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Anticorrosion properties of SrO–ZnO–B_2O_3–P_2O_5 pigments

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Abstract

Seven compositions of anticorrosion pigments of zinc–strontium borophosphates were prepared and then characterized by X-ray diffraction analysis, solubility measurements, particle size distribution, and the pH of their aqueous extracts. The pigments were dispersed in an alkyd resin formulation, and used in paints. Following application of the paints to steel sheets, they were subjected to standard anticorrosion tests, to assess their anticorrosive–inhibitory properties. Test results showed that 14.6SrO–43.7ZnO–8.3B_2O_3–33.3P_2O_5 and 37.5SrO–37.5ZnO–25B_2O_3 compositions surpassed the anticorrosive properties of standard pigments based on zinc orthophosphate and calcium metaborate.

Keywords: Pigments; Phosphate; Borate; Borophosphate; Anticorrosive paints; Corrosion tests

1. Introduction

Anticorrosive protection of metals cannot always be achieved by judicious materials selection, due to high materials costs. An alternative approach involves the use of a protection coating containing inorganic anticorrosion pigments. In this regard, recent ecological and toxicological measures have led to the search for potential replacements for lead- and chromium-containing pigments. Among the candidate pigments tested were metal cyanamides and phosphides [1], zinc, calcium and magnesium ferrites [2], zinc powder or zinc oxide [3,4], and molybdate pigments [5]. Barrier-type pigments, such as iron mica and wollastonite [6], and the compounds with ion-exchanging ability [7,8] were also investigated.

Prospective anticorrosive properties were also found among pigments containing phosphates and borates [9]. The first useful pigment in this group of compounds was zinc phosphate $Zn_3(PO_4)_2{\cdot}2H_2O$ [10]. Further studies led to phosphate pigments [11,12] such as $CaZn_2(PO_4)_2{\cdot}2H_2O$, $AlH_2P_3O_{10}{\cdot}2H_2O$, and phosphates containing Ba^{2+}, Ca^{2+}, Mg^{2+} ions. Other modifications of phosphate pigments involved combinations with various anions [13–15], or multiphase phosphate pigments based on the synergistic effects of phosphate pigments and organic corrosion inhibitors.

The anticorrosive properties of phosphate pigments are ascribed to their strong complexing behavior. Phosphates can form complexes with metal cations and functional groups of organic resins. The complex-forming ability is much higher for phosphates with a linear structure than for those with a cyclic structure. Chemical bonds between metal cations and phosphates with a cyclic

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structure are significantly weaker, due to steric interactions between functional groups in small size rings. Complex forming ability increases with increasing phosphate ring size. The anticorrosive properties of phosphates are also affected by their hydrolytic behavior. Generally, linear condensed phosphates undergo hydrolysis more easily than their cyclic counterparts.

Borate anticorrosion pigments possess a relatively high solubility in water and, therefore, exhibit inhibitory behavior, especially in the first stage of corrosion. These properties contrast those of phosphate pigments, which exhibit a slower interaction with water. The anticorrosion behavior of metal borates arises from their basicity, as they are able to maintain the high pH needed to protect pigment coatings. However, anticorrosion paints containing phosphates or borates are less effective than those containing lead and chromium compounds.

The goal of this work was to combine the effects of borate and phosphate groups, in order to take advantage of the good properties of both residues, and to help compensate for their negative properties.

2. Experimental

Anticorrosion $SrO–ZnO–B_2O_3–P_2O_5$ pigments were prepared from mixtures of ZnO, $SrCO_3$, H_3PO_4 a H_3BO_3, by homogenization followed by slow dehydration and calcination at temperatures up to 750°C. After cooling, the reaction products were subjected to dry grinding and grinding in ethanol. The pigment powders obtained were characterized by the X-ray diffraction using, an HZG 4B X-ray diffractometer (Freiberg, Germany). Pigment densities were measured using a helium pycnometer (Micromeritics, USA), and particle size distributions were measured on a Sedigraph 5000E (Micromeritics, USA) using ethylene glycol as a sedimentation liquid.

The aforementioned methods afforded pigment samples of the compositions given in Table 1. Before the preparation of coating formulations the critical volume concentration of the pigment (CVCP) in the coating formulation was calculated from the equation:

$$\mathrm{CVCP} = \frac{10000/\rho}{100/\rho + \mathbf{a}/0.93} \tag{1}$$

where is the pigment density (g cm^{-3}) and a is the oil consumption per 100 g of pigment.

