

PROPERTIES OF ORGANIC COATINGS CONTAINING PIGMENTS WITH SURFACE MODIFIED WITH A LAYER OF $ZnFe_2O_4$

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Received: 2015.10.09
Accepted: 2015.11.14
Published: 2015.12.04

ABSTRACT

This work is focussed on the properties of organic coatings containing pigments whose surface was chemically coated with zinc ferrite ($ZnFe_2O_4$) layer. Four silicate types with different particle shapes were selected as the cores: diatomite, talc, kaolin and wollastonite. The untreated particles exhibit a barrier effect. The aim of this project was to apply the surface treatment approach with a view to enhancing not only the model paint films' anticorrosion properties but also their resistance to physico-mechanical tests pursuant to ISO standards (cupping, bending, impact, adhesion). Other parameters examined included: particle size and morphology, density of the modified pigment, oil consumption, pH, conductivity, and electrochemical properties of the paint film. A solvent-based epoxy-ester resin was used as the binder and also served as the reference material. The pigment volume concentration (PVC) was 1% and 10%. During the last stage of the experiment, the paint films were exposed to a corrosive environment stimulating seaside conditions or conditions roads treated with rock salt. The accelerated cyclic corrosion test in a neutral salt mist atmosphere was conducted for 864 hours. The results served to ascertain a suitable environment for organic coatings.

Keywords: zinc ferrites, silicates, surface protection, organic coatings.

INTRODUCTION

Organic coatings represent one of many ways to protect objects (not only metallic) from degradation detracting from their performance. This degradation – material corrosion – is nearly always undesirable. Recent research has been focussing on the development of anticorrosion paints that provide better anticorrosion protection than the routinely used materials and, in addition, are reasonably environmentally friendly [1]. The present study was devoted to the properties of organic coatings containing silicon oxide based pigments with the surfaces modified with a chemical layer of zinc ferrite ($ZnFe_2O_4$). Zinc ferrite is a crystalline inorganic spinel type pigment. The structure of zinc ferrite can be described by the general formula AB_2O_4 where A and B are, e.g., Fe, Al, Ba, Mg, Zn, Ni, Co or Ca and where the

cations are arranged in octahedral and tetrahedral gaps [2, 3]. In this particular case, A was Zn^{2+} and B was Fe^{3+} [4]. Targeted selection of the cations modifying the spinel lattice can be used to change the properties or create new properties of the pigment dispersed in an organic binder [5]. The $ZnFe_2O_4$ spinels are thermally stable [6], exhibit a high covering power, are insoluble [7, 8], are resistant to aggressive media [9], and the cost of their preparation is reasonably low [2]. Spinel pigments enhance mechanical strength of the binder through a chemical reaction that produces cationic soaps, thereby reducing their solubility and tendency to saponify on exposure to a corrosive environment where hydroxy ions are created [10]. The objective of this work with zinc ferrite is to slow down or completely inhibit metal corrosion. Metal corrosion is an electrochemical process which can be suppressed by charge transfer aimed

at avoiding metal degradation. Generally, the corrosion process is promoted, e.g., by chloride ions, which dissolve iron oxides. To inhibit corrosion of a metallic substrate, ferrous ions (Fe^{2+}) must be transformed to ferric ions (Fe^{3+}), which act as inorganic corrosion inhibitors in the electrochemical process. In this manner it is possible to create a passivation layer which will suppress the cathodic and/or anodic reaction [5, 11]. Depending on the pigment, organic coatings do not act electrochemically only: they also provide barrier [12] or mechanical [13] protection against corrosive environments. The present paper describes the properties of the reasonably well available pigments diatomite, talc, wollastonite and kaolin, each modified with a layer of zinc ferrite on the particle surface. The advantage of this surface treatment is the synergistic effect of barrier protection and the inhibiting reaction in a region unsuitable for the corrosion reaction. A low amount of ZnFe_2O_4 can be used for the surface treatment, 16–20 wt.% of the volume, which is financially beneficial.

