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ANTICORROSION PROPERTIES OF ION-EXCHANGABLE PIGMENTS IN EPOXIDE COATINGS

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Hexavalent chromium compounds (chromates) have been widely used as inhibitive pigments in the formulation of anticorrosive paints. However, their high toxicity and carcinogenic effects are forcing the development of effective chromate-free organic coatings. One such alternative, which is very attractive from a scientific point of view, is the use of ion-exchangeable pigments (IEPs). The few studies conducted with this type of pigment are not conclusive about their anticorrosive efficiency and controversy surrounds their functioning mechanisms, interchange capacity and anticorrosive performance. In the present research, which focuses on the anticorrosive protection of this type of pigment, calcium/silica (Ca/Si) IEPs were synthesized in first step, next epoxide paint coatings were formulated. IEPs have been applied on low carbon steel panels. The effect of these non-toxic pigments on the protective properties of coatings has been tested by means of natural and accelerated corrosion tests (humidity, salt spray and SO_2*).*

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Experimental results have shown that IEPs are suitable to formulate anticorrosive paint films with improved anticorrosive effects.

Introduction

Paints initially insulate a metal substrate from the water and oxygen required for environmental corrosion. However, all organic film-forming polymers are to a greater or lesser extent permeable. Although paint coatings have been used for centuries to protect metals against atmospheric corrosion, their protection mechanisms have not yet been fully explained and for many years have been the subject of controversy. Anticorrosive protection by paints has recently been described as being a combination of a physical barrier, a chemical inhibitor and an electrical rezistor [1]. IEPs are relatively high surface area inorganic oxides loaded with ionic corrosion inhibitors by ion exchange with the surface hydroxyl groups. The oxides are chosen for their acidic or basic properties to provide cation or anion exchangers; thus, silica is used as a cation support and alumina for anions. So, calcium-exchanged silica [2], Al–Zn–decavanadate hydrotalcite [3], and cerium(III) and calcium(II) cation exchanged bentonites [4] have been incorporated as pigments in anticorrosive paints.

Cations permeating the paint film will release calcium from the pigment and at the same time be immobilised. The implications of such a release mechanism are that the inhibitor species is only released when the paint film is being permeated by corrosive species and the amount released is dependent on the severity of the environment. Calcium, released from the silica surface, migrates to the paint–metal interface where a thin, inorganic layer is deposited which is essentially impermeable to moisture/ions and hence prevents the corrosion reaction from proceeding. According to Goldie [5] the presence of this layer has been detected by X-ray photoelectron spectroscopy on painted metal plates exposed to a variety of environments. Other evidence supporting this layer theory has been obtained from electrochemical studies [5]. So, the anticorrosive effect of Ca/Si pigment can be described considering two mechanisms: the exchange of calcium ions for cations (H^+, etc.) penetrating the coating from the environment, neutralising the acid compounds and forming on the substrate a protective layer consisting of calcium and iron silicite [5,6].

Experimental

Preparation and Characterization of Pigment

IEPs were prepared by high-temperature synthesis based on reaction of silicates with calcium oxide. Calcium carbonate and silicates with different layered structure were chosen as starting raw materials. The first step was thermal decomposition of $CaCO_3$ to CaO and CO_2 according to Eq. (1). The reaction proceeded in solid phase. The resulting pigment had the silica matrix with CaO on the surface. The amount of CaO in the final pigment was 20 % by wt.

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (1)$$

The following silicates were chosen: Bentone SD2, Mica SFG 20, Talek A-60. The starting raw materials were weighed with an accuracy of ±0.001 g. The mixture of starting materials was homogenized in porcelain mortar for a period of 30 min. The second step was calcination in electric oven at the temperature of 1150 °C with 2-hour time lag at the peak temperature and the temperature increasing from the start at the rate of 5 °C min^{-1}.

The prepared calcinate was ground by wet way in planetary ball mill for a period of 5 hours at the rate of 400 rpm. Corundum balls were used as the mill balls.

