Efficiency of Anticorrosive Pigments Based on Modified Phosphates

Petr Kalenda[a*], *Andrea Kalendová*[a], *Petr Mošner*[b], *Michal Poledno*[a]

University of Pardubice, Faculty of Chemical Technology, [a] Institute of Polymeric Materials, [b] Department of General Inorganic Chemistry, nám. Cs. Legií 565, 532 10 Pardubice, Czech Republic

Summary: The paper deals with the study of modified phosphate compounds from their anticorrosion action point of view. The pigments start with zinc orthophosphate, the modification of which can give phosphosilicates, phosphomolybdates, or basic phosphates. In the region of cations the combination of zinc with calcium, strontium, barium, or aluminum are possible. The modified anticorrosive pigments differ in water solubility, inhibition efficiency of the aqueous extracts and anticorrosion actions in organic coatings. The various types of modified phosphates were studied. The effect of organic inhibitor in presence of anticorrosive inorganic pigments in coatings was determined.

Introduction

Zinc orthophosphate is presently the most widely used anticorrosive pigment for coatings determined to protecting steel to corrosion. Broadening this pigment in the region of organic coatings was strengthened by the ecological opinion regarding chromate and lead(II) anticorrosive pigments.[1] Zinc orthophosphate is, however, not a universal anticorrosive pigment and requires definite conditions.[2] The binder should contain carboxyl groups for securing the reaction between the pigment and the polymer chain, a result being the formation of an inhibition complex.[3] It is also important that zinc orthophosphate contains a definit amount of crystal water. Efforts to increase the anticorrosion efficiency of zinc orthophosphate lead to modifying this pigment by means of cations and also in the anionic part.[4] The modification can be applied also for adapting the pH value to an alkaline region.[5] Zinc orthophosphate in an untreated form exhibits a mild acidic nature in aqueous extracts.

The modified form is represented by double orthophosphates, in which one of the cations is represented by zinc.[6,7] This concerns primarily the Zn-Al, Zn-Ca, but also Zn-K, Zn-Fe, Zn-Ca-Sr or Ba-Ca and Sr-Ca combinations. In the anion part it is possible to combine the phosphate anion with further anticorrosively efficient anions,

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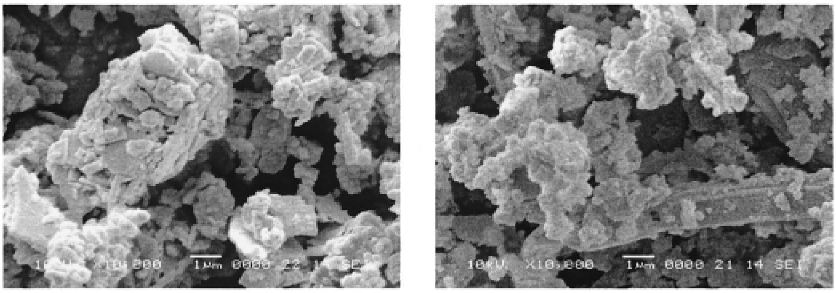
such as silicate, molybdate, or borate.[8,9] The modified phosphate pigments (as in the region of cations, so as in that of anions) can be modified by organic corrosion inhibitors in interest of increasing the anticorrosion efficiency.[10] The modified phosphate pigments can be exemplified by the following compounds: aluminum(III) zinc(II) phosphate, basic zinc phosphate, zinc phosphomolybdate, zinc calcium phosphomolybdate, zinc borophosphate. On combining the phosphate anion with silicates the combinations of cations giving the following pigments are used: zinc strontium phosphosilicate, calcium barium phosphosilicate, calcium strontium zinc phosphosilicate.[11]

