

ANTICORROSION PEROVSKITE PIGMENT BASED ON STRONTIUM TITANATE

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Abstract

Synthesized strontium titanate researched in the paper appears to be a promising anticorrosion pigment. Nowadays, strontium titanate is prepared from anatase and strontium carbonate by high temperature synthesis. The pigment was researched by means of X-ray diffraction, particle size distribution measurement, scanning electron microscopy, with specific mass, oil consumption and critical pigment volume concentration (CPVC). The strontium titanate was used to prepare solvent type of epoxy – ester resin based coatings with varying PVC of the strontium titanate pigment. The coating was tested for physical and anticorrosive efficiencies. It was analysed that strontium titanate of perovskite structure is a highly efficient anticorrosion pigment.

Keywords: perovskite, strontium titanate, coating, anticorrosive, pigment, anatase

1 Introduction

The anticorrosion efficiency of protective coatings depends on the perfect pre-treatment of the metal surface [1,2], the type and concentration of the anticorrosion pigment [3-6], the method of film creation [7,8], the adhesion of the coating to the metal base [9,10], and on the mechanical properties of the whole coating system [11-13].

The group of corrosion-inhibiting pigments includes the pigments that actively participate, in several ways, in extending the life of coating [4]. The anticorrosion pigments working on a chemical principle are soluble to a certain extent and their ions are thus capable of interacting, at the interface of their particles, with the surface of a metal base, or with the functional groups of a binder during the drying of coating films. Simultaneously, there can occur oxidation-reduction processes that are connected with the creation of new compounds with inhibitive effects [6]. The anticorrosion pigments with electrochemical effects passivate a metal base material electrochemically. Their effects are either in the anodic or cathodic area. The primary particles of barrier pigments have a nonisometric particle structure and assume a position that is parallel to the base during the drying of the coating film. This orientation contributes to the improvement of the film's mechanical properties, inhibits the direct permeation of humidity, oxygen and corrosive ions, and protects the binder from degradation by UV radiation.

The last ten years witnessed a nearly complete replacement of chromates and lead anticorrosion pigments with phosphate anion-based pigments of which zinc orthophosphate found most applications [14-16]. To enhance its anticorrosion efficiency, zinc orthophosphate was modified in several ways or combined with other effective components, including molybdates [17], organic inhibitors of corrosion [18] and oxides modifying a system's pH [19-20]. However, some negative aspects of the use of zinc compounds in paints have been revealed in the course of time [21].

One of possible solutions is the use of anticorrosive pigments containing calcium or strontium as a cation [22]. At present, the application of pigments whose inhibiting effects are based on the exchange of ions appears to be the most promising option in the area of anticorrosion paints.

Calcium ranks among the most widespread elements in the earth crust. Due to its high reactivity it never occurs in a metal form but always in compounds with other.

Research into the inhibitive behaviour of calcium salts started already in the past, concluding that unlike the Zn^{2+} ions the Ca^{2+} ions are nearly five times more efficient when inhibiting steel corrosion in their aqueous extract. However, when applying an anticorrosion pigment in a paint film consisting of a polymeric binder the solubility of the pigment has to be taken into account, because too low solubility in water results in low inhibitive efficiency while too high solubility results in the disturbance of the polymeric matrix and paint cohesion. Therefore, it is always necessary to find an appropriate compromise between substance solubility and its anticorrosion effects. The attempts to increase the calcium content led to the synthesis of strontium titanate whose perovskite structure comprises many more calcium ions [23].

In perovskite, the large ions of Ca^{2+} and O^{2-} together with a smaller Ti^{4+} cation that is individually placed in one of many gaps create a tightly arranged structure. Other double oxides with a perovskite structure are $SrTiO_3$ or $CaZrO_3$ [24].

2 Experimental materials and methods

2.1 Preparation of $SrTiO_3$ with a perovskite structure

Titanium dioxide of anatase kind and calcium carbonate were used at a molar ratio of 1:1 to prepare $SrTiO_3$ of perovskite structure acting as an anticorrosion pigment. Both starting substances were homogenized in a planetary spherical mill for six hours. The subsequent procedure completed the high-temperature calcinations of the homogenized mixture. The mixture was calcinated at 1180 °C, with a maximum holding period of three hours, and a heating rate of 5°C per minute. A sample was taken from the prepared product to be subjected to an X-ray diffraction analysis that identified the complete reaction of the starting substances. The product was transferred to a suspension in ethanol and then ground in the planetary spherical mill for seven hours. The obtained product was dried in a laboratory drier at 110°C. Using scanning electron microscopy (SEM), pictures of particles of the prepared pigment were taken (Fig. 1) and the distribution of particle sizes was measured.