Pigment solubility was measured in the distilled water (pH = 6) and in 0.3 M HCl at 25°C. To evaluate anticorrosive properties of the pigments, a standard coating formulation based on an alkyd resin was used [16]. Anticorrosion pigments were employed at the 10% (w/w) level in each formulation, and the pigment content corresponded to 80% of CVCP. After 30 days, the coating composition was applied to steel sheets (45×220 mm),

Table 1
X-ray diffraction data for the anticorrosive pigments employed in this study

Pigment symbol	Composition (mol%)				Identified crystalline phases
	SrO	ZnO	B_2O_3	P_2O_5	
AP1	29.17	29.17	8.33	33.33	ZnP_4O_{11}, $SrZnP_2O_7$, $SrB_6O_{10}/SrO·3B_2O_3$
Ap2	25	25	–	50	$Zn_3(PO_4)_2$, α-$Zn(PO_3)_2$, $Sr(PO_3)_2$
AP3	37.50	37.50	25	–	$SrB_2O_4/SrO·B_2O_3$, ZnO
AP4	14.59	43.75	8.33	33.33	$Zn_3(PO_4)_2$, ZnP_4O_{11}, α-$Zn(PO_3)_2$,$Sr_2P_2O_7/2SrO·P_2O_5$,$2SrO·P_2O_5·B_2O_3$, BPO_4
AP5	32.14	32.14	14.29	21.43	$Zn_3(PO_4)_2$, α-$Zn(PO_3)_2$, $2SrO·P_2O_5·B_2O_3$, $SrB_4O_7/SrO·2B_2O_3$
AP6	–	58.34	8.33	33.33	$Zn_2P_2O_7$, BPO_4
AP7	58.34	–	8.33	33.33	$Sr_2P_2O_7/2SrO·P_2O_5$, $Sr_2B_2O_5$
S1[a]	–	75	–	25	$Zn_3(PO_4)_2$
S2[a]	–	–	50	–	$Ca(BO_2)_2$

[a] Standard anticorrosive pigments.

using a special spreading tool, in 2 layers of 20-μm thickness, with a 48-h time lag between applications. After another 30 days, corrosion tests were carried out in a condensation chamber containing an SO_2 atmosphere (2 mg SO_2/dm^3, 35°C and 100% relative humidity), for 200, 400 and 600 h. Salt spraying tests were carried out using an aerosol of 5%-NaCl, at 35°C, for 120, 200 and 300 h. Before conducting the salt spraying test, the coating films were etched, by making a 15-cm X-shaped cut.

The corrosion behavior of the uncoated steel sheets was also studied, by extracting these sheets with aqueous extracts of pigments and coating compositions and determining the decrease in sheet weight after a 21-day exposure of the activated steel sheets with 100 g of a suspension of 10% pigment/90% water. The steel sheets were activated in a solution of 10% HCl and 1% urotropine, with subsequent washing in distilled water. The corrosion tests were carried out in triplicate for each pigment composition, the results of which are given as the averages. All tests included the standard commercial pigments based on zinc orthophosphate and calcium metaborate.

3. Results and discussion

The compositions of the borophosphate pigments and the standard (commercial) pigments used in this study are given in Table 1, including key X-ray data. From the results of X-ray diffraction studies, it can be seen that a mixture of phosphate and borate compounds of Zn and Sr is present in most of the pigments heated at 750°C. The presence of a $2SrO{\cdot}P_2O_5{\cdot}B_2O_3$ borophosphate phase was observed in pigments A4 and A5. Relatively strong diffraction lines for the crystalline BPO_4 phase were found in samples with a low SrO content (i.e. AP4, AP6). The composition of the identified phases provides evidence for a preferential reaction of amphoteric ZnO with the stronger phosphoric acid H_3PO_4 rather than with the weaker boric acid H_3BO_3. The more basic character of $SrCO_3$ results in its reactions with H_3PO_4 and H_3BO_3. The higher reactivity of $SrCO_3$ is evident from its decomposition during reaction with the acids. Its higher reactivity accounts for the results of the structural analysis of sample AP3 ($37.5SrO–37.5ZnO–25B_2O_3$), where only the diffraction lines of SrB_2O_4 and ZnO were observed.

The density of the borophosphate pigments AP1–AP6 was 3.29–4.08 g cm^{-3}, and their oil consumption per 100g of pigments was 19–37.2g (see Table 2). The density of the borophosphate pigments with the same molar ratio of ZnO and SrO increased with increasing B_2O_3 content, whereas the oil consumption number decreased. Table 2 also provides the critical volume concentration for the pigments examined.