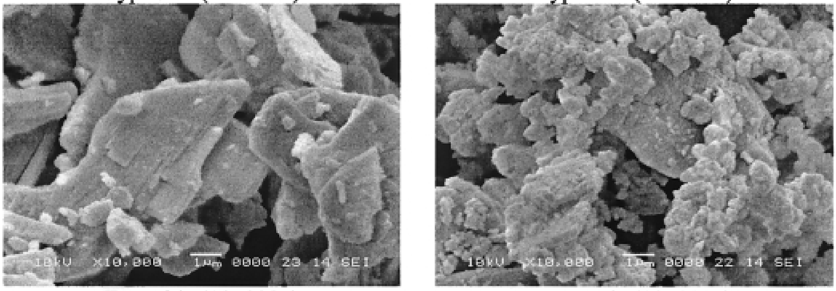
As an organic inhibitor for modifying and increasing the anticorrosion efficiency of the pigment the following compounds can be used: zinc 5-nitroisophthalate, calcium 5-nitroisophthalate, calcium cyanurate, metal salts of dinonylnaphthalene sulfonic acids.[12]

Experimental part

Table 1 and Figure 1 give some characteristic properties and morphology of pigment particles tested.



Type A/2 (10. 000x) Type A/6 (10. 000x)



Type C/2 (10. 000x) Type B/1 (10. 000x)

Figure 1. Morphology of pigment particles tested (SEM, *Jeol 5600 LV*).

Table 1. Characterization of anticorrosive pigments tested.

Type	Chemical composition %	Loss on ignition[a] %	Oil absorp.[b] g	Density g/cm^3	Water abs. g	CPVC[c] %
	Phosphosilicate anticorrosive pigments					
A/1	ZnO 55%,SiO_2 24%, P_2O_5 21%	0.05	40.4	3.5	41.1	39.7
A/2	ZnO 35.5%,SiO_2 7.3%, PO_4 24.2%, $BaSO_4$ 29%, MgO 4%	0.09	30.1	3.3	34.3	48.4
A/3	SiO_2 39.7%, PO_4 8.8%, SrO 12.5%, CaO 39%	0.17	43.8	2.9	34.4	42.3
A4	SiO_2 41.1%, P_2O_5 7.1%, BaO 14.4%, CaO37.4%	0.14	36.5	3.0	41.0	46.2
A/5	SiO_2 45.7%, PO_4 5.4%, K_2O 2.6%, CaO 19.4%, Al_2O_3 11.9%, BaO 5.4%, Na_2O 3.9%, Sb_2O_3 2.4%, ZnO 1.4%, org. 1,9%	0.08	37.6	2.8	35.5	47.4
A/6	ZnO 42%, SrO 7%, P_2O_5 19%, CaO 16.5%, SiO_2 15.5%	0.11	39.1	3.1	43.0	43.4
	Anticorrosive phosphomolybdate pigments					
B/1	ZnO 55.8%, MoO_3 1.7%, PO_4 42.5%	0.16	24.2	3.5	30.3	52.3
	Anticorrosive phosphate pigments					
C/1	ZnO 40%,Al_2O_3 4.5%, PO_4 55.5%.	0.10	46.4	2.8	48.5	41.7
C/2	ZnO 52.5%,PO_4 47.5%	0.30	27.6	3.2	35.6	51.3

[a] Detertmination of loss on ignition at 200°C

[b] Determination of oil absorption for pigments (DIN ISO 787/2)

[c] critical pigment volume concentration calculated by linseed oil consumption

Preparation of coatings

The coatings were prepared by dispersing anticorrosive pigments in a styrene-acrylate binder. All the pigmented systems were formulated to a pigment volume concentration (PVC) value = 10 vol. %. The test coatings were prepared on standard steel panels. The coating film thicknesses fluctuated in a range of 75 - 80 μm in a dry paint film. The coatings were conditioned at standard conditions for 30 days.