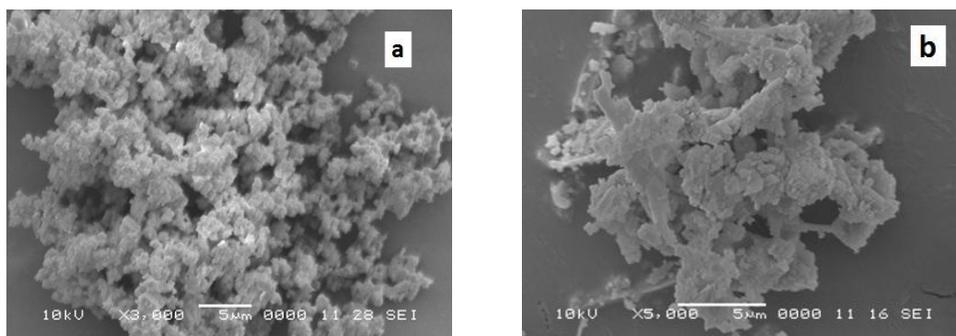


Fig. 1 SEM electron micrographs a) anatase, b) $SrTiO_3$

The structure of strontium titanate ($SrTiO_3$) of perovskite structure can be derived from the structure of CsCl by replacing all Cs atoms with Sr atoms and by subsequently replacing Cl atoms with TiO_6 octahedrons.

2.2 Formulation of paints containing a synthesized pigment

Paints were prepared by dispersing pigments in epoxy – ester resin of solvent type. Dispersion was first carried out in a dissolver and the obtained paste was later exposed to dispersion proper in a pearl mill. The SrTiO₃ to a binder ratio was defined so as to create a concentration line of 0-35 vol. % (PVC = 0, 5, 10, 15, 20, 25, 30 and 35 vol.%). **Table 1** indicates the charges of raw materials required for the preparation of testing paints with the SrTiO₃ content. The formulation of the paints containing TiO₂ employed the same concentration line PVC = 0-35 vol. %.

2.3 Testing paint preparation

Testing paints were prepared on steel, cold rolled sheets (by the Q-panel company) provided with a standard finish. For the purpose of selected tests, the paints were prepared on glass boards (measurement of paint hardness). The paints were performed by means of an applicator so that the final thickness of the dry film was 90±3 µm. Upon producing the paints, the samples were conditioned in an air-conditioned box at 23°C and a relative humidity of 50% for 30 days.

3 Results and discussion

Strontium titanate affects the physical-mechanical properties of epoxy coatings. Thanks to the shape and morphology of their particles as well as thanks to the possible ferroelectric properties displayed by M^{II}_nTiO₃-type substance, the mechanical properties of pigmented coatings are better than those of the binder alone, which applies mainly by the cupping test.

Table 1 Results of the mechanical test of the paints containing strontium titanate and titanium dioxide of varying concentrations (DFT = 65±3 µm)

PVC vol. %	Lattice adhesion /peel off [dg.]/[MPa]	Cupping [mm]	Bend [mm]	Impact [cm]
SrTiO₃				
0	0 / 4.5	5.0	< 4	100
5	0 / 4.5	6.2	< 4	100
10	0 / 4.7	≥10	< 4	100
15	0 / 4.4	≥10	< 4	100
20	0 / 4.5	10	< 4	75
25	0 / 4.3	10	4	60
30	0 / 3.8	10	4	60
35	0 / 3.5	9	5	55
40	1 / 3.2	9.0	5	50
TiO₂				
0	0 / 4.7	5.0	< 4	100
5	1 / 3.1	4.8	4	78
10	2 / 2.4	3.3	15	45
15	3 / 2.1	0.9	15	37
20	3 / 2.1	0.8	15	36
25	3 / 2.4	0.9	20	31
30	4 / 1.78	0.6	20	26
35	5 / 0.6	-	-	7
40	5 / 0.4	-	-	5

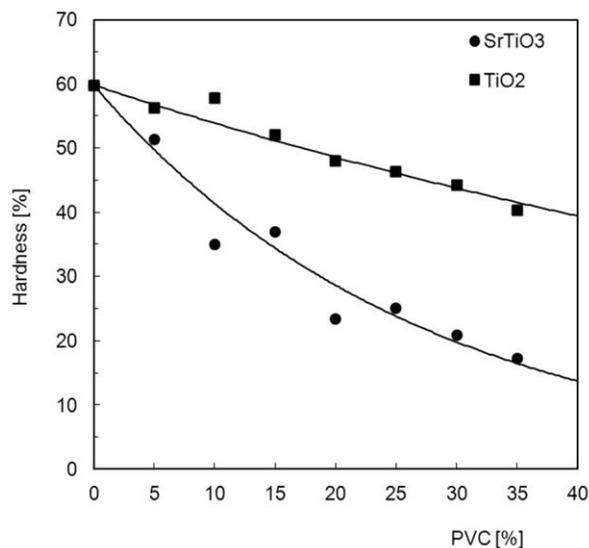


Fig. 2 Dependence of the final hardness of the coatings pigmented with SrTiO₃ and TiO₂ to their concentration (the hardness of the coatings after 50 days of ageing)