The goal of this work was to use the pigment surface treatment to enhance not only the anticorrosion efficiency of model paint films but also their resistance in physico-mechanical tests performed according to CSN ISO standards (cupping, bending, impact, adhesion). The assets of the surface-modified pigments should also include non-toxicity and the use of traditional natural sources.

EXPERIMENTAL

Preparation of the surface-treated pigment, specification of the pigment

The pigment surface treatment procedure was conducted in laboratory conditions. An amount

of 50 g of the pigment was suspended in 4 litres of distilled water acidified with 5 ml of H_2SO_4 , and $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ and urea were added. The system was heated to boil and pH was measured during the reaction. The reaction was terminated on attaining pH 8. The product was decanted, filtered out, rinsed with water, and dried at 110 °C, and the dry material was annealed at 800 °C for 2 hours. The pigments so prepared were specified as stipulated in EN ISO 787-10 and EN ISO 787-5, and the critical pigment volume concentration (CPVC) was determined. The particle shape was examined on a JEOL – JSM 5600 electron microscope.

Paint formulation and preparation

A solvent-type epoxy-ester resin (Worlée-Dur D46, Worlée Chemie, Germany) was used as the coating material binder. The model paints were prepared by adding the pigment to the binder and homogenizing the system. The pigment volume concentration (PVC) in the paint was 1% and 10%. The paints were pre-prepared on a dissolver and dispersed in a bead mill at 3000 rpm for 45 minutes. Nuodex Combi (Sigma-Aldrich) was added (0.1 wt.%) as a siccativ. The paints were applied to glass and steel panels. The non-pigmented epoxy-ester resin served as the reference material for comparing the properties of the paints.

Relative surface hardness measured on a pendulum apparatus

Surface hardness relative to a glass standard (%) was measured on a Persoz type pendulum apparatus as per CSN 67 3076 during 120 days.

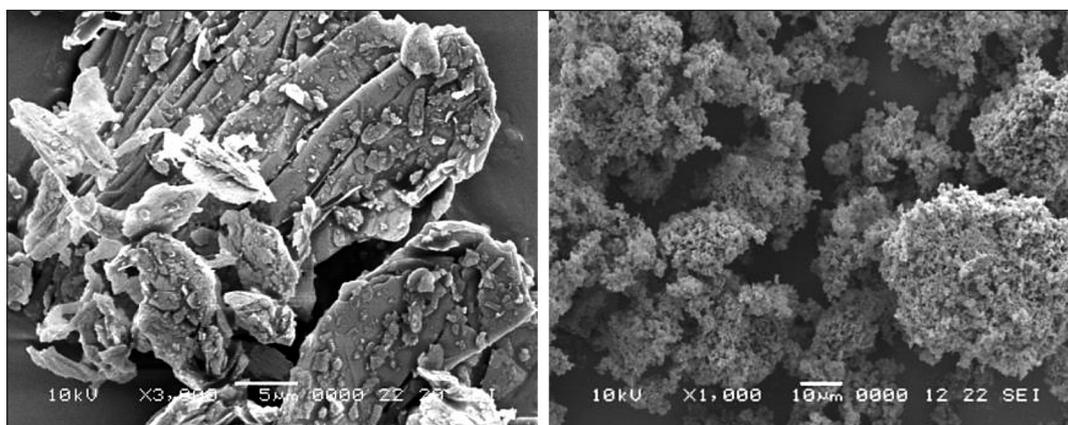


Fig. 1. An untreated talc particle, magnification 3000× (left); a talc particle with its surface treated with a chemical layer of ZnFe_2O_4 , magnification 1000× (right)

Physico-mechanical tests

The physico-mechanical properties of the paint films were determined by subjecting the films to mechanical and destructive stress according to ISO standards 2409, 6272, 1519, and 1520.