The measurement of the particle size distribution of the new pigments revealed that the mean particle size ranged from 1.5 μm (AP7) to 5.5 μm (AP3), while the mean particle size of commercial

Table 2
Physico-chemical properties of the pigments employed in anticorrosive coatings

No.	Pigment composition (mol%)				Density	Oil consumption	CVCP	Solubility at 25°C	
	SrO	ZnO	B_2O_3	P_2O_5	(g cm^{-3})	(g/100 g)		(g/100 g H_2O)	(g/100 g 0.3 M HCl)
AP1	29.17	29.17	8.33	33.33	3.62	27.9	47.9	0.04	0.83
AP2	25	25	–	50	3.29	37.2	43.3	0.08	0.31
AP3	37.50	37.50	25	–	4.08	19.0	54.5	0.35	1.62
AP4	14.59	43.75	8.33	33.33	4.91	27.9	40.4	0.05	0.89
AP5	32.14	32.14	14.29	21.43	3.72	24.8	50.2	0.13	1.89
AP6	–	58.34	8.33	33.33	3.70	21.7	53.7	0.14	0.84
AP7	58.34	–	8.33	33.33	3.59	31.0	45.5	0.05	0.92
S1	–	75	–	25	3.30	27.9	50.3	0.13	2.92
S2	–	–	50	–	2.75	19.0	64.0	0.02	0.87

pigments was 3 μm for S1 and 12 μm for S2. The samples with a high B_2O_3 content (AP3, AP5, and S2) tended to form of aggregates, despite the use of ultrasonic disintegration before measurements, which could have influenced the results of particle size measurements.

The results of solubility measurements are given in Table 2. From these data it is evident that pigment solubility in water and in HCl increased with an increasing B_2O_3 content. These results reflect the higher resistance of the phosphate chains to dissociation in aqueous solutions. Pigment solubility was also influenced by the stoichiometric ratio of metal cations to borate and phosphate anions.

The first test for the evaluation of anticorrosive–inhibitory properties of the borophosphate pigments consisted of determining the weight loss (WL) of steel sheets immersed for 21 days in aqueous extracts of pigment and coating formulations. The results obtained are given in Table 3. WL values reflected the acido-basic properties of the extracts. The lowest loss was observed for borophosphate pigment AP5, while the WL values for pigments S2 and AP2 were the highest, and were close to that in the distilled water. The WL values generated from the extracts of coating formulations were generally higher than those obtained from pigment extracts, probably due to the lower water solubility of the coating formulations. These results were attributed to the formation of donor-acceptor bonds between the pigments and binder. Acidity of the pigment extracts decreased slightly with time, whereas the pH of the extracts of coating formulations reached a maximum after 1 week and then decreased with time.

Corrosion resistance of pigment films, following deposition on activated steel sheets, was determined in an SO_2 atmosphere and in the salt spray (fog) test. These tests were carried out according to standard methods [17,18]. The assessment of corrosion was based mainly on the size and density of paint blisters formed in SO_2 and salt spray atmospheres, and on the size of the corroded area produced after removing the damaged paint. For the evaluation of the corrosion of etched specimens, both the depth of undercorrosion of the film in the etched places and the overall corroded area after paint removal were assessed. The results of these tests are given in Tables 4 and 5.

From the results of the corrosion test in an SO_2 atmosphere (Table 4), it can be seen that for three samples (AP4, AP2, AP3) the degree of corrosion did not change substantially with exposure time. These pigment compositions exhibited the highest corrosion resistance in this test. By comparison, the corrosion resistance of the paint with commercial pigment S2 was lower after 600 h of exposure, exhibiting the worst corrosion resistance.

The best corrosion resistance in the salt spray test (see Table 5) was observed with the paint containing pigment AP3. Slightly inferior results

Table 3
pH of aqueous extracts of the borophosphate pigments and coating formulations and weight losses (WL) of steel sheets after 21 days immersion in aqueous extracts

No.	Pigment composition (mol %)				Pigments					Coating formulations				
					pH of aqueous extracts				WL	pH of aqueous extracts				WL
	SrO	ZnO	B_2O_3	P_2O_5	1 day	7 days	14 days	21 days	(g m^{-2})	1 day	7 days	14 days	21 days	(g m^{-2})
AP1	29.17	29.17	8.33	33.33	4.9	5.3	5.5	5.6	29.6	4.9	6.0	5.7	5.4	51.7
AP2	25	25	–	50	2.4	3.5	3.7	3.3	87.8	4.1	5.8	5.8	5.1	68.3
AP3	37.50	37.50	25	–	12.7	12.9	13.0	13.0	1.1	4.3	5.6	5.6	5.3	25.2
AP4	14.59	43.75	8.33	33.33	6.5	7.1	7.2	7.0	52.3	5.9	6.2	5.5	5.1	73.2
AP5	32.14	32.14	14.29	21.43	8.6	8.7	8.8	8.7	0.5	5.6	6.3	5.4	5.2	45.5
AP6	–	58.34	8.33	33.33	5.7	6.4	6.4	6.4	12.5	5.1	6.0	5.6	5.3	48.7
AP	58.34	–	8.33	33.33	6.3	6.9	7.1	7.1	25.7	5.5	6.9	6.6	6.5	53.5
S 1	–	75	–	25	7.2	6.9	6.8	6.7	71.4	5.3	5.9	5.4	5.2	58.5
S 2	–	–	50	–	9.2	9.4	9.3	9.2	83.1	7.2	7.6	7.2	7.2	0
H_2O	–	–	–	–	5.4	6.2	5.9	5.6	90.8	–	–	–	–	–

