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TESTING OF CORROSIVE-INHIBITIVE PROPERTIES OF ZINC ORTHOPHOSPHATE DOPED WITH LANTHANUM ORTHOPHOSPHATE

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This paper deals with the study of corrosion-inhibition properties of commercially used pigment $Zn_3(PO_4)_2$ *after the modification with lanthanum orthophosphate in various molar ratios. The system* $Zn_3(PO_4)_2/LaPO_4$ *was prepared in one step synthesis by crystallization method. Individual pigments were examined in the synthetic-based paint and water-based paint. The samples were exposed to influences in the condensation chamber, atmosphere of 100 % humidity and to the content of 0.2 a 1* dm^3 SO_2*. The prepared pigments were evaluated from the viewpoint of the degree of rusting, the blistering, degree of cracking, corrosion in the surroundings of cut and corrosion in the surface. The evaluation, which took place in the comparison with commercially available samples and laboratory prepared* $Zn_3(PO_4)_2$*, show very good efficiency for the protection of metallic materials.*

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Introduction

The laws and regulations in the ecological and toxicological area insit on replacement of known inorganic pigments, which often contain toxic elements, by pigments more friendly for environment or by less toxic compounds. The discovery and development of the new and improved inorganic pigments are desired [1].

The protection of metallic materials can be successful thanks to, e.g., increasing purity of metals, alloying of metals, metallization of materials, covering of materials with paints and inhibitors of corrosion. Zinc orthophosphate belongs to the inhibitors of corrosion [2].

Zinc orthophosphate was used for substitution of zinc by chromium. This change had lower efficiency. Next it was used with different compounds, unfortunately with the opposite results. Its efficiency in the accelerated tests is not as good as in long-term tests (outdoor exposing). Probably, it can not be only changed zinc for chromium. This was the reason for many tests with aim to modify zinc orthophosphate. Zinc orthophosphate showed good results in the industrial environment [3].

Lanthanide orthophosphates occurr in nature in the form of mineral monazit and xenotime, which secondarily occur in magmatits, granites or Alpine veins. Big deposits of these ores are found in Scandinavia, USA, China and Vietnam [4]. Synthetic lanthanide of orthophosphates can be prepared as hydrate $LnPO_4.nH_2O$, the so-called rhabdophan types, or as waterless salt $LnPO_4$, the so-called monazit type. The monazit type changes crystalline structure from hexagonal to monoclinic, the so-called xenotime type, at higher temperatures [5-7]. This group of compounds has high thermal and chemical resistance and belongs among high-temperature pigments. Unfortunately, they have not high-quality colour tones. These compounds are most frequently used in the ceramic industry as additives still.

Many authors have dealt with the preparation of the modified phosphates. The anticorrosive behaviour was examined in zinc molybdate, zinc calcium molybdate, zinc phosphomolybdate and zinc calcium phosphomolybdate [8,9]. Also studied were the properties of zinc aluminium polyphosphate representing the modification of zinc phosphate pigment [10]. The polyaniline phosphate pigments were synthesized by reaction in aqueous solution of ammonium peroxodisalfate and phosphoric acid [11]. The modification of this pigment was dioctyl phosphate doped with polyaniline [12]. The synergic effect of polyaniline and anticorrosive pigment was tested in epoxy coatings. This effect was tested in $Zn_3(PO_4)_2.2H_2O$ [13].

Experimental

The working procedure of mixing of these orthophosphates was suggested on the basis of gained theoretical and practical knowledge about zinc orthophosphates and lanthanide orthophosphates. The results of preceding research show corrosion-inhibition efficiency of lanthanide orthophosphates. This fact leads to the idea of possible synergic effect of classical anticorrosive pigment doped by this compound [14].

