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Properties of Metal Oxide Pigments Surface Modified with Polyaniline Phosphate and Polypyrrole Phosphate in Corrosion Protective Organic Coatings

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Additional information is available at the end of the chapter

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Abstract

The objective of this work was to describe the properties of metal oxide-based pigments whose surface has been coated with a conductive polymer, if used as pigments in organic coating materials. The perovskite-type pigments were synthesized by high-temperature solid-phase reaction, and their surface was modified with a conductive polymer, specifically polyaniline phosphate or polypyrrole phosphate, by chemical oxidative polymerization. The pigments' structure and physicochemical properties were examined by XRD, XRF, and SEM. The composite pigments (pigment/conductive polymer) were dispersed in a solvent-type epoxy-ester resin binder to obtain a series of paints whose anticorrosion properties were assessed by means of corrosion tests in simulated corrosion atmospheres and by the linear polarization method. The anticorrosion and mechanical properties of the paints were compared with those of a paint containing the routinely used zinc phosphate hydrate pigment as a reference material. The pigments were found to possess a high anticorrosion efficiency, comparable to or higher than that of the commercially available zinc phosphate-based anticorrosion pigment. The highest anticorrosion efficiency was observed with the paints containing the Ca-Ti, Sr-Ti, and Sr-Mn perovskite pigments modified with polypyrrole phosphate.

Keywords: organic coating, anticorrosion pigment, polyaniline phosphate (PANI), polypyrrole phosphate (PPY), perovskite

1. Introduction

The most widespread method to protect the surfaces of metallic materials consists in coating them with paints possessing anticorrosion properties [1, 2]. The mechanism consists in an electrochemical reaction of the anticorrosion pigment with the metal itself or with the corrosive substances penetrating through the paint film from the outer atmospheric environment [3]. Corrosion-inhibiting pigments include materials that are actively engaged in the paint film lifetime extension [4]. Anticorrosion pigments acting on the chemical principle are soluble to some extent, contain water-soluble components that may maintain a constant pH in the paint layer, such as is more favorable for reducing the corrosion rate [5]. Electrochemically acting anticorrosion pigments passivate the substrate metal protected by the layer of the organic coating, acting either in the anodic region or in the cathodic region.

Many of the compounds are toxic or not entirely harmless/environment-friendly. So, new anticorrosion pigments are sought, equally efficient as the existing ones, but free from the harmful heavy metals (Pb, Cr (VI), Cd, Ni ...) [6–8]. Nontoxic pigment types started to be sought in the 1960s, but no equivalent substitutes for lead or chromium (VI)-based pigments have been found so far [9].

Among substances showing promise from the anticorrosion protection aspect are conductive polymers [10]. Added to paints on their own, conductive polymers cause certain troubles which must be addressed, for example, their effect on the liquid paint stability, paint adhesion if exposed to a high humidity/moisture, good dispersion in the binder and in the film, and the conductive polymer's efficient concentration in the organic binder to hinder corrosion of the substrate metal. So, it is frequently more convenient, rather than use the conductive polymer alone, to use composite pigment particles where a layer of the conductive polymer is deposited on an inorganic carrier particle. Metal oxides can be used as inorganic carrier particles.

Metal oxides of predominantly ionic nature of the MO (or M_2O) type include, for example, MgO, SrO, or NiO, which are not routinely used as ingredients in organic coating materials and paints. The M_3O_4 type is an exception, reminding of double oxides, such as the oldest anticorrosion pigment minium, Pb_3O_4 , in which lead exists in two oxidation states. The other type includes oxides whose lattice, in contrast to the former type, is dissimilar to the structure of simple compounds. Most important in this group are three oxide types: ilmenite, $FeTiO_3$; spinel, $FeAl_2O_4$; and perovskite $CaTiO_3$ [11]. The basic formula of perovskites is ABO_3 , where cation *A* is relatively bulky and its valency is low (e.g., Sr^{2+} , Ca^{2+} , La^{3+}), whereas cation *B* is relatively small (e.g., Ti^{4+} , Zr^{4+} , W^{6+} , Fe^{3+} , Mn^{3+} , Zn^{2+}). The perovskite-type oxides, whose properties can be modified through the selection of the structural lattice-forming elements, were selected owing to the stability of their physical and chemical properties [12, 13], insolubility, and thermal stability. It is also an asset of perovskites that they can be synthesized from a wide range of starting materials that are nontoxic and are reasonably environment-friendly. The Ca^{2+} and Sr^{2+} cations were selected owing to their properties, which may be beneficial in suppressing corrosion of the metal surface beneath the paint film. The choice of those cations (Ca or Sr) in the perovskite structure can also be made use of to improve the inhibiting behavior of the pigments, viz., through their rate or ease with which the cation can be released from the

elementary lattice to act in the paint film. The perovskite carrier as well as the conductive polymer should modify the electric conductivity of the composite pigment particles and affect favorably the properties of the paint film when hindering electrochemical corrosion in environments with enhanced humidity/moisture, acid-nature corrosive substances, and corrosion initiators. If the perovskites prove to be good carriers for the conductive polymer layers (pigment/conductive polymer system), they may open up the door to additional interesting applications of the pigments as well as of the conductive polymers [10, 14].

2. Formulation of the anticorrosion organic coatings with polyaniline (PANI) phosphate

Thanks to its high electrical conductivity, PANI phosphate (hereinafter referred to as “polyaniline” or “PANI”), a conducting polymer, appears to be a possible inhibitor of corrosion reactions. Because all redox processes involving polyaniline are based on a transfer of electrons, the concentration of PANI is likely to be also important. If its inhibition properties and efficiency were proven in a paint film, it would suggest its prospective applications in organic binders where it would function as an organic corrosion inhibitor or in the form of an anti-corrosion pigment.

Analyses of results of the laboratory tests of corrosion resistance concluded that the best anticorrosion efficiency was displayed by an epoxy-ester coating pigmented with polyaniline to pigment volume concentration, $PVC_{PANI} = 15 \text{ vol.}\%$. This concentration facilitates the best anticorrosion effects of PANI in all the applied corrosion environments and approximately corresponds to the percolation threshold of conducting polyaniline dispersed in the nonconducting matrix (**Figure 1**) [15–17].

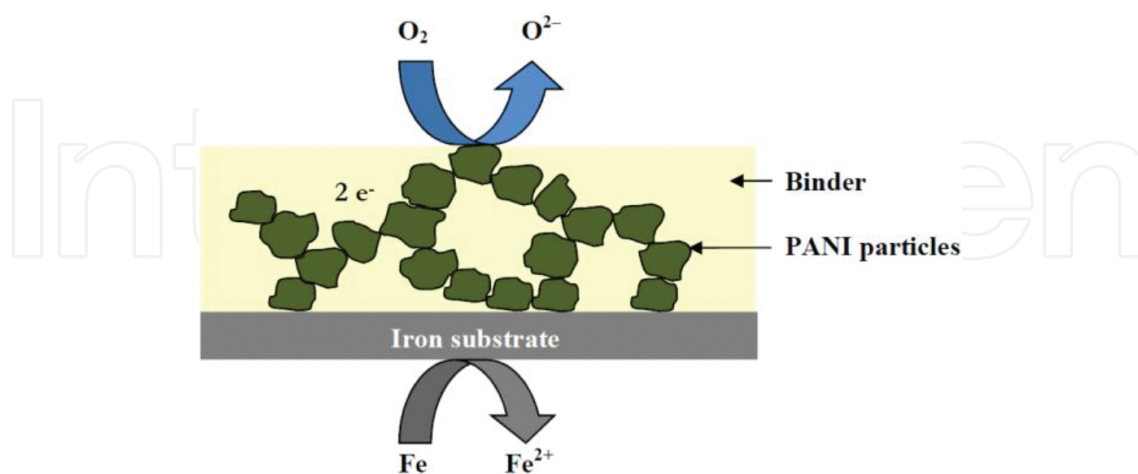


Figure 1. The possible role of polyaniline, at concentrations above the percolation threshold in the corrosion.