The ground pigment was washed with distilled water to remove the non-reacted particles of starting materials that would negatively affect the pigment characteristics, whereupon the pigment was heated at the temperature of 110 °C to constant weight.

The powdery pigment was characterized by the following parameters: specific mass, oil consumption, pH value, and specific conductivity of aqueous extract of the pigment. The values of critical pigment volume concentrations (CPVC) were calculated.

Preparation of Coatings

Model paints based on epoxy emulsion (producer Spolchemie a.s., dry mass = 55 %) and epoxy resin (producer Spolchemie a.s., dry mass = 75 %) containing the synthesized pigments were prepeared in order to assess properties of the pigment. For estimation of physical-mechanical and anticorrosion properties the cjosen volume concentration of pigment in PVC-based coating was 10 %.

The prepared paints were coated on a steel panel (approx. dimensions 152×102×0.8 mm) by means of a double-layer applicator blade with 200 μm slot. The second layer of paint was applied (after sufficient curing of first layer) by means of an applicator blade with the slot producing a film of approx. 100 μm final thickness. For the corrosion tests the panels were cut (approx. 8 cm cuts except the steel basis in the distance of 1 cm from the edges).

Corrosion Tests

The tested coatings were exposed to corrosive environment chambers with general condensation of water, corrosive environment combination chambers with salt fog and corrosive environment condensation chamber containing SO_2. The general anticorrosion efficiency (A) was derived from the test evaluating the corrosion of flat basis (A_1) according to ASTM D 610- 85), the test evaluating the corrosion in cuts (A_2) according to ASTM 1654- 92), and the test evaluating production of blisters in the coating (A_3) according to ASTM D 714- 87). The samples were exposed to corrosive environment for a period of ca. 500 hours (paints based on epoxy emulsion) or ca. 2000 hours (paints based on epoxy resin).

The value of general efficiency (A) is in the interval of 0-100. A higher numeric value means higher value of anticorrosive efficiency — Eq. (2). Overall assessment was derived after Heubach scale. Equation for general anticorrosive efficiency A for corrosion test in chamber with NaCl content, condensation chamber with general evaporation of water and in chamber with SO_2 content reads as follows

$$A = \frac{A_1 + A_2 + A_3}{3} \tag{2}$$

Results and Discussion

Properties of Pigments

Parameter	Mica	Bentone	Talek
Specific mass, g cm^{-3}	2.78	2.51	2.86
Oil consumption, g/100 g pigment	64.6	75.9	44.4
CPVC, %	34.1	32.76	42.1
pH of aqueous leach	11.3	9.76	12.31

Note. In the table, there are properties of finished IEPs pigments. The names of these pigments are identical with the names of silicates.

Anticorrosion Properties

In the chambers with salt fog, all coatings on the basis of epoxy resin had very good anticorrosion efficiency. The best of all was the coating pigmented with Mica SFG + 20 % CaO. The paint with Talek A60 + 20 % CaO had the minimum anticorrosion efficiency in epoxy emulsion coatings. The other two coatings had a similar, higher than average anticorrosion protection. The results are presented in Diagram 1.