Laboratory tests

The mass steel losses in aqueous pigment extracts

The steel panels were exposed to aqueous extracts prepared in 10% anticorrosive phosphate pigments in water. Following a 800 h exposure the panels were freed of the corrosion products (using etching solution) and gravimetrically the mass loss (K), the corrosion velocity (v_k), and the corrosion loss (X) calculated to blank experiment (corrosion in pure water) were determined as follows:

$$K = \frac{(m_1 - m_2).10000}{S} \quad [g.m^{-2}] \qquad (1)$$

$$v_k = \frac{K}{t_1} \quad [g.m^{-2}.d] \qquad (2)$$

$$X = \frac{K}{K_{H_2O}}\,.\,100 \quad [\%] \qquad (3)$$

m_1	mass of steel panel prior to exposure [g]
m_2	mass of steel panel after the exposure [g]
S	surface area of steel panel [m^2]
t_1	time of exposure [d]

Corrosion tests

Determination of the corrosion resistance in a condensation chamber

The test was performed according to ISO 6988 in a medium of 100% relative humidity and a temperature of 35°C. The coatings were exposed for 500, 1000, and 2100 h.

Determination of the corrosion resistance in a neutral salt fog

The testing principle consists in exposing the coatings to a fog of neutral 5% aqueous sodium chloride (NaCl) solution at a temperature of 35°C. The test starts with ISO 9227. The samples were exposed for 100 and 200 h.

Prohesion test

The method is a modification of salt-chamber test using the aqueous solution spray of 0.35% $(NH_4)_2SO_4$ and 0.05% NaCl. The samples were exposed also for 100 and 200 h.

Evaluation of the results

The overall evaluation of the anticorrosion protection of coatings was performed according to the already described method.[13] The result is expressed as a numerical value giving all the followed corrosion manifestations. The relation for the complete degree of corrosion (anticorrosion protection) after the salt chamber test (4) and to the condensation chamber test (5):

$$Overall\ rating = \frac{[Rating\ 1] + [Rating\ 2] + 2\ x\,[Rating\ 3]}{4} \quad (4)$$

$$Overall\ rating = \frac{[Rating\ 1] + 2\ x\,[Rating\ 3]}{3} \quad (5)$$

[Rating 1]	evaluation of the blistering degree with the coatings acording to ASTM D 714/87
[Rating 2]	evaluation of the failure in a cut with the coatings according to ASTM D 1654/92
[Rating 3]	evaluation of the corrosion degree with a steel substrate according to ASTM D 610/85

Results and discussion

Table 2. The properties of phosphate anticorrosive pigments.

Type	pH[a]	Conductivity µS/cm	Water-soluble matter[b] %		K_m g/m^2	v_k g/(m^2.h)	X %
			at 20 °C	at 100 °C			
A/1	8.40	774	1.51	1.82	54.78	1.52	79.60
A/2	7.08	337	0.24	0.31	6.10	0.17	8.86
A/3	9.10	240	0.30	0.53	50.77	1.41	73.77
A/4	8.93	190	0.19	0.55	82.95	2.30	120.54
A/5	8.18	2270	2.51	2.41	3.44	0.10	4.99
A/6	7.19	97	0.10	0.16	49.77	1.38	72.33
B/1	6.89	154	0.14	0.16	65.09	1.81	94.59
C/1	6.28	75	0.08	0.11	55.89	1.64	89.63
C/2	6.44	94	0.06	0.06	54.96	1.49	79.87
Water	-	-	-	-	62.35	1.83	100.00

[a] Determination of the pH value of water extracts for pigments (DIN ISO 787/9)

[b] Determination of water soluble matter for pigments (CSN EN ISO 787/3, CSN EN ISO 787/9)

Table 2 shows that the anticorrosive pigments based on phosphosilicates (types A) have an alkaline extract at a pH value in a range of 7-9. Phosphomolybdate and phosphate pigments exhibit slightly acidic extracts with pH values of 6-7. The results show that at the corrosion steel losses in aqueous pigment extracts, the anticorrosion properties are positively affected by the organic inhibitors. The A/1 type pigment (zinc phosphosilicate) in comparison with an identical pigment A/2 (zinc phosphosilicate + organic inhibitor) differ in the velocity of steel corrosion running in aqueous extracts of these pigments. The A/1 type exhibits a corrosion velocity of 1.52 g/(m^2.h) compared to the A/2 type with a value of 0.17 g/(m^2.h). The inhibition efficiency of zinc phosphosilicate containing an organic inhibitor is thus by10 times higher than with zinc phosphosilicate alone.