The pigments affect not only the anticorrosion properties of the coating materials but also the physicomechanical properties of the coating films. The role of percolation threshold of

polymer-conductive materials can be connected with the role of the CPVC value of the powdery pigment and with the optimum performance properties of the pigmented paint film (**Figure 2**). When present in a volume concentration much less than the critical level, the pigment particles are isolated, mutually separated by the binder. Such a coating material is glossy and nearly impermeable by water vapor. As the PVC is increased, the pigment particles become closer to one another, although still separated by the binder. The film acquires hardness and tensile strength, while its elongability and gloss decrease. The properties of the film change depending on the type of pigment, till the PVC reaches its critical value ($PVC = CPVC$). At this point, the amount of binder is just sufficient to fill the space between the pigment particles. When the pigment concentration is further increased, the amount of binder is insufficient to fill the space between the pigment particles. The film contains air, and its properties change dramatically. Mechanical properties fail, and substrate metal corrosion and film blistering are appreciable in cases where the coating contains inorganic pigments. The optimum performance of pigmented coating is usually achieved below the CPVC value [18].

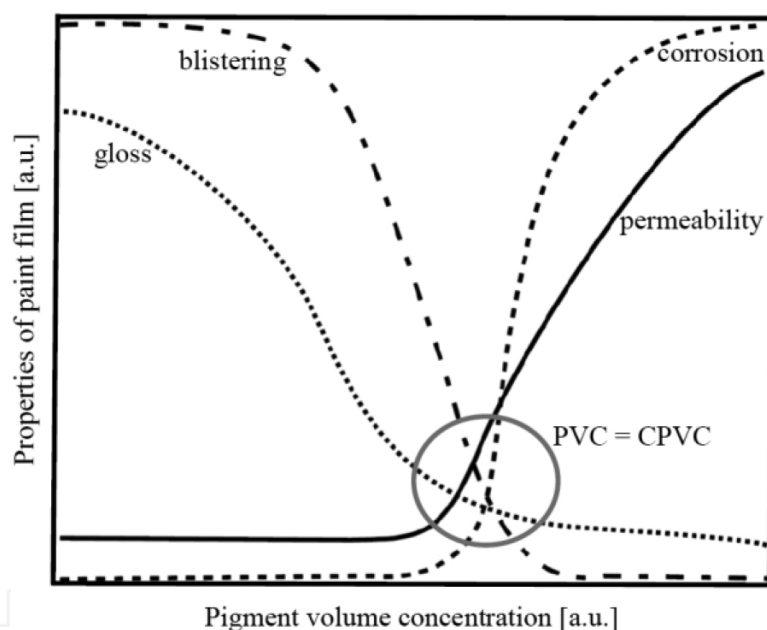


Figure 2. Coating properties depending on the degree of pigmentation (PVC). Notes: (a) The dependence of the properties of a pigmented film on PVC.

The goal of this study was to prepare a series of perovskites, coat their surfaces with layers of a conductive polymer—polyaniline phosphate (PANI) or polypyrrole phosphate (PPY) to obtain composite pigments (pigment/conductive polymer) with anticorrosion properties, and use them in paints for metallic substrate corrosion protection. The pigments with particles coated with a layer of a conductive polymer should exhibit properties of the conductive polymer, in particular, a higher conductivity for active protection of the metal against electrochemical corrosion, anticorrosion efficiency when exposing the system to corrosive substances with pH in the acid region, and passivation of the metal surface during corrosive damage of the organic coating.

2.1. Experimental

2.1.1. Laboratory preparation of the perovskite-type pigments

Perovskites with a generally isometric particle [13, 19] shape were synthesized to serve as the pigment cores for coating with conductive polymers and to be added to a binder to form anticorrosion paints. Pigments possessing the simple perovskite structure, $MeTiO_3$, $MeMnO_3$ ($Me = Ca, Sr$), were synthesized by calcination (Eqs. (1)–(2)).



The materials for the preparation of the pigments were as follows: titanium oxide (Precheza a.s. Prerov, CZ, composition: TiO_2 anatase); calcium carbonate (Omya a.s. Austria, composition: $CaCO_3$, natural calcite); strontium carbonate (Sigma-Aldrich Chemie, Germany, composition: $SrCO_3$); manganese (III) oxide (Sigma-Aldrich Chemie, Germany, composition: Mn_2O_3).

The pigments were synthesized by solid-phase reaction, viz., by high-temperature calcination of the homogenized mixtures of the starting materials [20] by following the general principles of preparation of high-temperature inorganic pigments [21]. The process of preparing the pigments consists of four operational steps: homogenization of starting compound mixtures, calcination procedure, leaching the calcination products by washing with water, and adapting the product to obtain the size of particles as necessary by a wet grinding process. The process was conducted as a two-stage procedure: the pigments were first calcined at 1000°C for 2 h and then at 1180°C . Since a suitable size of the pigment particles is a very important factor, the calcination step was followed by wet milling, performed in a planetary ball mill Pulverisette 6 (Netzsch, Germany). The pigment powder was placed in a milling container made from zircon-silicate ceramics and milled with rollers made from the corundum ceramics. The rotation speed was 400 rpm, and the process was conducted for 4–5 h. The milled pigments were followed rinsed with a multiply larger volume of distilled water followed by drying at 105°C in a hot-air dryer for 10 hours.

2.1.2. Perovskite structure examination

The structure of the perovskites was examined by X-ray diffraction (XRD) analysis. The results gave evidence that the required structure had been attained. ABO_3 was found to be the majority phase in most of the pigments. Some of the pigments contained traces of the starting TiO_2 or of reaction by-products. The pigment $CaTiO_3$ contained the main crystalline phase of $CaTiO_3$ and a small amount of rutile (TiO_2), $Ca(OH)_2$, and $CaCO_3$; $SrTiO_3$ contained the $SrTiO_3$ crystalline phase by TiO_2 (rutile) and $Sr_3Ti_2O_7$; $CaMnO_3$ contained the $CaMnO_3$ crystalline phase; and $SrMnO_3$ contained the $SrMnO_3$ crystalline phase and a small amount of $CaMn_2O_4$.

The results gave evidence that the pigments intended for surface modification with the conductive polymers had been obtained as intended, and are in agreement with previous studies [22].

2.1.3. Laboratory preparation of pigments with conductive polymer surface layers

Four perovskite-type pigments, CaTiO_3 , SrTiO_3 , CaMnO_3 , and SrMnO_3 , were subjected to surface treatment with the conductive polymers with a view to optimizing (enhancing) their anticorrosion properties.

2.1.3.1. Preparation of the perovskites modified with a surface layer of polyaniline phosphate

The pigment was suspended in 250 ml of 0.2 M aniline solution in 0.8 M *ortho*-phosphoric acid, and 250 ml of 0.25 M ammonium peroxodisulfate, also in 0.8 M *ortho*-phosphoric acid, was added to initiate the aniline polymerization process. The suspension was stirred for 1 h during which aniline polymerized on the surface of the pigment particles. Next day, the solids were filtered out and rinsed with 0.4 M phosphoric acid followed by acetone. The pigment particles coated with the polyaniline phosphate (PANI) overlayer were dried in air and then at 60°C in a laboratory drier [23].

2.1.3.2. Preparation of the perovskites modified with a surface layer of polypyrrole phosphate

The pigment was suspended in 250 ml of distilled water with 0.8 M *ortho*-phosphoric acid, and 0.2 M pyrrole was added. The system was stirred vigorously by using a glass stirrer, and an oxidant solution consisting of 0.25 M ammonium peroxodisulfate in 250 ml of distilled water was added. The whole solution was stirred for approximately 1 h. Next day, the solids were filtered out and rinsed with 0.4 M phosphoric acid followed by acetone. The pigment particles coated with the polypyrrole phosphate (PPY) overlayer were dried in air and then at 60°C in a laboratory drier [23].