Determination of pH and specific electric conductivity of and corrosion losses in aqueous extracts

The pH and specific electric conductivities of 10% aqueous extracts of the loose paint films were measured as specified in EN ISO 789-9 and EN ISO 787-14 during 4 weeks. The suspension was filtered, and a pre-cleaned and pre-weighed steel panel was submerged in the aqueous extract. The panel was removed from the extract after 10 days and the weight loss due to corrosion (K_m) was determined.

Accelerated corrosion test in an NaCl mist (EN ISO 92 27)

The corrosion test was performed on steel panels $152 \times 102 \times 0.8$ mm size, coated with the paint films. A test cut 7 cm long was made through each paint film. The panels were exposed to the neutral salt mist / condensed moisture environment during 864 hours, and the corrosion effects were evaluated as per EN ISO 4628-2 to 4628-5 after terminating the exposure. The parameters measured included blistering on the paint film surface (ASTM D 714-78), degree of metal corrosion on the test cut (ASTM D 1654-92) and degree of corrosion of the metal surface (ASTM D 610-85).

Electrochemical method

Electrochemical examination consisted in linear polarisation measurements using a cell with a reference electrode (SCE), a Pt cathode, and the sample as the working electrode (anode). A 3.5% NaCl solution constituted the working medium. The samples were polarised from -10 mV/EOC to $+10$ mV/EOC at 0.166 mV/s. The parameters measured for each paint included the spontaneous corrosion potential (E_{corr}), current density (I_{corr}), and polarisation resistance (R_p). The corrosion rate (v_{corr}) was calculated.

RESULTS AND DISCUSSION

Model paints containing SiO_2 based pigments whose surface had or had not been modified with a layer of ZnFe_2O_4 were prepared. The pigment volume concentrations were 1% and 10%. A solvent-based epoxy-ester resins was used as a binder, and when containing no pigment, also as the reference material. The physico-mechanical and anticorrosion properties of the paint films were examined. The results are listed in Table 1.

Relative surface hardness (RSH) of the films was measured during 120 days. This parameter increased (with some exceptions) also for films with pigments that on their own (no surface treatment) are rather soft, such as talc. Generally, surface hardness is increased by the presence of the zinc ferrite layer, particularly at PVC = 10%. The tearing-off force required to detach the paint film (or a part of it) from the substrate increases as well. The situation is opposite with talc: surface-untreated talc exhibits a very good particle adhesion both to the resin and to the substrate metal. The force required to tear off the epoxy-ester resin was 235 N, and it was lower if the pigment was present. The overall physico-mechanical resistance (OPMR) of the paint film was 100%, only the paint film with talc as the pigment (film thickness 0.5 mm) did not attain the maximum value in the cupping test on the Erichsen instrument; the paint film, though, was no less efficient, actually it was more elastic. The pH and specific electric conductivities of aqueous extracts of the loose paint films were measured during 28 days.

The suspensions were filtered on day 21, and clean and pre-weighed steel panels were submerged in them and left there for 10 days. Subsequently, the panels were removed, rinsed and weighed to determine the corrosion losses (K_m) relative to a blank, i.e. redistilled water; RW: pH 5.29–5.79. Submersion of the panels brought about pH increase by 1–2 units. The pH shift was due to the effect of the pigment itself and by the effect of the surface treatment, owing to which the system had a tendency to saponification. Although the pH remained in the acid region, the effect of the resin itself, the pH of the pigment powders was in the range of 7.56–8.49.

Specific electric conductivity (S) increased with electron exchange in the pigment-paint-substrate system. The paint films were exposed to the effect of condensed moisture with salt mist during 864 hours. The apparent corrosion effects