The purpose of this work was to synthesize and to verify corrosion-inhibition properties of system $Zn_3(PO_4)_2.nH_2O/LaPO_4.nH_2O$ in molar ratios 1.2:1; 2:1; 4.5:1 a 12:1. The method of crystallisation from phosphoric acid was used for the synthesis. The starting compounds were zinc carbonate (Lachema Brno, CZ), lanthanide oxide (Bochemie Bohumín, CZ) and phosphoric acid (85%, Lachema Brno, CZ). For comparison of results the sample of classical zinc phosphate $Zn_3(PO_4)_2.4H_2O$ was prepared by the same method. The synthesis was based on the mixing of lanthanide oxide and zinc carbonate with distilled water for the crystallisation process (100 cm^3 of 0.04 M of suspension). Then phosphoric acid in 50 % volume surplus against stoichiometric volume was added to the suspension by intensive mixing at room temperature. The volume of phosphoric acid was increased by a half volume, because it was proved that stoichiometric volume of acid did not lead to the formation of required compounds. The mixture was left overnight or for a longer period of time and then transferred to a flask equipped with reflux condenser, heated, and kept boiling for 2 hours with continuous stirring. The obtained solid was filtered off, washed with distilled water until a neutral pH was obtained, and dried at the temperature of 85 °C [14,15].

The industrially produced and often used pigments ZP-BS-M, Silcal “A” and ZP 10 was chosen for comparison of corrosion-inhibition properties. The pigment ZP-BS-M and Silcal “A” was used for application to the synthetic-based paints and ZP 10 to the water-based paints. The ZP-BS-M is dihydrate of zinc phosphate with the content of free zinc oxide (S.N.C.Z., France). The ZP 10 is zinc phosphate — a mixture of dihydrate and tetrahydrate (Heubach, Germany). The pigment Silcal “A” is a mixture of hydrates of zinc phosphates and the pigment based on calcium silicate (AV Eco-Color, CZ).

The prepared pigments were milled in the mill Pulverissette 5 (Fritsch, SRN). The medium value of particle size was lower than 10 μm, which is sufficient for application to the chosen types of paints. The measurement took place in the water suspension, and the size was evaluated by laser diffraction using Frauenhofer aproximation (Mastersizer MU, Malvern, GB). The prepared pigments were studied by X-ray diffraction. The X-ray diffraction patterns were obtained (D8 Advance, Bruker AXS, UK) by using monochromated CuK_α radiation and a scintillation detector.

The prepared pigments were applied in water-based and synthetic-based paints. The formulas for the preparation of paints were provided by the company

Barvy a Laky Teluria, s.r.o. Primer paint with the trade name Pragoprimer was chosen as the synthetic paint (SP). This paint is used first of all as the primer paint on steel for inside and outside environment. Pragoprimer is a dispersion of inorganic pigments and additives in solution of modified resin and organic solvents with addition of siccative. As the water-based paint (WP) was chosen “Bakrylex primer antikor”, which is used also as primer paint on metallic constructions. It is a mixture of watered down alkyd resin with special additives.

The paints with the content of prepared pigments and comparative standards were applied on a steel plate (steel category 11 370). The steel plates were exposed to the action of 100 % relative humidity in the apparatus Hygrotherm 519 (Erichsen, SRN) according to the valid ČSN norm [16]. The period of testing in the condensation chamber was 80 days. Another set of the steel plates was exposed to the action of 100 % relative humidity and with atmosphere of 0.2 dm^3 SO_2 in the same apparatus according to the valid ČSN norm [17] for a period of 30 days. The last test was performed on the steel plates, which were exposed to the action of 100 % relative humidity and with atmosphere of 1 dm^3 SO_2 in the same apparatus according to the valid ČSN norm [17]. The period of testing in the chamber with the content of 1 dm^3 SO_2 was 10 days.

Results and discussion

The prepared pigments were verified by X-ray diffraction. On the basis of this analysis it was stated that the prepared pigments correspond with zinc orthophosphate doped by lanthanum phosphate in the defined ratio. In Fig. 1, the example of the sample $Zn_3(PO_4)_2/LaPO_4$ (1.2:1) is presented.