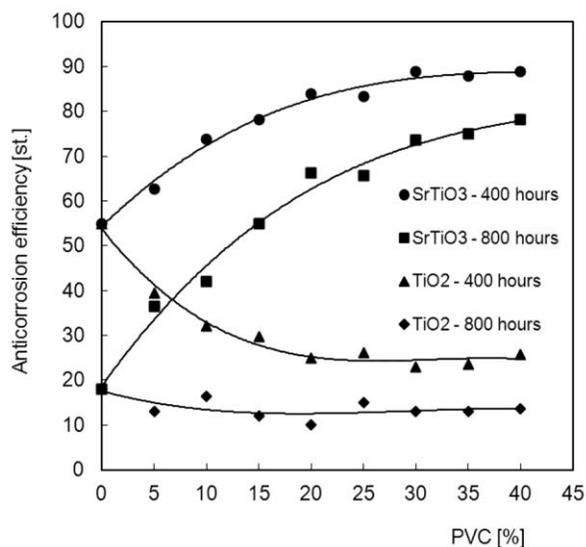


Fig. 3 Anticorrosion efficiency of the coatings pigmented with SrTiO₃ and TiO₂ in dependence on pigment concentration (PVC) following 400 and 800 hours of exposure in a condenser chamber

Throughout the entire PVC concentration line = (0;40 vol.%), the mechanical properties are either substantially better than or fully comparable to a pure non-pigmented coating (PVC = 0 vol. %). For the purpose of comparison, **Table 1** indicates the results of the mechanical properties of epoxy-ester based coatings pigmented in the same concentration line with titanium

dioxide of anatase type. The results are fully in harmony with the knowledge of the deterioration of the mechanical properties of the paints during their pigmentation with isometric particles, particularly in the area of CPVC.

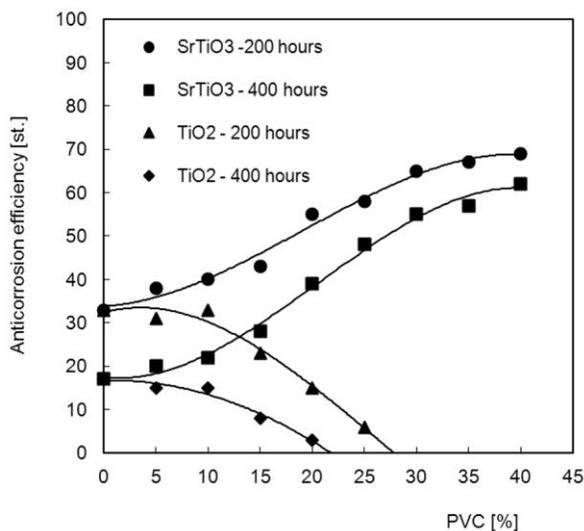


Fig. 4 The anticorrosion efficiency of the coatings pigmented with CaTiO_3 and TiO_2 depending on pigment concentration (PVC) after 200 and 400 hours of exposure in a NaCl salt spray chamber

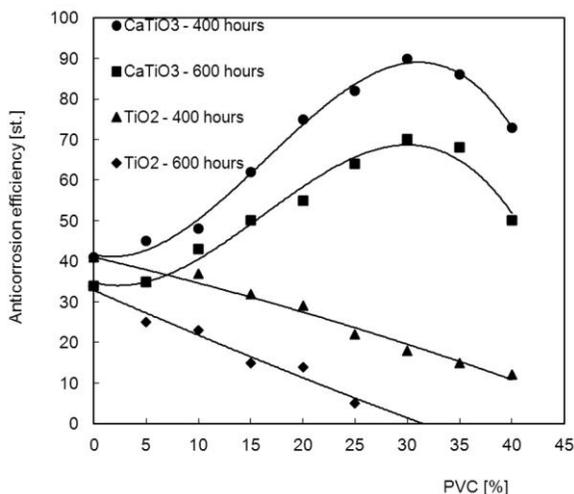
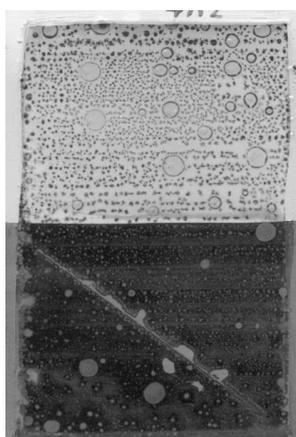


Fig. 5 Anticorrosion efficiency of the paints pigmented with CaTiO_3 and TiO_2 in dependence on pigment concentration (PVC) after 400 and 600 hours of exposure in a condenser chamber with the SO_2 content

As the obtained results imply, strontium titanate has positive effects on the adhesion of the coatings to the steel substrate. These lattice adhesion test results are shown in **Table 1**.