2.1.4. Characterization of the composite pigments containing a layer of a conductive polymer—PANI or PPY

A total of eight perovskite-type pigments with their surfaces modified with PANI or PPY were prepared and subjected to X-ray fluorescence (XRF) analysis on a Philips PW 1404 X-ray spectrometer equipped with a Rh cathode, in conjunction with UniQuant software enabling 74 elements (from fluorine to uranium) semiquantitatively determined (10% relative error). XRD spectra of the synthesized perovskites were measured on an X'Pert PRO MPD 1880 X-ray diffractometer (PANalytical, the Netherlands). The diffraction data were evaluated by means of the X'Pert programs (X'Pert HighScore Plus Software version 2.1b and X'Pert Industry Software version 1.1g); the phases were identified using data from the ICDD PDF2 diffraction database. The pigment surface and particle shape were examined on a JEOL-JSM 5600 LV scanning electron microscope (JEOL, Japan) in the secondary electron mode [24].

2.1.5. Determination of the physicochemical properties of the pigments with conductive polymer surface layers

Determination of particle size and the distribution of pigment particle size were identified by means of Mastersizer 2000 (Malvern, Instruments Ltd., UK), which is able to measure the distribution of particle sizes from 0.01 to 2000 μm . Particle size is represented by the diameter of the equivalent sphere, that is, sphere whose laser radiation dispersion patterns are identical with those of the particle in question. The pigments' specific weights were determined by using a AccuPyc II 1340 gas pycnometer (Micromeritics, USA). Linseed oil absorption was measured by the pestle-mortar method. The outcome, called the oil number (in g/100 g), is a prerequisite for calculation of the CPVC and for the formulation of the paints [25, 26]. The determination of the pH level of aqueous extracts of the pigments was based on the ISO 789-9 standard. 10% pigment suspensions in redistilled water ($\text{pH} = 7$) were prepared and measured periodically during 28 days, after which they were filtered, and the ultimate (constant) pH value of the filtrate (pH_p), was recorded. Specific electrical conductivity of the 10% pigment suspensions (χ_p) was based on the ISO 787-14 standard. The pH values of aqueous extracts (pH_f) prepared from 10% suspensions of loose paint films and the specific electric conductivity values of aqueous extracts (χ_f) prepared from suspensions of loose paint films at PVC=1, 5, 10, and 15% were determined by the same method. The water-soluble fraction was measured gravimetrically by extraction of the powdered pigment, weighed with a precision of ± 0.01 g in distilled water at 20°C (W_{20}). This procedure was derived from the ČSN EN ISO 787-3 standard.

2.1.6. Assessment of the anticorrosion efficiency of the pigments with conductive polymer surface layers

Model solvent-based epoxy-ester resin-based paints were formulated for investigation of the pigments' anticorrosion properties. Description of binder is as follows: a 60% solution of a medium high-molecular weight epoxy resin esterified with a mixture of fatty acids of dehydrated ricin oil and soy oil, trade name WorléeDur D 46, acid number 4, viscosity 2.5–5.0 Pa·s, flow time (DIN 53211-4200) 250 s. The PVCs in the paints were invariably 1, 5, 10, and 15%. The PVC/CPVC ratio was adjusted in all the model paints to 0.50 by means of the anticorrosion-neutral filler calcite CaCO_3 . The total pigment plus filler concentration in the paint film was 50%, whereby a constant total concentration of the powder fractions in the dry paint film was assured, while varying only the proportion of the composite pigment. The paints were prepared by dispersing the powders in the liquid binder in a pearl mill Dispermat CV (VMA Getzmann GmbH Verfahrenstechnik, Germany). Co-octoate in a fraction of 0.3 wt.% was used as the siccative.

Test samples were prepared by applying the paint to steel panels (deep-drawn cold-rolled steel, manufactured by Q-panel, UK) 150 mm \times 100 mm \times 0.9 mm size, by using a box-type application ruler with a 250 μm slot, modified as per ISO 1514. The dry film thickness (DFT) was measured with a MiniTest 110 magnetic thickness gauge fitted with a F16-type probe (ElektroPhysik, Germany) in accordance with ISO 2808 [27]. A total of 10 test panels was prepared for each paint. A thin cut (groove) 7 cm long, which penetrated through the paint film and reached the substrate metal, was made by means of a sharp blade. The samples on the test panels were allowed to dry in standard conditions (temperature, 20°C ; relative

humidity, 50%) in a conditioned laboratory for 6 weeks. Paint films on polyethylene sheets were also prepared, peeled off when dry, and cut to pieces approximately 1 mm × 1 mm size. The unsupported films were used to prepare aqueous paint film suspensions in distilled water.

2.1.7. Laboratory corrosion tests

2.1.7.1. Cyclic corrosion test in an atmosphere with NaCl mist and condensing moisture

In this cyclic corrosion test, the test panels were exposed to the mist of a 5% NaCl solution at $35 \pm 2^\circ\text{C}$ for 10 h (first cycle stage) and to condensing distilled water at $40 \pm 2^\circ\text{C}$ for 1 h (second cycle stage), followed by drying at $23 \pm 2^\circ\text{C}$ (third cycle stage). The test encompassed 59 cycles, that is, its total time was 1416 h. The tests were conducted in a Liebis S 400 salt chamber (Liebis Labortechnik, Germany). The procedure was based on the ISO 7253 standard.

2.1.7.2. Cyclic corrosion test in an atmosphere of condensed moisture and SO_2

This test consisted of 24-hour cycles comprising condensation of water with SO_2 at $36 \pm 2^\circ\text{C}$ for 8 h (first cycle stage), followed by drying at $23 \pm 2^\circ\text{C}$ for 16 h (second cycle stage). The test was conducted in a Liebis V 400 corrosion chamber (Liebis Labortechnik, Germany), and the samples were evaluated after completing 67 test cycles, that is, in 1608 h. The test procedure was based on the ISO 3231 standard.

2.1.8. Corrosion test evaluation methods

After completing the corrosion tests, the paints were evaluated by methods derived from the ASTM D 714-87, ASTM D 610, and ASTM D 1654-92 standards. The corrosion phenomena evaluated included formation (size and frequency of occurrence) of blisters in the paint film surface and near a cut made in the film, percent fraction of substrate metal surface area affected by corrosion, and distance of propagation of substrate metal corrosion near the cut (in mm, both evaluated after removing the paint film).

By connecting all the three (four) methods for the evaluation of various manifestations of the corrosion substrate attacks and of protective film alone, we can obtain a single value of the protective efficiency. The results were converted to scores on a 100–0 scale, and a parameter called the overall anticorrosion efficiency of the paints was calculated by a mathematical relation [28]. The total anticorrosion efficiency from the cyclic corrosion tests ($E_{\text{NaCl}}, E_{\text{SO}_2}$) was calculated as the arithmetic mean of the scores [29].

2.1.9. Linear polarization

The linear polarization method is applied to corrosion monitoring. It is designed specifically for the determination of the polarization resistance R_p and current density I_{corr} . Linear polarization was measured in a cell accommodating the reference electrode (saturated calomel electrode—SCE), counter-electrode (platinum electrode), and working electrode constituted by the sample. The method is based on the fact that a linear segment near the corrosion potential occurs on the polarization curve in linear coordinates.

A 1 cm² area of the working electrode in the measuring cell was exposed to a 3.5 wt.% NaCl solution. The cell was connected to a potentiostat/galvanostat (VSP-300/France). The paint films were exposed to the NaCl solution for 24 h, after which they were measured by the linear polarization method. The polarization region was from -10 mV/*E*_{OC} to +10 mV/*E*_{OC} at a rate of 0.166 mV/s. The following parameters were evaluated for each paint: spontaneous corrosion potential (*E*_{corr}), tafel region slopes (β_a and β_c), current density (*I*_{corr}), polarization resistance (*R*_p), and corrosion rate (*v*_{corr}). Polarization resistance *R*_p is defined as the inverse values of the current density *I* against the curve of the spontaneous corrosion potential *E* (at which *dE* → 0) [29, 30].