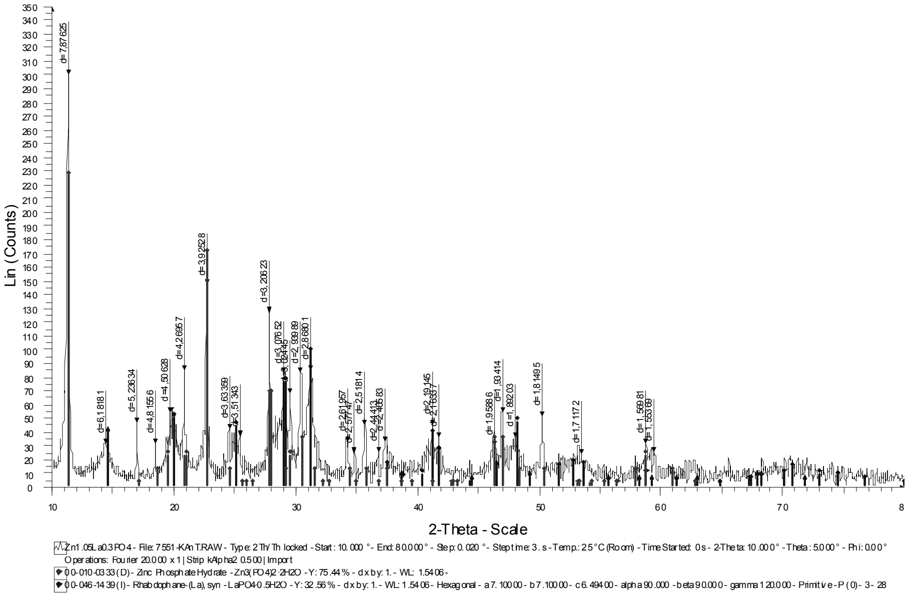

Fig. 1 Diffractogram of $Zn_3(PO_4)_2/LaPO_4$ sample (1.2 : 1)

Table I Evaluation of degradation of coat of paint in condensation chamber

		Blistering	Rusting	Cracking	Corrosion in surrounding of cut	Corrosion in surface	Average thickness of coating, µm ng, µm	Standard deviation of thickness, µm
SP	Silcal “A”	0	10 % Ri 2 (S4)	5 % 3 (S4) c 95 % 0	3	30 %	144	38
	ZP-BS-M	0	Ri 0	0	1	10 %	146	32
	$Zn_3(PO_4)_2$	0	Ri 0	0	2	20 %	132	22
	$Zn_3(PO_4)_2/LaPO_4$ (12 : 1)	0	50 % Ri 5 (S5) 50 % Ri 3 (S4)	40 % 5 (S4) c 60 % 0	4	40 %	99	17
	$Zn_3(PO_4)_2/LaPO_4$ (4.5 : 1)	0	20 % Ri 3 (S4) 80 % Ri 0	20 % 5 (S5) c 80 % 0	2	20 %	120	28
	$Zn_3(PO_4)_2/LaPO_4$ (2 : 1)	0	5 % Ri 1 (S4) 95 % Ri 0	5 % 1 (S4) c 95 % 0	2	40 %	117	32
	$Zn_3(PO_4)_2/LaPO_4$ (1.2 : 1)	0	50 % Ri 5 (S5) 50 % Ri 2 (S4)	70 % 5 (S5) c 30 % 0	1	10 %	105	24
WP	ZP 10	0	Ri 0	0	2	40 %	161	38
	$Zn_3(PO_4)_2$	0	Ri 0	0	0	0 %	200	32
	$Zn_3(PO_4)_2/LaPO_4$ (12 : 1)	0	Ri 0	0	0	0 %	193	36
	$Zn_3(PO_4)_2/LaPO_4$ (4.5 : 1)	0	Ri 0	0	1	0 %	190	26
	$Zn_3(PO_4)_2/LaPO_4$ (2 : 1)	0	Ri 0	0	0	0 %	196	29
	$Zn_3(PO_4)_2/LaPO_4$ (1.2 : 1)	0	Ri 0	0	0	0 %	186	28

The pigments were applied to paints, and with the help of an application rule with the aperture of 100 µm the coatings were prepared on the steel plates. The sides and back parts of the steel plates were treated with a commercial anticorrosive paint. The comparative commercial standards were applied according to their determination in the original formulas, i.e., the samples of Silcal “A” and ZP-BS-M were applied to the synthetic-based paint and the sample ZP 10 to the water-based paint.