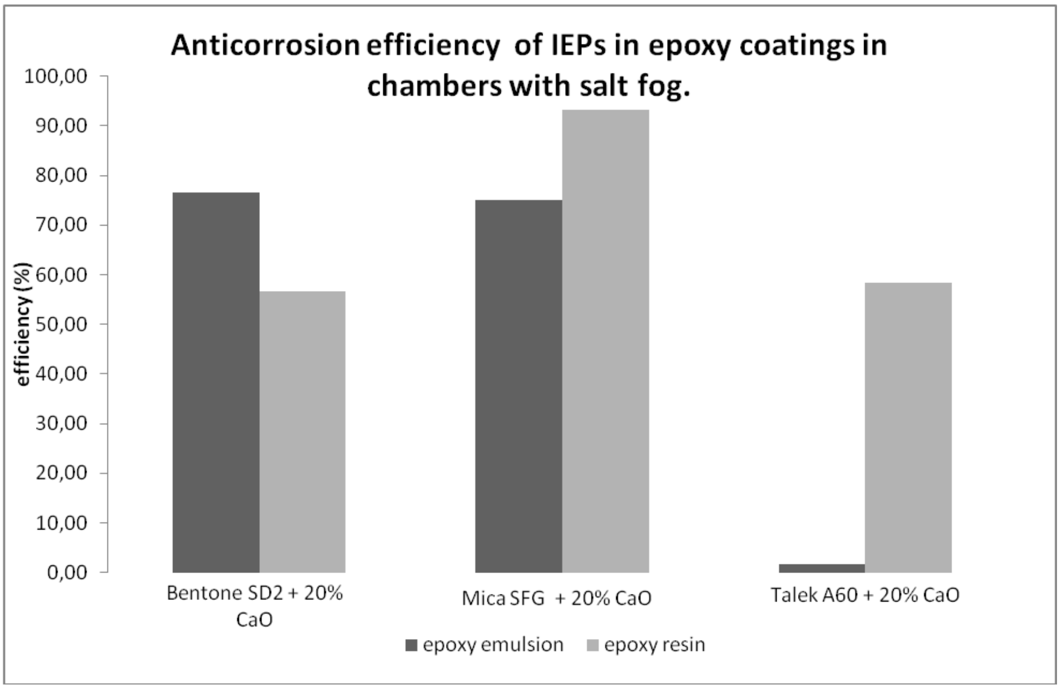

Diagram 1

In chambers with general condensation of water, epoxy resin coatings showed very high anticorrosion protection. The coating pigmented with Talek A60 + 20 % CaO had almost maximal protection. The coating on the basis of epoxy emulsion had a different anticorrosion efficiency. The best of all was the coating with Talek A60 + 20 % CaO. This paint showed 100 % efficiency. The results are presented in Diagram 2.

In the chamber containing SO_2 all the coatings (in both types of binders), except coatings pigmented with Bentone SD2 + 20 % CaO, showed higher than average anticorrosion protection. The paint containing Mica SFG + 20 % CaO had the best anticorrosion efficiency in epoxy emulsion coatings . Talek A60 + 20 % CaO had the best protection against corrosion in coatings on the basis of epoxy resin. The results are presented in Diagram 3.