The A/4 type pigment (barium-calcium phosphosilicate) and an A/5 type pigment (barium-calcium phosposilicate + organic inhibitor) exhibit similar differences. The organic corrosion inhibitor increases the conductivity of extract from a value of 190 μS/cm up to a value of 2270 μS/cm. Water-soluble compounds in both the pigments A/4 = 0.1% and A/5 = 2.51% give also a testimony of such a system, in which the organic inhibitor considerably increases the anticorrosion efficiency in an aqueous extract, but in the coating film the formation of osmotic blisters or an increase of film permeability to water and water vapor can take place. Comparing the anticorrosive pigments without any content of organic inhibitor (types: A/1, A/3, A/4, A/6, B/1, C/1, C/2) from the corrosion inhibition in an aqueous extract point of view shows clearly a comparatively nonexpressed anticorrosion effect. It is thus evident that the synergic effect accompanying the action of cations takes place. The anions in the followed anticorrosive pigments affect the inhibition properties of extracts in such a way that they create a series starting with the most efficient ones: phosphosilicates > phosphates > phosphomolybdates.

The results obtained after the exposure of coatings to a condensation chamber medium of 100% relative humidity do not give too expressive differences after 500 h between the anticorrosive pigments tested. 1000 h and 2100 h exposures to these conditions allow already to take conclusions from the state of coatings and steel corrosion under the coatings. If we consider the overall anticorrosion coating efficiencies in dependence on the solubilities of anticorrosive pigments in or the conductivities of the extracts thereof we find a striking agreement (Tab. 3).

The anticorrosively most efficient pigments comprise zinc-aluminum phosphate, zinc orthophosphate, calcium-strontium-zinc phosphosilicate, and zinc phosphomolybdate. It is surprising that always the compounds are concerned, which contain zinc as a cation. The effect of anion on the anticorrosion properties is of low demonstration ability.

Table 3. Order of anticorrosive pigment efficencies in a condensation chamber after 2100 h of exposure.

Pigment type	C/1	C/2	A/6	B/1	A/4	A/3	A/2	A/1	A/5
Overall anticorrosion efficiency	97	83	82	70	68	57	65	65	63
Conductivity of water extract μS/cm	75	94	97	154	190	240	337	774	2270

The contrary to following the corrosion inhibition in aqueous extracts whereat the better soluble pigments manifest themselves. A high pigment solubility or the content of water soluble compounds in the pigment lead to the increase in water penetration, when the pigments are used in coatings. In the most simple case the blisters and subsequently the corrosion of substrate metal appear just in the blister places. Having this in mind the pigments containing organic inhibitors do not manifest themselves in the test of exposure to a condensation chamber medium. These pigments are characterized by a higher water solubility.

In studying the inhibition effects of anticorrosive pigments it was necessary to derive a model which allows application in more porous binder matrix and which can demonstrate its inhibition properties. Owing to these reasons the coatings were subjected at first to 200 hour ultravioleght (UV) radiation of xenone arc. This exposure disturbs the coating surface, and at the same time, the hardening of binder takes place. The coating samples were after the irradiation transferred to a condensation chamber, salt spray chamber, and exposed for 500, 1000, and 2100 h. These modified test results give an image of that how a reaction of steel with pigment extract appears. The coatings are more permeable for water, and the amounts of water and water vapor having passed through the coating film are higher than at the preceding test in a condensation chamber. This corrosion test with a UV radiation also better reproduces the real atmospheric conditions which the coatings meet in practice.

Fig. 2 gives the results of corrosion tests performed with the coatings containing the pigments studied. A similar trend was observed in both test types without exposure to UV radiation and also after this exposure.