The prepared pigments were evaluated, apart from degree of rusting, also from the viewpoint of the blistering, degree of cracking, corrosion in the surround-

Table II Evaluation of degradation of coat of paint in chamber with 100 % humidity and with atmosphere of 0.2 dm^3 SO_2

		Blistering	Rusting	Cracking	Corrosion in surrounding of cut	Corrosion in surface	Average thickness of coating, µm	Standard deviation of thickness, µm
SP	Silcal “A”	30 % 4(S2)	20 % Ri 1 (S3) 80 % Ri 0	0	5	95 %	90	29
	ZP-BS-M	0	30 % Ri 1 (S3) 70 % Ri 0	0	2	85 %	109	28
	$Zn_3(PO_4)_2$	0	Ri 0	0	1	50 %	128	28
	$Zn_3(PO_4)_2/LaPO_4$ (12 : 1)	10 % 4(S2)	10 % Ri 1 (S3) 90 % Ri 0	0	1	60 %	136	30
	$Zn_3(PO_4)_2/LaPO_4$ (4.5 : 1)	30 % 4(S2)	40 % Ri 2 (S3) 60 % Ri 0	85 % 5 (S3) b 15 % 0	5	95 %	100	22
	$Zn_3(PO_4)_2/LaPO_4$ (2 : 1)	0	10 % Ri 1 (S4) 90 % Ri 0	10 % 3 (S4) b 90 % 0	4	95 %	166	26
	$Zn_3(PO_4)_2/LaPO_4$ (1.2 : 1)	20 % 4(S3)	Ri 0	0	3	85 %	134	22
WP	ZP 10	0	Ri 0	0	0	0 %	118	26
	$Zn_3(PO_4)_2$	0	Ri 0	0	0	0 %	169	42
	$Zn_3(PO_4)_2/LaPO_4$ (12 : 1)	0	Ri 0	0	0	0 %	168	40
	$Zn_3(PO_4)_2/LaPO_4$ (4.5 : 1)	0	Ri 0	0	0	0 %	139	22
	$Zn_3(PO_4)_2/LaPO_4$ (2 : 1)	0	Ri 0	0	0	0 %	160	13
	$Zn_3(PO_4)_2/LaPO_4$ (1.2 : 1)	0	Ri 0	0	0	0 %	138	30

ing of cut and corrosion in the surface according to the standard ČSN EN ISO 4628 [18].

This practical test provided information about efficiency of inhibitor corro-

Table III Evaluation of degradation of coat of paint in chamber with 100 % humidity and with atmosphere of 1.0 dm^3 SO$_2$