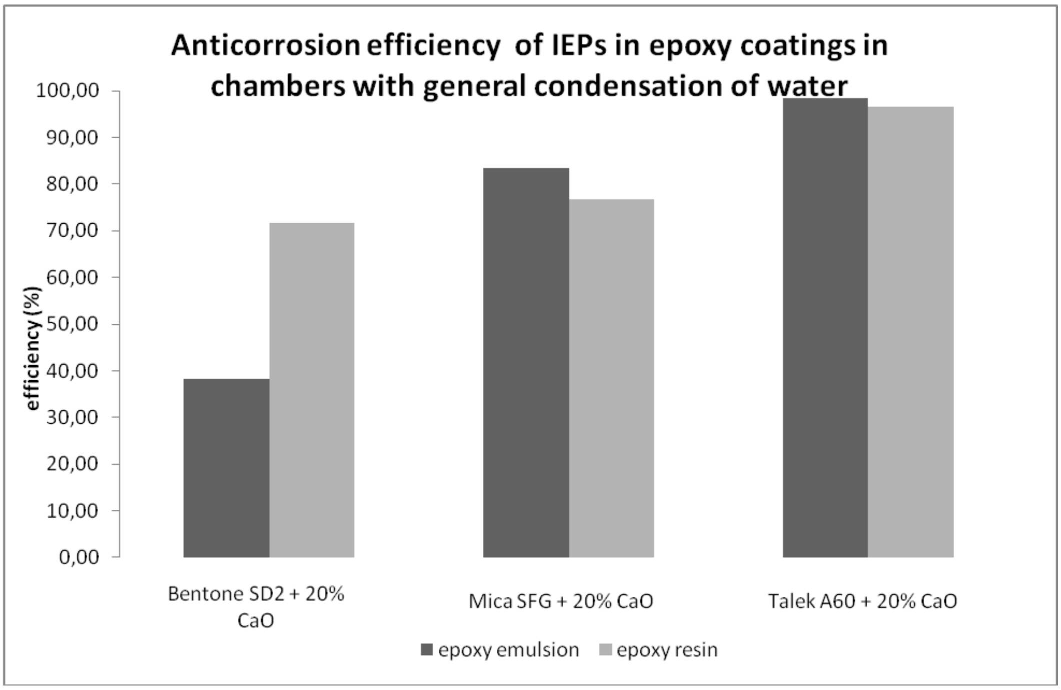

Diagram 2

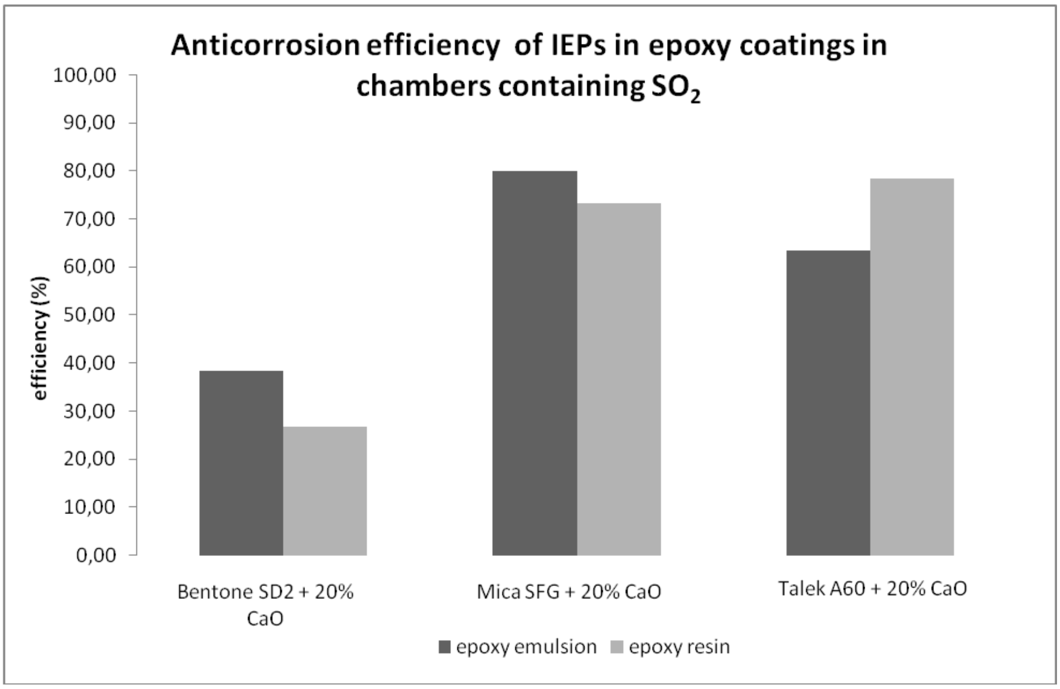

Diagram 3

Conclusion

Several IEPs of calcium/silica (Ca/Si) type were synthesized. The pigments in powdery state were characterized by the following parameters: specific mass, oil consumption, pH value and specific conductivity of aqueous extract of the pigment. Coatings based on aqueous epoxy emulsion and on solvent epoxy resin were formulated and prepared. The IEPs were applied on low carbon steel panels. The effect of these non-toxic pigments on the protective properties of coatings was tested by means of natural and accelerated corrosion tests (humidity, salt spray and SO_2). Generally, all the pigments showed very good anticorrosion protection. Especially coatings on the base of epoxy resin showed extreme efficiency. The best of all pigments was Mica SFG + 20 % CaO.

Acknowledgments

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