2.1.10. Comparison experiments

The anticorrosion pigment based on the zinc phosphate hydrate Zn₃(PO₄)₂·*x*H₂O (PVC = 15%) was also tested as a reference material, allowing us to compare the results obtained with the pigments synthesized by us with those obtained with a commercially available product. Films of the coating materials free from any pigment were also used in some tests, in the linear polarization measurements.

2.2. Results evaluation

2.2.1. Structure and morphology of the composite pigment particles

Four perovskite-type pigments were subjected to surface treatment with the conductive polymers PANI and PPY. Like the bare perovskite pigments, the pigments coated with the conductive polymers were subjected to XRD and XRF analyses to elucidate their structure and composition. The results of the XRF data of the initial untreated pigments are listed in **Table 1**.

Parameter [wt.%]	CaMnO ₃	SrMnO ₃	CaTiO ₃	SrTiO ₃
Al ₂ O ₃	3.00	0.70	3.20	3.40
SiO ₂	0.25	0.16	0.41	0.11
CaO	43.61	–	39.44	–
MnO	53.14	57.72	–	–
SrO	–	41.42	–	52.98
TiO ₂	–	–	56.95	43.51

Table 1. Results of XRF analysis of the untreated pigments (the data are in wt.%; elements present at concentrations lower than 0.01% are omitted).

The pigments contained Al₂O₃ in the order of tenths to units percent (0.7–3.4%) due to wear of the corundum milling bodies in the milling equipment. For the same reason, the samples also contained trace amounts (0.11–0.41%) of SiO₂. The two substances are neutral with respect to the chemical properties of the anticorrosion pigments. Analysis results (XRF) of surface-treated pigments are given in **Tables 2** and **3**. The surface-modified (composite) pigments contained

the respective oxides (TiO_2 , Mn_2O_3 , SrO , CaO), and also some amounts of compounds from the surface treatment procedure: P_2O_5 and SO_3 (associated with the polypyrrole phosphate/polyaniline phosphate layer). The surface treatment procedure was associated with weight loss of the oxides (of Ti, Mn, Ca, Sr) due to the nature of the medium (strongly acidic, with acids). What is important, however, is the fact that the pigment matrices for the conductive polymers and the mixed oxide contents were ensured (Tables 2 and 3). Once enveloped in a PANI or PPY layer, the oxides were protected from additional dissolution in an aqueous solution of phosphoric acid.

Parameter [wt.%]	$\text{CaTiO}_3/\text{PANI}$	$\text{SrTiO}_3/\text{PANI}$	$\text{CaMnO}_3/\text{PANI}$	$\text{SrMnO}_3/\text{PANI}$
Al_2O_3	2.40	2.40	2.21	1.10
SiO_2	0.25	–	0.11	0.13
P_2O_5	9.50	10.70	8.20	17.80
SO_3	10.10	17.50	41.80	39.10
CaO	27.70	0.10	33.80	0.07
TiO_2	48.60	35.00	–	–
MnO	–	–	13.20	7.53
SrO	–	30.00	–	33.40

Table 2. Results of XRF analysis of the treated pigments/PANI (the data are in wt.%; elements present at concentrations lower than 0.01 % are omitted).

Parameter [wt.%]	$\text{CaMnO}_3/\text{PPY}$	$\text{SrMnO}_3/\text{PPY}$	$\text{CaTiO}_3/\text{PPY}$	$\text{SrTiO}_3/\text{PPY}$
Al_2O_3	2.20	1.30	2.35	2.10
SiO_2	0.12	0.18	0.13	–
P_2O_5	4.90	5.40	2.65	5.50
SO_3	37.20	42.70	16.90	11.50
CaO	34.10	0.08	29.70	0.12
TiO_2	–	–	46.80	42.80
ZnO	–	–	–	–
SrO	–	42.00	–	36.30
MnO	20.80	7.32	–	–

Table 3. Results of XRF analysis of the treated pigments/PPY (the data are in wt.%; elements present at concentrations lower than 0.01% are omitted).

The composite pigments contained amorphous fractions of the conductive polymer and crystalline fractions of the carrier pigment. In addition to the amorphous fractions, which were invariably present, the composite pigments contained the following phases: $\text{CaTiO}_3/\text{PANI}$: a

crystalline phase of CaTiO_3 , a small amount of a by-phase of rutile (TiO_2), and a small amount of corundum (Al_2O_3); $\text{CaTiO}_3/\text{PPY}$: a crystalline phase of CaTiO_3 , minor phases of rutile (TiO_2) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and a small amount of anatase (TiO_2); $\text{SrTiO}_3/\text{PANI}$: a crystalline phase of SrTiO_3 and small amounts of corundum (Al_2O_3) and rutile (TiO_2); $\text{SrTiO}_3/\text{PPY}$: a crystalline phase of SrTiO_3 and a small amount of SrSO_4 ; $\text{CaMnO}_3/\text{PANI}$: crystalline phases of CaMnO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; $\text{CaMnO}_3/\text{PPY}$: a crystalline phase of CaMnO_3 and a smaller fraction of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 ; $\text{SrMnO}_3/\text{PANI}$: a crystalline phase of SrMnO_3 and SrSO_4 ; and $\text{SrMnO}_3/\text{PPY}$: a crystalline phase of SrMnO_3 and a minor phase of SrSO_4 .

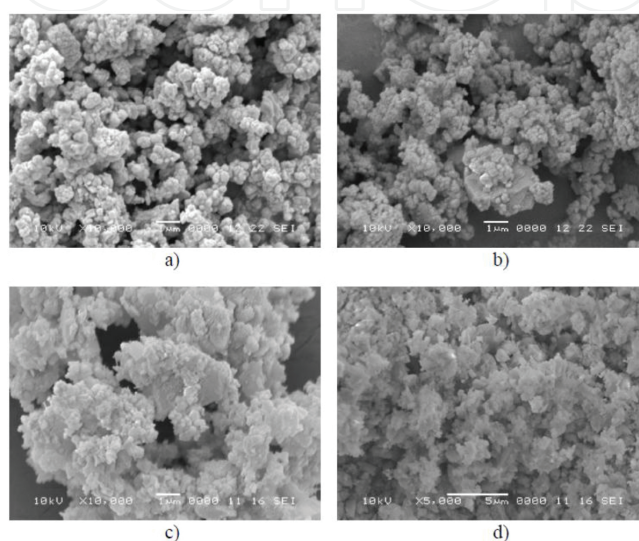


Figure 3. Morphology of perovskite particles with PANI and PPY as observed by SEM (magnification 10,000×). Notes: (a) $\text{CaTiO}_3/\text{PANI}$; (b) $\text{SrTiO}_3/\text{PANI}$; (c) $\text{SrMnO}_3/\text{PANI}$; (d) $\text{CaMnO}_3/\text{PANI}$.