		Blistering	Rusting	Cracking	Corrosion in surrounding of cut	Corrosion in surface	Average thickness of coating, µm ng, µm	Standard deviation of thickness, µm
SP	Silcal “A”	5 % 2(S5)	0	0	1	20 %	186	22
	ZP-BS-M	5 % 2(S4)	0	0	0	10 %	187	36
	$Zn_3(PO_4)_2$	5 % 3(S5)	0	0	1	20 %	181	36
	$Zn_3(PO_4)_2/LaPO_4$ (12 : 1)	70 % 5(S5)	5 % Ri 2 (S3) 95 % Ri 0	0	1	50 %	146	22
	$Zn_3(PO_4)_2/LaPO_4$ (4.5 : 1)	5 % 4(S5)	5 % Ri 1 (S3) 95 % Ri 0	0	3	50 %	148	26
	$Zn_3(PO_4)_2/LaPO_4$ (2 : 1)	10 % 4(S5)	5 % Ri 1 (S3) 95 % Ri 0	0	2	30 %	158	39
	$Zn_3(PO_4)_2/LaPO_4$ (1.2 : 1)	20 % 4(S4)	0	0	1	40 %	134	21
WP	ZP 10	10 % 5(S5)	Ri 0	0	0	0 %	138	26
	$Zn_3(PO_4)_2$	0	Ri 0	0	3	40 %	191	23
	$Zn_3(PO_4)_2/LaPO_4$ (12 : 1)	30 % 3(S3)	Ri 0	0	3	50 %	136	25
	$Zn_3(PO_4)_2/LaPO_4$ (4.5 : 1)	0	Ri 0	0	3	40 %	188	56
	$Zn_3(PO_4)_2/LaPO_4$ (2 : 1)	0	Ri 0	0	0	5 %	136	40
	$Zn_3(PO_4)_2/LaPO_4$ (1.2 : 1)	5 % 2(S5)	Ri 0	0	3	60 %	117	28

sion (prepared pigment). At the same time the action of prepared samples was compared with corresponding commercial standards.

Rusting

The water-based paints showed the best results. The standard pigments and newly prepared pigments did not show any defects from the viewpoint of rusting after the exposition in corrosive apparatus with 100 % humidity (Table I). The standard ZP-BS-M and laboratory produced zinc phosphate showed the best resistance of the pigment applied to synthetic-based paint. Very low degree of rusting was reached by using $Zn_3(PO_4)_2/LaPO_4$ (2:1) in the paint. The worst result was achieved with pigment $Zn_3(PO_4)_2/LaPO_4$ (12:1). It is necessary to note, that although the production of coat paints was the same in all the cases, the thickness of coatings of prepared samples of synthetic-based paint was lower than in standards. The thickness of coatings of water-based paints was similar in all the coatings.

The paints with apllied pigments were exposed to the atmosphere of 100 % humidity and to the content of 0.2 dm^3 SO_2 (Table II) and they were evaluated in the same way. The rusting did not appear in any paint of water-based system. The synthetic-based paint containing our prepared pigments $Zn_3(PO_4)_2$ and $Zn_3(PO_4)_2/LaPO_4$ (1.2:1) did not show any rusting either. The paints with the content of compounds $Zn_3(PO_4)_2/LaPO_4$ (4.5:1) and $Zn_3(PO_4)_2/LaPO_4$ (2:1) showed relatively the worst results.

The prepared pigments and standards resisted very well the influence of high concentration of sulphur dioxide for 10 days. The rusting did not show in pigments applied to water-based paints. The defects in synthetic-based paints appeared in two cases, but only little (Table III).

Blistering

The steel plates treated with the coatings (synthetic- or water-based paint) did not show the blistering in condensation chamber. The blistering was observed in the samples exposed to the action of the atmosphere of 100 % humidity and the content of 0.2 dm^3 SO_2. The worst hit surface was shown in the standard Silcal “A”, which was about 30 %. All prepared pigments, except for the sample $Zn_3(PO_4)_2/LaPO_4$ (2:1), in the synthetic-based paint exposed to low concentration of SO_2 showed from 10 % to 30 % similar type of blisters. The sample $Zn_3(PO_4)_2/LaPO_4$ (2:1) did not show any blisters. The samples of water-based paints by action of low concentration of SO_2 did not show any blistering

All prepared pigments and standards showed blisters in synthetic-based paint, which were exposed to atmosphere of 100 % humidity and the content of 1 dm^3 SO_2. The best results were in the standards. The worst blistering was in the sample $Zn_3(PO_4)_2/LaPO_4$ (12:1). The blistering was in all samples including standards similar to this case. Other situation was in the samples of the water-based paints. The worst blistering was shown in standard ZP 10. The blistering was found also in the pigments with the lowest and the highest content of La in water-based paint. The other samples did not show any blisters.