Table 4
Corrosion resistance of the paints in a condensation chamber with SO_2

Pigment	Blister size (mm); blister density[a]						Corroded area (%)			Corrosion degree[b]		
	Duration of exposure (h)						Duration of exposure (h)			Duration of exposure (h)		
	200		400		600		200	400	600	200	400	600
AP1	1–3	D	1–3	D	3–5	MD	25	45	45	3	4	4
AP2	< 1	M	< 1	M	< 1	F	8	12	12	2	2	2
AP3	1–3	M	1–3	F	1–3	F	1	3	3	2	2	2
AP4	< 1	F	< 1	F	< 1	F	1	1	3	1	1	2
AP5	1–3	MD	< 1	MD	< 1	M	7	10	30	2	2	3
AP6	< 1	M	< 1	M	1–3	M	25	45	45	3	4	4
AP7	1–3	M	1–3	D	1–3	MD	25	45	45	3	4	4
S1	< 1	D	< 1	D	< 1	D	10	50	75	2	4	5
S2	1–3	M	1–3	MD	3–5	MD	6	12	12	2	2	3

[a] Blister density: F, few; M, medium; MD, medium dense; D, dense.

[b] Corrosion degree is evaluated on a scale of 1–5, where 1 = the lowest corrosion level and 5 = complete corrosion.

Table 5
Corrosion resistance of the paints in the salt spray testing

Pigment	Under-film corrosion (mm)			Corroded area (%)			Corrosion degree[a]		
	Time of exposure (h)			Time of exposure (h)			Time of exposure (h)		
	120	200	300	120	200	300	120	200	300
AP1	0–0.5	1–2	2–3	10	10	15	2	2	3
AP2	0–0.5	0.5–1	0.5–1	1	3	3	1	2	2
AP3	0	0–0.5	1–2	1	1	1	1	1	2
AP4	0–0.5	0.5–1	0.5–1	3	3	3	1	2	2
AP5	0–0.5	0.5–1	1–2	1	3	3	1	2	2
AP6	0–0.5	1–2	2–3	10	10	15	2	2	3
AP7	0–0.5	1–2	2–3	10	15	35	2	2	4
S1	0–0.5	1–2	2–3	1	3	5	1	2	2
S2	0	1–2	1–2	3	10	10	1	2	2

[a] Corrosion degree is evaluated on a scale of 1–5, where 1 = the lowest corrosion level and 5 = complete corrosion.

were obtained with paints containing pigments AP2, AP4, AP5 and the commercial pigment S2.

The adhesion of the paints to the steel sheets was also evaluated [19], both before the corrosion tests and after their exposure to the SO_2 atmosphere. The degree of adhesion for paints before the corrosion tests was high; but after the exposure, it became worse for most paints. The exception was the paint containing pigment AP4 ($14.5SrO–43.8ZnO–8.3B_2O_3–33.3P_2O_5$), where the degree of adhesion did not change — even after the exposure for 600 h in an SO_2 atmosphere. The worst adhesion properties were obtained with paints containing pigments AP1 and S2.

4. Conclusion

The results of anticorrosion tests reflected relatively good anticorrosion properties in alkyd paints prepared with borophosphate pigments. The best results were obtained with pigments $14.6SrO–43.8ZnO–8.3B_2O_3–33.3P_2O_5$ (AP4) and $37.5SrO–37.5ZnO25B_2O_3$ (AP3). Satisfactory results were obtained with pigments 25SrO–25ZnO–50P_2O_5 (AP2) and 32.14SrO–32.14ZnO–14.29B_2O_3–21.43P_2O_5 (AP5), which were comparable to commercial pigments based on $Zn_3(PO_4)_2$ and $Ca(BO_2)_2$, respectively. The good properties of pigment AP3 can probably be attributed to its high solubility and the high pH of its aqueous extracts. The presence of the $Zn_3(PO_4)_2$ constituent has a positive effect on the anticorrosive behavior of the paints, as both the anticorrosion resistance and mechanical properties of the paints improved with increasing $Zn_3(PO_4)_2$ content. It is clear that the paints prepared from the zinc orthophosphate pigment did not have the best anticorrosion properties but it seems that the presence of more alkaline strontium cations improved anticorrosion properties. Also the alkyd resin contributed substantially to satisfactory results in anticorrosion tests.

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