The hardness of the pigmented coatings was measured by means of a pendulum apparatus, type Perzos, as the time dependence of hardness on the time of film hardening-through applicable to varying concentrations of the studied pigments. **Fig. 2** displays time dependencies of film hardness. It is obvious that the improved mechanical properties of the coatings are connected with their lower hardness. Strontium titanate reduces the hardness of the coatings and the pigmented films are even less hard than the binder alone. In case the pigmentation lies within a range of 0 – 30 vol.%, the hardness of the coatings diminishes; whereas, the same hardness is enhanced if PVC is 30 vol.% or higher.



Epoxy-ester binder (PVC = 0%)

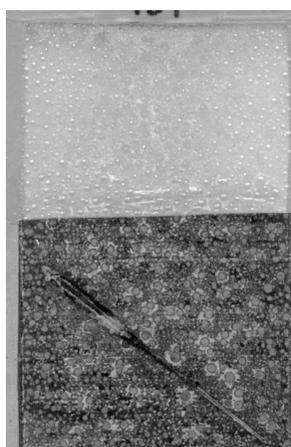
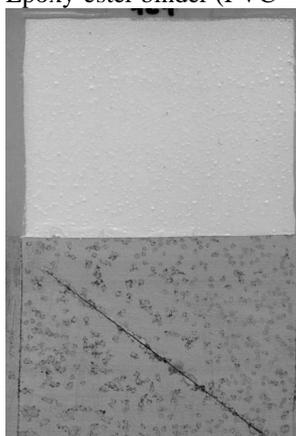
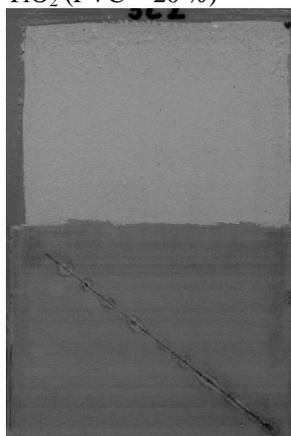
TiO₂ (PVC = 20 %)SrTiO₃ (PVC = 10 %)SrTiO₃ (PVC = 20 %)

Fig. 6 Photographs of the test steel panels following 400 hours' exposure in the NaCl salt spray cabinet

Strontium titanate shows maximum anticorrosion efficiency in a range from 15 to 20 vol. %. Strontium bonded in the lattice of perovskite is released by controlled hydrolysis to react on the surface of the substrate with the products of a cathodic corrosion reaction, thus forming a highly efficient passivation layer.

In general, corrosion tests performed in salt spray cabinets provide exacting test for water-borne coatings. This is why the test panels were evaluated after completing only 300 hours of

exposure, which exposure time was long enough to exhibit obvious differences between a non-pigmented coating (PVC=0%), a pigmented coating with the SrTiO₃ content and a coating containing inert TiO₂ – anatase. 500 hours of exposure in a salt spray cabinet unambiguously demonstrated the inhibiting properties of the coatings pigmented with strontium titanate. **Fig. 3-5** present the dependencies of the anticorrosion efficiency of the epoxy ester resin based coatings on their PVC. The corrosion tests results after 200 and 400 hours of exposure in the condenser chamber with the SO₂ content are featured in **Fig. 5**. The illustrated dependencies indicate that in this test the optimum concentration of the paints pigmented with strontium titanate is between 15 and 20 vol. % of the effective substance. Like in the previous tests of corrosion stress, TiO₂ – anatase does not have positive effects on the anticorrosion properties of the epoxy coatings. **Fig. 6** depicts the test steel panels after the removal of some of the coating, specifically its condition after 800 hours of exposure in the condenser chamber.

4 Conclusion

Synthesized strontium titanate pigment provides promising anticorrosive properties. In corrosion tests, epoxy-ester coatings containing 15-20 vol. % of this pigment exhibit high anticorrosion efficiency compared to coatings pigmented with TiO₂ only. The physical-mechanical properties of the paints with the SrTiO₃ content have more advantages than in pigmentation with titanium dioxide. The properties of the paints containing strontium titanate are favourably affected mainly by the convenient shape and distribution of the size of the particles. The hot-temperature method described in this research paper was employed to formulate an anticorrosion pigment that finds appropriate applications especially in water-borne paints.

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