Degree of Cracking

The cracks and the wrinkling damage appeared in all samples of synthetic-based paint except for standard ZP-BS-M and zinc orthophosphate prepared in our laboratory and exposed to the environment in the condensation chamber. Very low damage showed standard Silcal "A" and the sample $Zn_3(PO_4)_2/LaPO_4$ (2:1). The worst result was in the sample $Zn_3(PO_4)_2/LaPO_4$ (1.2:1), which hit about 70 %.

The cracks were shown in samples $Zn_3(PO_4)_2/LaPO_4$ (4.5:1) and $Zn_3(PO_4)_2/LaPO_4$ (2:1) after the action of the atmosphere with low concentration of SO_2. The degree of cracking was large in the sample $Zn_3(PO_4)_2/LaPO_4$ (4.5:1). All changes were found only in synthetic-based paints. The samples in synthetic-based paint and water-based paint, which were exposed to atmosphere of 100 % humidity and the content of 1 dm^3 SO_2, did not show cracking.

Corrosion in Surrounding of Cut

This type of corrosion appeared in all standards and samples of the synthetic-based paint. The worst result was in the sample $Zn_3(PO_4)_2/LaPO_4$ (12:1). Quite bad result was also in the standard Silcal "A". The least corrosion in the cut was found in the standard ZP-BS-M and in the sample $Zn_3(PO_4)_2/LaPO_4$ (1.2:1). Two steel plates were damaged by corrosion in the surrounding of cut, namely standard ZP 10 and the sample of $Zn_3(PO_4)_2/LaPO_4$ (4.5:1) applied to the water-based paint exposed in the condensation chamber.

The low concentration of SO_2 caused corrosion in the cut only in synthetic-based paints. Particularly the standard Silcal "A" and the sample $Zn_3(PO_4)_2/LaPO_4$ (4.5:1) showed the worst results. On the other hand, the sample $Zn_3(PO_4)_2/LaPO_4$ (12:1) and zinc orthophosphate prepared in our laboratory showed the best results.

The corrosion appeared in all tested compounds in the synthetic-based paint, except the standard ZP-BS-M exposed to higher concentration of SO_2. The sample $Zn_3(PO_4)_2/LaPO_4$ (4.5:1) showed the worst damage of the steel plate. The standard ZP 10 and sample $Zn_3(PO_4)_2/LaPO_4$ (2:1) in water-based paints did not show defects. All remaining samples showed very similar corrosion in the cut.

Conclusion

We prepared pigments on the basis of zinc phosphate doped with lanthanide orthophosphate in molar ratios $Zn_3(PO_4)_2$:$LaPO_4$ 1.2:1; 2:1; 4.5:1 a 12:1. The method of crystallization from phosphoric acid in water medium was chosen for the preparation of the pigments. The pigments were verified by X-ray diffraction. This analysis confirmed the defined ratios of $Zn_3(PO_4)_2.nH_2O$: $LaPO_4.nH_2O$.

We performed corrosion-inhibition tests of the pigments in the condensation chamber for a period of 80 days, in the condensation chamber with the content of 0.2 dm^3 SO_2 for a period of 30 days and in the condensation chamber with the content of 1 dm^3 SO_2 for a period of 10 days. The degree of rusting through the coat, blistering of the coat, degree of cracking after taking from the chambers. The results showed good corrosion-inhibitive properties of the pigments. The prepared pigments are fully compatible with water-based paints. Primarily the standard Silcal “A” does not resist to any parameters (cracking, blistering) action of humidity and to the atmosphere of sulphur dioxide so well as the newly prepared pigments. The dependence of corrosive-inhibitive properties on the quantity of lanthanide orthophosphate in the sample was not proved.

The light stability was next measured property. The marked change of the colour was in the samples $Zn_{1.44}La_{0.04}PO_4$ and $Zn_{1.35}La_{0.1}PO_4$. These two samples are not suitable for white paints.

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