced at the stage of design and construction of installations by applying selected materials, which are more intrinsically resistant to corrosion. Unfortunately, sometimes it is impossible since the most frequently used metals in the constructions such as iron, aluminum, zinc or magnesium are vulnerable to the destruction caused by corrosion. The other materials (e.g. plastics or

ceramics) can be damaged by corrosion as well [4]. Nevertheless, the corrosion rate can be slow down by using the organic protective coatings containing anticorrosive pigments. These coatings act as a barrier, which separates the covered material from an aggressive environment. The addition of anticorrosive pigments has a positive impact on enhancement of the corrosion inhibition process of the applied coating [5]. Anticorrosive pigments used so far contained barium chromate, zinc chromate, strontium chromate and lead mostly used in powdered form and also mixed oxides of lead [6]. They are currently being replaced by less harmful compounds, most often inorganic having the crystalline structure [7,8]. One of the most popular and the oldest pigments regarded to be more environmentally friendly than those previously reported is zinc phosphate, the toxicity of which is several times lower than that of chromates [9–11]. Data from 2008 show that the annual production of zinc pigments in the European Union is 22,000 tones [12]. However, according to the European regulation CLP [13] Zn₃(PO₄)₂ has been classified as hazardous and designated by the symbol H400 (Very toxic to aquatic life), and H411 (Very toxic to aquatic life with long lasting effects). This has led to increased interest in pigments with reduced zinc content or completely free of zinc. More recently, there have been several studies aiming to develop novel anticorrosive pigments, which would be at least as effective as zinc chromate or zinc phosphate and at the same time, pose no threat to the environment or human health. Therefore, researchers have begun to

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replace totally or partially the zinc ions by other ions, e.g. magnesium, calcium, strontium, aluminum, and even sodium, and to incorporate into the system other compounds such as borates, molybdates, phosphomolybdates, triphosphates or pyrophosphates [9,14–23].

The aim of this study was to obtain modified phosphate pigments containing strontium, calcium and aluminum and determination of their physicochemical properties, i.e. chemical and phase composition, oil absorption number, specific surface area, average particle size, and the usefulness for preparation of anticorrosion coatings.

2. Experimental

2.1. Materials and preparation

Reagent grade substrates such as: 85 wt.% H_3PO_4 (POCh, Basic, Gliwice, Poland), $SrCO_3$ (AKTYN, Suchy Las, Poland), $CaCO_3$ (EURO-CHEM BGD Sp. z.o.o., Tarnów, Poland), freshly precipitated $Al(OH)_3$, and an aqueous NaOH solution (CHEMPUR, Piekary Śląskie, Poland) were utilized for the preparation of modified phosphates. In order to obtain a fresh aluminum hydroxide, an aqueous solution of KOH was gradually added to an aqueous solution of $Al(NO_3)_3$, until the pH value of the reaction mixture was 7. The obtained precipitate was separated from the mother liquor, triple-washed with distilled water and dried for 3 h at 105 °C (378,15 K).

Synthesis was carried out in an unpressurized reactor at an ambient temperature. The solid reactants were added into an aqueous solution of phosphate acid at constant stirring velocity and the pH of the reaction mixture was adjusted to 6 by using the aqueous NaOH solution. The process was continued for 30 min. For all experiments the salt concentration in a suspension was 40 wt.%. After each reaction the obtained precipitate was separated from the mother liquor using a vacuum filter, followed by triple washing with distilled water (weight ratio of liquid phase to solid phase was 3:1). Finally, the obtained product was dried for 3 h at 70 °C (343.15 K).

The preparation processes of strontium and calcium phosphates as well as strontium and aluminum phosphates were performed varying the molar ratios of $Ca^{2+}/Al^{3+}:Sr^{2+}:PO_4^{3-}$, which amounted to 0:1:1, 0.25:0.75:1, 0.5:0.5:1, 0.75:0.25:1, and 1:0:1 in the consecutive experiments.

A compilation of the process parameters for all the experiments was presented in Table 1.

The presence of foreign ions in the filtrates is not recommended due to difficulty with its further utilisation. That is why the insoluble carbonates ($SrCO_3$ and $CaCO_3$) were used in phosphate synthesis, instead of the soluble salts (e.g. chlorides, nitrates). Moreover, studies have shown that the presence of unreacted carbonates in the obtained materials improves their anticorrosive properties.