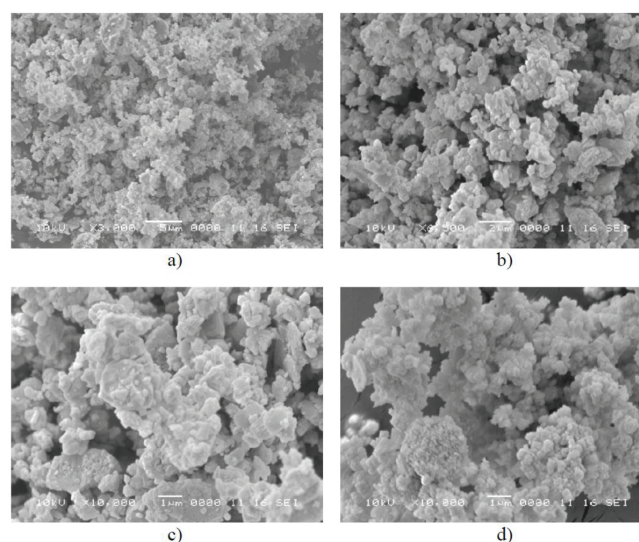


Figure 4. Morphology of perovskite particles with PANI and PPY as observed by SEM (magnification 10,000×). Notes: (a) $\text{CaTiO}_3/\text{PPY}$; (b) $\text{SrTiO}_3/\text{PPY}$; (c) $\text{SrMnO}_3/\text{PPY}$; (d) $\text{CaMnO}_3/\text{PPY}$.

The pigment particle morphology is illustrated by scanning electron micrographs for the perovskites and for the surface-modified perovskites in **Figures 3** and **4**. The micrographs were taken in the secondary electron imaging (SEI) mode. The composite pigments had a tendency to form clusters [30]. The particles of the initial perovskite pigments had a regular nodular shape, which remained unaffected by surface treatment with conducting polymers.

2.2.2. Physicochemical properties of the powdered pigments

The physicochemical properties of the powdery pigments are given in **Tables 4** and **5**, including density, linseed oil consumption, CPVC, pH, specific electric conductivity, particle size distribution, and water-soluble fractions W_{20} . **Table 5** lists the specific electric conductivities of the pigments in dependence on their concentrations in the paint films. The particle size distribution values $D(0.5)$, $D(0.9)$, and $D(0.1)$ show that the size of 50, 90, or 10% particles, respectively, in the volume is smaller than the specified value. $D(4.3)$ is the mean particle size.

Pigment	^a Density (g/cm ³)	^a Oil consumption (g/100 g pigment)	CPVC (%)	Particle size Percent fraction below the specified size			
				$D(0.1)$ (μm)	$D(0.5)$ (μm)	$D(0.9)$ (μm)	$D(4.3)$ (μm)
CaTiO ₃ /PANI	2.97	37	46	1.11	17.29	23.63	19.37
SrTiO ₃ /PANI	2.76	49	41	4.52	12.23	24.89	20.43
CaMnO ₃ /PANI	2.17	57	43	2.45	8.70	16.06	13.87
SrMnO ₃ /PANI	1.42	55	80	2.65	13.61	39.16	38.86
CaTiO ₃ /PPY	2.83	22	60	1.93	21.79	40.29	34.44
SrTiO ₃ /PPY	1.44	49	57	1.86	15.93	17.67	20.45
CaMnO ₃ /PPY	2.54	31	54	1.28	9.17	28.25	13.24
SrMnO ₃ /PPY	2.87	33	50	2.21	15.56	33.22	29.34
Zn ₃ (PO ₄) ₂ ·xH ₂ O	3.28	34	45	0.13	4.78	9.96	5.34
CaCO ₃	2.72	14	71	0.20	5.60	9.99	6.14

^aParameters are given as arithmetic averages within 10 measured values.

Table 4. Physicochemical properties of the powdered pigments.

The mean particle size ($D_{4.3}$) of the perovskites coated with layers of PANI and of PPY lay within the similar ranges of 13.87–38.86 μm and 13.24–34.44 μm , respectively (**Table 4**). The densities of the perovskites coated with layers of PANI and of PPY lay within the ranges of 1.42–2.97 g cm^{-3} and 1.44–2.87 g cm^{-3} , respectively (**Table 4**), that is, less than the densities of the initial inorganic perovskites. The densities of the PANI and PPY powders themselves are 1.58 g cm^{-3} and 1.76 g cm^{-3} , respectively [18].

Pigment/coating	Aqueous extracts of the pigments			Aqueous extracts of the paint films
	W_{20} (%)	$^a\text{pH}_p$	$^b\text{Specific electric conductivity } (\mu\text{S/cm})$	$^a\text{pH}_f$
CaTiO ₃ /PANI	9.46	4.34	2220	6.54
SrTiO ₃ /PANI	5.09	3.00	1450	6.16
CaMnO ₃ /PANI	12.78	5.62	2260	7.44
SrMnO ₃ /PANI	9.78	5.03	994	7.27
CaTiO ₃ /PPY	10.69	5.29	2390	7.28
SrTiO ₃ /PPY	10.07	6.02	1008	7.65
CaMnO ₃ /PPY	18.47	6.26	2100	7.73
SrMnO ₃ /PPY	3.36	6.17	949	7.46
Zn ₃ (PO ₄) ₂ ·xH ₂ O	0.26	6.65	50	7.28
CaCO ₃	0.51	8.47	10	8.47
Nonpigmented film	–	–	–	3.71

^apH was measured with an accuracy ± 0.01 .

^bConductivity was measured with an accuracy $\pm 0.5\%$.

Table 5. Physicochemical properties of the pigments.

Oil consumption of the composite pigments with PANI and with PPY lies within the ranges of 37–57 g and 22–49 g per 100 g of the pigment, respectively (**Table 4**). The values were higher than those measured for the initial perovskite pigments due to the presence of the porous layers of the conductive polymers. The oil consumption data for the composite pigments depended on the pigment particle heterodispersity; in fact, the oil consumption is generally dependent on the particle size and particle shape (i.e., on the specific surface area of the particle) [31].

Knowledge of the critical pigment volume concentration (CPVC) value was a prerequisite for a correct formulation of the pigmented organic coating material [26]. The CPVC value depends on the density and on the pigment's oil number. The CPVC levels were calculated to be about from 41 to 80% for the surface-modified perovskites with PANI and from 50 to 60% for the perovskite pigments surface modified with PPY. From the above data, it follows that the CPVCs of the composite pigments are lower for PANI than for PPY as the surface-modifying conductive polymer (**Table 4**).

2.2.3. Water-soluble contents

The water-soluble contents (W_{20}) of the pigments are listed in **Table 5**. The water-soluble content was higher in the pigments modified with the conductive polymers than in the initial inorganic perovskites due to the presence of minor by-phases, such as CaSO₄ or SrSO₄. The lowest content of substances soluble in cold water, $W_{20}=3.36\%$, was found in the SrMnO₃/PPY

system, and the highest content, $W_{20}=18.47\%$, in the $\text{CaMnO}_3/\text{PPY}$ system due to the presence of the by-phase of CaSO_4 . The differences in the water-soluble contents between the pigments coated with PPY and the pigments coated with PANI were units percent only: for example, the maximum value observed with PPY was $W_{20}=18.47\%$, and the maximum value observed with PANI was $W_{20}=12.78\%$. The increased water-soluble content of the modified pigments compared to the nonmodified pigments also supports the concept of deprotonation of the conductive polymer layers in the former [32]. A high water-soluble content is indicative of a potentially increased occurrence of osmotic blisters on the surfaces of the paint films [18]. It is concluded that the pigments are not “hazardous” because of this parameter [23].

2.2.4. pH values of aqueous extracts of the pigments and of loose paint films

The observed pH values of the pigment powders (pH_p) and of loose paint films containing the pigments (pH_f) are listed in **Table 5**. The values of extracts of the nonmodified perovskite pigments (pH_p) lay within the region of Ph range of 9–12, and the values of extracts of the pigments coated with the conductive polymer layers (pH_p) lay within the range of 3.0–6.3. Hence, the pigment surface treatment brought about a pH shift toward more acid values: modification with PPY shifted the pH to a slightly acidic region, and modification with PANI, to the acid region. This shift can be explained in terms of deprotonation of the phosphate salts of PANI/PPY in aqueous solutions. The presence of the PANI or PPY salt in the composite pigment reduced the individual differences in the pH values between the initial perovskites. The pH values of extracts of the loose pigmented paint films lay within the region of pH_f (6.2–7.7); within this region, the paint films containing PPY occupied the basic side pH_f (7.3–7.7); within this region, the paint films containing PANI occupied the basic side pH_f (6.2–7.4). The pH of the extract of the nonpigmented film lay in the acid region, at $\text{pH}_f = 3.7$. The pH values for the paints containing the composite pigments were also affected by the presence of CaCO_3 in the paint, or by release of the basically reacting calcium and strontium cations (Ca^{2+} , Sr^{2+}). The pH of the extract of the paint film containing calcite at $\text{PVC} = 50\%$ lay in the slightly basic region, at $\text{pH} = 8.47$. This is beneficial with respect to suppression of corrosion on the metal surface beneath the paint film.