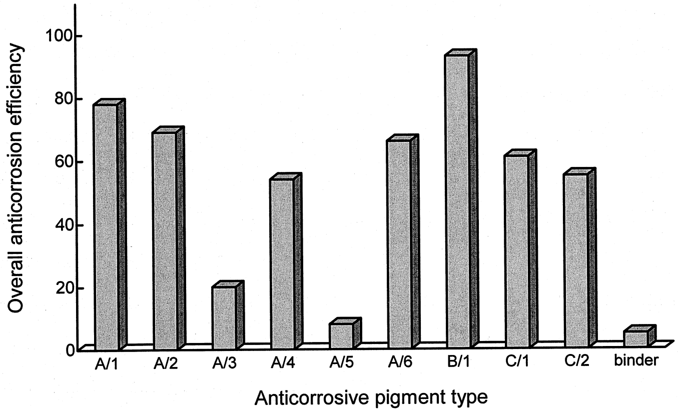


Figure 2. Overall anticorrosion coating efficiency in dependence on the type of anticorrosive pigment after a two-stage corrosion exposure for 200h to UV radiation and a subsequent 200h exposure to a salt chamber medium with the expression of blistering degrees.

The evaluation of anticorrosion efficiencies of the studied pigments was executed on the basis of all performed corrosion tests. Tab. 4 brings for every corrosion test the order of pigments in a series from the most efficient one to the pigments of low efficiency. The addition of anticorrosion efficiency values (in every test the max. value equals 100) for all five performed accelerated corrosion tests a value of ≤ 500 was obtained.

Table 4. The order of anticorrosive pigment efficiencies for all the corrosion tests performed.

	Corrosion test	Pigment type / order of efficiency								
n_1	Condensation chamber 2100 h	C/1	C/2	A/6	B/1	A/4	A/3	A/2	A/1	A/5
n_2	200 h UV + condensation chamber 2100 h	A/6	A/4	B/1	A/2	A/5	A/1	C/2	A/3	C/1
n_3	Salt chamber 200 h	A/6	B/1	A/1	A/2	C/1	A/3	A/5	A/4	C/2
n_4	200 h UV + salt chamber 200 h	B/1	A/1	A/2	A/6	C/1	C/2	A/4	A/3	A/5
n_5	200 h UV + Prohesion test 200 h	A/1	B/1	A/4	A/2	C/2	C/1	A/5	A/3	A/6

Example of evaluation: Pigment A/1 has in the test n_1 the anticorrosion efficiency of or the test $n_2 = 43$, $n_3 = 81$, $n_4 = 78$, $n_5 = 83$.

$$\text{Anticorrosion efficiency} = \sum_{i=5} n_i = 350$$

The value 350 expresses the anticorrosion efficiency of pigment A/1 for all the performed corrosion tests. Table 5 reports the summary results for each anticorrosive pigment from the anticorrosion efficiency point of view in all the corrosion tests.

Table 5. Resulting anticorrosion efficiency values for the tested pigments.

Anticorrosive pigment type	A/1	A/2	A/3	A/4	A/5	A/6	B/1	C/1	C/2
Anticorrosion efficiency $\sum_{i=5} n_i$	350	338	198	313	214	349	389	261	263

Conclusion

In the conclusion we can say that the pigments based on modified phosphates are effective corrosion inhibitors in the coatings.

The results obtained allow to conclude:

- From the studied anticorrosive pigments the most effective one is zinc phosphomolybdate.
- Highly efficient pigments comprise also phosphosilicates containing zinc cation either alone or in combination with further elements such as strontium and calcium in their molecules.
- Zinc orthophosphate in comparison with modified phosphates exhibits only average anticorrosion properties.
- The combination of zinc and aluminum in orthophosphate brings no improvement of the anticorrosion properties.
- Phosphosilicates which do not contain zinc (barium-calcium and strontium-calcium phosphosilicates) are characterized by inferior anticorrosion properties to zinc orthophosphate.
- The effect of organic inhibitor in modified phosphate anticorrosive pigments is not too significant.

The order of anticorrosive pigments by the dropping efficiency was established:

Basic hydrated zinc phosphomolybdate
Zinc phosphosilicate
Calcium-strontium-zinc phosphosilicate
Zinc phosphosilicate + organic inhibitor
Barium-calcium phosphosilicate
Zinc orthophosphate
Zinc-aluminum phosphate
Barium-calcium phosphosilicate + organic inhibitor
Strontium-calcium phosposilicate

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