Table 1. Properties of the test paint films

Sp.	PVC	RSH [%]	OPMR [%]	Fmax [N]	pH 0 day	pH 21 day	pH 28 day	S 0 day [μ S/cm]	S 21 day [μ S/cm]	S 28 day [μ S/cm]	K_m [%]	E_{corr} [mV]	R_p [Ω]	NaCl [%]
Non-modified pigments														
D	1	32	100	110	3.41	3.18	4.42	133	207	197	48.8	-280	$4.86 \cdot 10^5$	65
	10	33	100	114	3.65	3.48	5.08	85	138	214	87.8	-395	$1.64 \cdot 10^5$	86
T	1	31	100	178	3.63	3.39	4.83	93	153	219	63.4	-458	$4.40 \cdot 10^4$	63
	10	33	100	302	3.74	3.43	4.09	61	116	131	51.2	-155	$2.45 \cdot 10^4$	94
K	1	33	100	157	3.54	3.22	4.27	102	181	171	17.1	-277	$1.12 \cdot 10^5$	66
	10	35	100	160	3.53	3.26	4.15	103	179	172	52.3	-368	$8.51 \cdot 10^3$	67
W	1	36	100	180	3.85	4.01	5.07	48	61	79	36.6	-652	$1.17 \cdot 10^5$	17
	10	36	100	159	6.04	6.36	5.73	46	111	105	9.76	-584	$1.47 \cdot 10^4$	75
Surface modified pigments with layer $ZnFe_2O_4$														
D	1	36	100	150	3.57	4.81	4.64	103	166	146	48.8	-136	$1.85 \cdot 10^4$	90
	10	33	100	178	3.89	3.70	4.93	75	151	183	65.9	-293	$1.41 \cdot 10^5$	47
M	1	36	100	127	3.76	3.47	5.23	62	119	129	70.7	-206	$1.64 \cdot 10^6$	85
	10	34	98.8	195	4.21	3.38	5.43	36	70	104	137	-208	$5.16 \cdot 10^4$	69
K	1	37	100	139	3.61	5.10	4.50	168	185	350	65.9	-132	$1.64 \cdot 10^6$	61
	10	36	100	189	3.70	4.02	4.91	65	138	138	65.9	-225	$1.02 \cdot 10^6$	80
W	1	35	100	141	3.50	3.36	4.01	13	245	228	36.6	-351	$9.28 \cdot 10^4$	74
	10	29	100	168	4.03	3.39	5.38	131	149	12	156	-146	$1.10 \cdot 10^6$	84
Blank sample														
E	x	33	100	235	3.42	3.38	3.30	92	195	232	88	-586	$4.41 \cdot 10^3$	50
RW	x	-	-	-	5.29	5.87	5.79	2	2	82	100	-	-	-

Notes: D – diatomite; T – talc; K – kaolin; W – wollastonite; E – epoxy-ester resin; RW – redistilled water.

were evaluated and the overall anticorrosion efficiency of the system was calculated (see Table 1, NaCl [%]). Talc at PVC = 10% exhibited the best results among the untreated pigments, and diatomite at PVC = 1% provided the best results among the pigments whose surface had been treated with $ZnFe_2O_4$. Although not all surface treatments led to higher corrosion protection values, all the surface-treated pigments at either of the two PVC levels reduced appreciably corrosion of the steel panel surface because corrosive medium penetration to the substrate was prevented or hindered by the protective film. The overall anticorrosion protection values agreed well with the electrochemical measurement results: a lower degree of corrosion protection was accompanied by a lower E_{corr} value. For instance, wollastonite at PVC = 1 % exhibited $E_{corr} = -652$ mV, and the corrosion test resulted in many blisters on the paint film surface and appreciable metal corrosion in the cut. The trend was opposite with the polarisation resistance (R_p): the higher the order of magnitude, the better the anticorrosion protection of the metal; and surface treatment of the pigments brought about increase by 1–2 orders of magnitude.

CONCLUSIONS

Paints containing pigments whose surface had been chemically modified with a zinc ferrite layer were studied. The paint films exhibited higher relative surface hardness and better physico-mechanical properties. The anticorrosion efficiency improvement was associated with a shift of the spontaneous corrosion potential to values slowing down corrosion of the metal; the polarisation resistance values were also consistent with the corrosion protection efficiency trend. The samples were resistant to a salt mist environment for the 864 hours of the test. so the paints are categorised as C5-I according to ISO 12 500 (medium degree-resistance to enhanced salinity environment).

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