2.2.5. Specific conductivities of aqueous extracts of the pigments and of the loose paint films

Some electric conductivity is necessary for the anticorrosion pigments to passivate the metal surface beneath the paint film. The specific conductivities of extracts of the pigment powders modified with the conductive polymers lay within the regions of $949\text{--}2390\ \mu\text{S}\cdot\text{cm}^{-1}$ for PPY and $994\text{--}2260\ \mu\text{S}\cdot\text{cm}^{-1}$ for PANI and increased in time due to the release of the soluble components into the aqueous environment. The specific electric conductivities did not differ appreciably between the individual surface-modified pigments: the differences lay within one order of magnitude—from 2390 to $949\ \mu\text{S}\cdot\text{cm}^{-1}$. Hence, the specific conductivity was one to two orders of magnitude higher for the composite pigments than for the initial perovskites.

The specific conductivity of the aqueous extracts of the loose films (χ_f) increased with increasing conductive polymer content of the paint (**Table 6**).

Pigment modified with PANI	PVC (%)	^a Specific electric conductivity ($\mu\text{S}/\text{cm}^{-1}$)	Pigment modified with PPY	PVC (%)	^a Specific electric conductivity ($\mu\text{S}/\text{cm}^{-1}$)
CaTiO ₃ /PANI	1	313	CaTiO ₃ /PPY	1	542
	5	318		5	584
	10	348		10	626
	15	465		15	992
SrTiO ₃ /PANI	1	332	SrTiO ₃ /PPY	1	446
	5			5	454
	10			10	461
	15			15	521
CaMnO ₃ /PANI	1	381	CaMnO ₃ /PPY	1	530
	5	443		5	645
	10	1353		10	887
	15	1894		15	1204
SrMnO ₃ /PANI	1	364	SrMnO ₃ /PPY	1	398
	5	421		5	503
	10	513		10	558
	15	851		15	639
Zn ₃ (PO ₄) ₂ ·xH ₂ O	15	176	Nonpigmented film	-	50

^aSpecific electric conductivity was measured with an accuracy $\pm 0.5\%$.

Table 6. Specific electric conductivity of aqueous extracts of loose paint films containing the composite pigments.

The specific conductivities were lowest for the paints with PVC = 1%, from 313 to 381 $\mu\text{S}/\text{cm}^{-1}$ for the pigments modified with PANI and from 398 to 542 $\mu\text{S}/\text{cm}^{-1}$ for the pigments modified with PPY. The specific conductivities were higher at PVC = 5% and lay within the ranges of 318 to 443 $\mu\text{S}/\text{cm}^{-1}$ for PANI and from 503 to 645 $\mu\text{S}/\text{cm}^{-1}$ for PPY. When the pigment concentrations were further increased to PVC = 10% and to PVC = 15%, the specific conductivities also increased, viz. to 348–1353 and 465–1894 $\mu\text{S}/\text{cm}^{-1}$, respectively, for PANI, and to 461–887 and 521–1204 $\mu\text{S}/\text{cm}^{-1}$, respectively, for PPY. The higher specific conductivities of the aqueous extracts of the paint films with the pigments modified with the conductive polymers as compared to the untreated pigments were due to the presence of free charge carriers on the polymeric chain, providing charge transfer across the chain. The positive charge at the chain is counterbalanced by the anion of the acid used for the protonation, that is, phosphoric acid (and the phosphate anion derived from it) in this case. The layers of the conductive polymers undergo partial deprotonation in aqueous solutions [31]. The extent of release and deprotonation of increased amounts of the conductive polymers in the paint films in aqueous systems was higher for paints with higher pigment concentrations (PVC).

Pigment	PVC (%)	Paint assessment		Substrate metal assessment		Calculated anticorrosion efficiency E_{NaCl}
		Degree of blistering		Corrosion in	Surface	
		ASTM D		a cut	corrosion	
		714-87		ASTM D	ASTM D	
		In	Metal	(mm)	(%)	
CaTiO ₃ /PANI	1	2F	4F	0.5–1.0	0.3	79
	5	–	–	0.0–0.5	0.03	98
	10	–	–	1.5–2.0	1	90
	15	–	2F	0.5–1.0	0.5	85
SrTiO ₃ /PANI	1	2M	–	1.5–2.0	0.1	79
	5	2M	–	0.5–1.0	0.03	82
	10	4M	4F	0.5–1.0	0.3	74
	15	4F	2MD	1.5–2.0	>50	44
CaMnO ₃ /PANI	1	2F	4F	1.5–2.0	0.3	75
	5	–	6F	0.5–1.0	3	84
	10	–	4F	2.0–2.5	10	76
	15	–	4F	1.5–2.0	50	65
SrMnO ₃ /PANI	1	–	2M	1.0–1.5	1	77
	5	–	4F	2.0–2.5	3	79
	10	2F	2F	2.5–3.0	10	65
	15	–	2D	3.0–4.0	50	42
CaTiO ₃ /PPY	1	–	–	0	0.3	98
	5	–	–	0	0.1	99
	10	–	4F	0.0–0.5	0.3	90
	15	–	–	1.5–2.0	33	75
SrTiO ₃ /PPY	1	4F	–	0	0.01	93
	5	–	6F	0–0.5	0.01	92
	10	2F	4F	1.0–1.5	0.03	79
	15	–	2F	1.0–1.5	0.1	86
CaMnO ₃ /PPY	1	–	–	0	0.01	100
	5	–	–	0–0.5	0.01	99
	10	–	8F	0–0.5	1	90
	15	4F	6F	1.0–1.5	33	63
SrMnO ₃ /PPY	1	–	6F	0	0.1	93
	5	–	8M	0–0.5	0.3	85
	10	2F	8F	0–0.5	3	79
	15	2F	8F	0–0.5	3	77
Zn ₃ (PO ₄) ₃ ·xH ₂ O	15	2M	–	3.0–4.0	3	68
Nonpigmented film	–	6M	–	1.5–2.0	50	60

Table 7. Results of accelerated corrosion tests of the paints containing the composite pigments in the NaCl mist atmosphere (exposure 1416 h, DFT = 95 ± 10 μm).

2.3. Exposure of the paint films in the atmosphere with the mist of a neutral NaCl solution

The results of the accelerated corrosion test in which the steel panels coated with the paints were exposed to a salt mist atmosphere for 1416 h are included in **Table 7**.

Osmotic blisters were observed on the surface of the paint films containing the composite pigments $\text{CaMnO}_3/\text{PANI}$ and $\text{SrMnO}_3/\text{PANI}$ at higher pigment concentrations, due to the presence of water-soluble substances (e.g., 12.78% in CaMnO_3) and higher concentration of the composite pigments playing a role in the film exposed to the mist of the neutral aqueous solution of chloride ions and to increased humidity/moisture. Therefore, the protective effect of the paint films was lower for the two pigment systems at PVC 15%, also due to the higher degree of corrosion (affected fraction > 50%) of the metal surface beneath the paint film. So, a compromise pigment concentration must be sought for the above paints in order to achieve the optimum anticorrosive effect [31].