Table 1
Process parameters of the experiments.

Experiment number (Phosphate acronym ^a)		Molar ratio in substrates				pH	Process temperature (K)	Process time(min)			
		Ca^{2+}	:	Al^{3+}	:				Sr^{2+}	:	PO_4^{3-}
1	SP	0.00	:	0.00	:	1.00	:	1.00	6	293	30
2	SCP1	0.25	:	0.00	:	0.75	:	1.00			
3	SCP2	0.50	:	0.00	:	0.50	:	1.00			
4	SCP3	0.75	:	0.00	:	0.25	:	1.00			
5	CP	1.00	:	0.00	:	0.00	:	1.00			
6	SAP1	0.00	:	0.25	:	0.75	:	1.00			
7	SAP2	0.00	:	0.50	:	0.50	:	1.00			
8	SAP3	0.00	:	0.75	:	0.25	:	1.00			
9	AP	0.00	:	1.00	:	0.00	:	1.00			

^a SP – strontium hydrophosphate; SCP – calcium and strontium phosphates; CP – calcium phosphates; SAP – aluminum and strontium phosphates; AP – aluminum phosphate.

2.2. Sample characterization

The phase composition of the prepared samples was studied with X-ray diffraction ($CuK\alpha$ radiation, Empyrean PANalytical) [24]. Identification of the crystalline phases was accomplished using HighScore+ software and the ICDD PDF-4+ 2015 database. The content of aluminum, calcium, strontium and sodium was determined by ICP-AES technique (Optima 5300 DV, Perkin-Elmer). The phosphates content was determined spectrophotometrically (Spekol 11, Carl Zeiss Jena) [25]. The oil absorption number (amount of oil needed for complete wetting of tested substance in powder form) was determined according to PN-EN ISO 787-5 standard [26]. The specific surface area (S_{BET}) was calculated from the BET equation based on the results of nitrogen adsorption and desorption process performed at 77 K (Quadrachrome SI Quantachrome Instrument). The average particle size of obtained materials was measured by using the laser scanning microscope (VK-9700, Keyence, USA).

Anticorrosive properties of obtained phosphates were investigated by an electrochemical noise method [27]. For this purpose, two identical samples of the low-carbon non-alloy steel (CRS SAE 1008/1010, Q-Lab, Germany) were placed in a glass cell containing a suspension of a tested pigment (0.1 wt.%) in a solution of NaCl (3.5 wt.%) in distilled water. A saturated calomel electrode was used as a reference electrode. The whole system was aerated during the test. The fluctuation of the corrosive current density between working electrodes was monitored for 24 h (12 partial measurements every 2 h) using the FAS2 femtostat and EN120 software (Gamry, USA). For the analysis of the results, the corrosive current density values after 6 h and 24 h of the test as well as the average value of all 12 partial measurements were selected. In addition, the density value of the charge exchanged between the electrodes during the entire test was calculated using the Echem Analyst software (Gamry).

3. Result and discussion

The X-ray powder diffraction patterns of materials are shown in Figs. 1–3.

The X-ray powder diffraction pattern of material SP corresponds to the presence of two crystalline phases: unreacted $SrCO_3$ (ICDD: 00-001-0556) and synthesized $SrHPO_4$ (ICDD: 00-012-0359). In the case of CP experiment, the compounds contained in the obtained material include unreacted $CaCO_3$ (ICDD: 01-086-2340) and also calcium monohydrogen phosphates: $CaHPO_4$ (ICDD: 00-001-0653) and $CaHPO_4 \cdot 2H_2O$ (ICDD: 00-009-0077). In comparison to the product from SP experiment, the amount of unreacted carbonate in that experiment was lower, although the molar ratio of $Ca^{2+}/Sr^{2+}:PO_4^{3-}$ was 1:1 in the both experiments. No crystalline phase was detected in the AP material. Nevertheless, on the basis of the chemical composition is assumed that $AlPO_4$ is present in the amorphous phase. In the diffraction pattern there is one wide reflection with its maximum at the scattering angle 2 θ

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