PPY was found superior to PANI at PVC = 1%. The highest possible efficiency $E_{\text{NaCl}} = 100\%$ at PVC = 1 (and also at PVC = 5%) was achieved by the paints containing the $\text{CaTiO}_3/\text{PPY}$ and $\text{CaMnO}_3/\text{PPY}$ systems, followed by the $\text{SrMnO}_3/\text{PPY}$ and $\text{SrTiO}_3/\text{PPY}$ systems ($E_{\text{NaCl}} = 93$ in both cases). In the paints with PVC = 5%, PPY was again superior to PANI in this respect. The overall anticorrosion efficiency values (E_{NaCl}) were only slightly poorer at PVC = 5% than at PVC = 1%. The highest corrosion-inhibiting efficiency at PVC = 5% was observed with the paints containing the $\text{CaTiO}_3/\text{PPY}$ system and the $\text{CaMnO}_3/\text{PPY}$ system ($E_{\text{NaCl}} = 99$ in both cases). Slightly lower corrosion resistance was observed with the paint with $\text{SrTiO}_3/\text{PPY}$ ($E_{\text{NaCl}} = 92$). The above paints exhibited a high ability to protect the substrate metal against surface corrosion and against corrosion near the cut, and virtually no blisters were observed on the paint films.

2.3.1. Findings from the corrosion-inhibiting efficiency of pigmented paint films in NaCl atmosphere

1. Paints providing high substrate metal surface protection against corrosion (affected area fraction $\leq 0.0\text{--}0.03\%$) contained the following composite pigments at the following concentrations: $\text{CaTiO}_3/\text{PANI}$ at PVC = 5% (corroded surface fraction, 0.03%); $\text{SrTiO}_3/\text{PANI}$ at PVC = 5% (corroded surface fraction, 0.03%); $\text{SrTiO}_3/\text{PPY}$ at PVC = 1 and 5% (corroded surface fraction, 0.01%), and at PVC = 10% (corroded surface fraction, 0.03%); $\text{CaMnO}_3/\text{PPY}$ at PVC = 1 and 5% (corroded surface fraction, 0.01%).
2. Paints providing high substrate metal protection against corrosion in the cut (i.e., corrosion propagation within 0.5 mm from the cut) contained the following composite pigments at the following concentrations: $\text{CaTiO}_3/\text{PPY}$ at PVC = 1 and 5% (corrosion propagation 0 mm), and at PVC = 10% (corrosion propagation ≤ 0.5 mm); $\text{SrTiO}_3/\text{PPY}$ at PVC = 1 and 5% (corrosion propagation ≤ 0.5 mm, respectively); $\text{CaMnO}_3/\text{PPY}$ at PVC = 1, 5, and 10% (corrosion propagation ≤ 0.5 mm, respectively); $\text{SrMnO}_3/\text{PPY}$ at PVC = 1, 5, 10, and 15% (corrosion propagation ≤ 0.5 mm, respectively).
3. Paint films exhibiting high resistance to surface blistering (score 0–8 F) contained the following composite pigments at the following concentrations: $\text{CaTiO}_3/\text{PPY}$ at PVC = 1, 5, and 15% (no blisters); $\text{SrTiO}_3/\text{PPY}$ at PVC = 1% (no blisters); $\text{CaMnO}_3/\text{PPY}$ at PVC = 1–10% (no blisters, no blisters, 8 F); and $\text{SrMnO}_3/\text{PPY}$ at PVC = 10 and 15% (8 F and 8 F).

4. Paint films exhibiting an anticorrosion effect at a pigment concentration as low as PVC = 1% included the following composite pigments: $\text{CaTiO}_3/\text{PPY}$ ($E_{\text{NaCl}} = 98$); $\text{SrTiO}_3/\text{PPY}$ ($E_{\text{NaCl}} = 93$); $\text{CaMnO}_3/\text{PPY}$ ($E_{\text{NaCl}} = 100$); and $\text{SrMnO}_3/\text{PPY}$ ($E_{\text{NaCl}} = 93$). The pigments with PANI exhibited lower efficiencies: $\text{CaTiO}_3/\text{PANI}$ ($E_{\text{NaCl}} = 79$); $\text{SrTiO}_3/\text{PANI}$ ($E_{\text{NaCl}} = 79$); $\text{CaMnO}_3/\text{PANI}$ ($E_{\text{NaCl}} = 75$); and $\text{SrMnO}_3/\text{PANI}$ ($E_{\text{NaCl}} = 77$).
5. Paint films that attained overall anticorrosion efficiency levels higher than the reference paint, that is, $E_{\text{NaCl}} > 68$, contained the following composite pigments at the following concentrations: $\text{CaTiO}_3/\text{PANI}$ at PVC = 1, 5, 10, and 15%; $\text{SrTiO}_3/\text{PANI}$ at PVC = 1, 5, and 10%; $\text{CaMnO}_3/\text{PANI}$ at PVC = 1, 5, and 10%; $\text{SrMnO}_3/\text{PANI}$ at PVC = 1, 5%; $\text{CaTiO}_3/\text{PPY}$ at PVC = 1, 5, 10, and 15%; $\text{SrTiO}_3/\text{PPY}$ at PVC = 1, 5, 10, and 15%; $\text{CaMnO}_3/\text{PPY}$ at PVC = 1, 5, and 10%; and $\text{SrMnO}_3/\text{PPY}$ at PVC = 1, 5, 10, and 15%.
6. The following paints containing pigments at PVC = 15% provided anticorrosion efficiency better than or roughly identical with that provided by the reference paint (zinc phosphate at PVC = 15%, $E_{\text{NaCl}} = 68$): $\text{CaTiO}_3/\text{PANI}$ ($E_{\text{NaCl}} = 85$); $\text{CaTiO}_3/\text{PPY}$ ($E_{\text{NaCl}} = 75$); $\text{SrTiO}_3/\text{PPY}$ ($E_{\text{NaCl}} = 86$); and $\text{SrMnO}_3/\text{PPY}$ ($E_{\text{NaCl}} = 77$).

2.4. Corrosion-inhibiting efficiency of pigmented paint films with SO_2 and water condensation

The results of the accelerated corrosion test of the paint films in a condensation chamber with an SO_2 mist are listed in **Table 8**. The following PVCs were found optimal with respect to the anticorrosion efficiency (E_{SO_2}) of the paints containing the pigments modified with PANI: $\text{CaTiO}_3/\text{PANI}$: PVC = 10% ($E_{\text{SO}_2} = 99$); $\text{SrTiO}_3/\text{PANI}$: PVC = 5 and 10% ($E_{\text{SO}_2} = 100$); $\text{CaMnO}_3/\text{PANI}$: PVC = 1% ($E_{\text{SO}_2} = 95$); and $\text{SrMnO}_3/\text{PANI}$: PVC = 1% ($E_{\text{SO}_2} = 92$). The analogous values for the pigments modified with PPY were as follows: $\text{CaTiO}_3/\text{PPY}$: PVC = 1% ($E_{\text{SO}_2} = 100$); $\text{SrTiO}_3/\text{PPY}$: PVC = 10 and 15% ($E_{\text{SO}_2} = 97$); $\text{SrMnO}_3/\text{PPY}$: PVC = 1% ($E_{\text{SO}_2} = 99$); and $\text{CaMnO}_3/\text{PPY}$: PVC = 5% ($E_{\text{SO}_2} = 88$).

Pigment	PVC (%)	Paint assessment		Substrate metal assessment		Calculated anticorrosion efficiency E_{SO_2}
		Degree of blistering ASTM D 714-87	Metal base	Corrosion in a cut ASTM D 1654-92 (mm)	Surface corrosion ASTM D 610-85 (%)	
CaTiO ₃ /PANI	1	–	–	3.0–4.0	0.1	89
	5	–	–	1.0–1.5	0.1	94
	10	–	–	0–0.5	0.03	99
	15	–	–	0.5–1.0	0.1	96
SrTiO ₃ /PANI	1	–	–	1.5–2.0	0.03	94
	5	–	–	0	0.03	100

Pigment	PVC (%)	Paint assessment		Substrate metal assessment		Calculated anticorrosion efficiency E_{SO_2}
		Degree of blistering ASTM D 714-87	Metal base	Corrosion in a cut ASTM D 1654-92 (mm)	Surface corrosion ASTM D 610-85 (%)	
CaMnO ₃ /PANI	10	–	–	0	0.03	100
	15	–	–	0–0.5	3	90
	1	–	–	1.0–1.5	0.01	95
	5	6F	–	2.0–2.5	0.03	86
	10	6F	–	1.5–2.0	0.3	86
SrMnO ₃ /PANI	15	4F	–	3.0–4.0	0.3	81
	1	–	–	2.0–2.5	0.03	92
	5	–	–	1.5–2.0	1	90
	10	–	–	1.5–2.0	3	88
	15	–	–	1.0–1.5	10	86
CaTiO ₃ /PPY	1	–	–	0	0.03	100
	5	–	–	0–0.5	0.03	99
	10	–	–	0.5–1.0	0.03	96
	15	–	–	1.0–1.5	0.03	95
	SrTiO ₃ /PPY	1	–	–	2.0–2.5	0.01
5		–	–	1.5–2.0	0.1	94
10		–	–	0.5–1.0	0.03	97
15		–	–	0.5–1.0	0.03	97
CaMnO ₃ /PPY		1	4F	–	2.0–2.5	0.03
	5	4F	–	1.0–1.5	0.03	88
	10	4F	–	2.0–2.5	0.1	85
	15	2F	–	3.0–4.0	0.1	81
	SrMnO ₃ /PPY	1	–	–	0–0.5	0.03
5		–	–	0–0.5	0.3	98
10		4F	–	1.0–1.5	0.3	86
15		4F	–	2.5–3.0	3	77
Zn ₃ (PO ₄) ₃ ·xH ₂ O		15	8MD	0	1.5–2.0	0.03
Nonpigmented film	–	6MD	–	2.5–3.0	0.01	75

Table 8. Results of accelerated corrosion tests of the paints containing composite pigments in the SO₂ atmosphere (exposure 1608 h, DFT = 95 ± 10 µm).

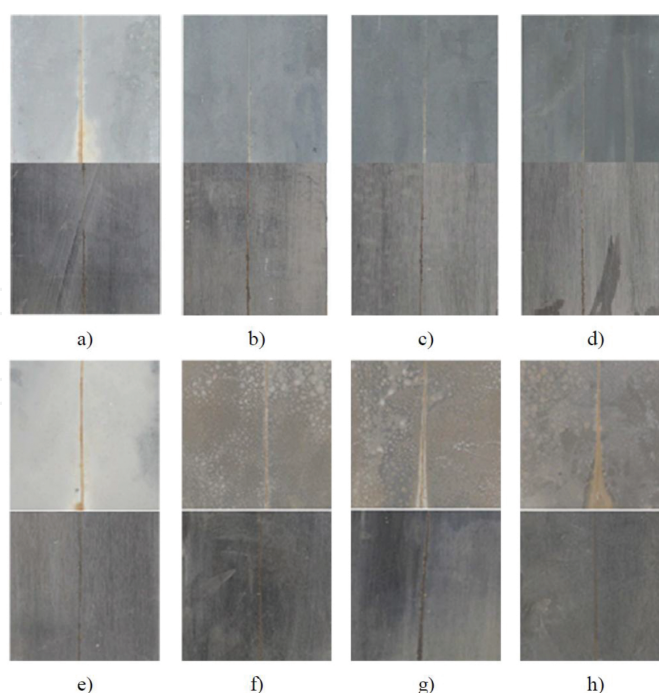


Figure 5. Results of exposure of a steel panel coated with the paint containing $\text{CaTiO}_3/\text{PANI}$ and $\text{CaTiO}_3/\text{PPY}$ in the SO_2 atmosphere.

2.4.1. Findings from the corrosion-inhibiting efficiency of pigmented paint films in SO_2 atmosphere

1. Paint films providing high protection against substrate metal surface corrosion (corroded area fraction $\leq 0.03\%$) contained the following composite pigments at the following concentrations: $\text{CaTiO}_3/\text{PANI}$ at PVC = 10% (corroded surface fraction, 0.03%); $\text{SrTiO}_3/\text{PANI}$ at PVC = 1–10% (corroded surface fraction, 0.03%); $\text{CaMnO}_3/\text{PANI}$ at PVC = 1% (corroded surface fraction, 0.01%), PVC = 5% (corroded surface fraction, 0.03%); $\text{SrMnO}_3/\text{PANI}$ at PVC = 1% (corroded surface fraction, 0.03%); $\text{CaTiO}_3/\text{PPY}$ at PVC = 1–15% (corroded surface fraction, 0.03%); $\text{SrTiO}_3/\text{PPY}$ at PVC = 1% (corroded surface fraction, 0.01%), PVC = 10 and 15% (corroded surface fraction, 0.03%); $\text{CaMnO}_3/\text{PPY}$ at PVC = 1–5% (corroded surface fraction, 0.03%); and $\text{SrMnO}_3/\text{PPY}$ at PVC = 1% (corroded surface fraction, 0.03%).
2. Paints providing high protection against corrosion propagation from the cut (corrosion propagation to ≤ 0.5 mm) contained the following composite pigments at the following concentrations: $\text{CaTiO}_3/\text{PANI}$ at PVC = 10% (corrosion propagation to 0.5 mm); $\text{SrTiO}_3/\text{PANI}$ at PVC = 5 and 10% (corrosion propagation 0 mm), PVC = 15% (corrosion propagation to 0.5 mm); $\text{CaTiO}_3/\text{PPY}$ at PVC = 1% (corrosion propagation 0 mm), PVC = 5% (corrosion propagation to 0.5 mm), $\text{SrMnO}_3/\text{PPY}$ at PVC = 1–5% (corrosion propagation to 0.5 mm). No blisters on the paint surface or near the cut were observed with the following composite pigments at any of the pigment concentrations applied: $\text{CaTiO}_3/\text{PANI}$, $\text{SrTiO}_3/\text{PANI}$, $\text{SrMnO}_3/\text{PANI}$, $\text{CaTiO}_3/\text{PPY}$, $\text{SrTiO}_3/\text{PPY}$.

3. The following pigments were efficient at a concentration as low as PVC = 1%: CaTiO₃/PANI (E_{SO_2} = 89), SrTiO₃/PANI (E_{SO_2} = 94), CaMnO₃/PANI (E_{SO_2} = 95), SrMnO₃/PANI (E_{SO_2} = 92), CaTiO₃/PPY (E_{SO_2} = 100), SrTiO₃/PPY (E_{SO_2} = 93), CaMnO₃/PPY (E_{SO_2} = 85), and SrMnO₃/PPY (E_{SO_2} = 99). All of the above overall anticorrosion efficiency levels are higher than that of the reference paint (i.e., E_{SO_2} > 79). Paints with PVC = 15% that were more efficient than the reference paint (zinc phosphate as the pigment at PVC = 15%, E_{SO_2} = 79) contained the following composite pigments: CaTiO₃/PANI (E_{SO_2} = 96); SrTiO₃/PANI (E_{SO_2} = 90); CaMnO₃/PANI (E_{SO_2} = 81); SrMnO₃/PANI (E_{SO_2} = 86); CaTiO₃/PPY (E_{SO_2} = 95); SrTiO₃/PPY (E_{SO_2} = 97); CaMnO₃/PPY (E_{SO_2} = 81). The majority of the paint films containing the composite pigments at any of the PVC levels applied attained an overall anticorrosion efficiency better than or comparable to that of the reference paint. The anticorrosion efficiencies of the paints containing CaTiO₃/PANI and CaTiO₃/PPY are graphically documented in Figure 5.

2.5. Assessment of the corrosion protection of coatings with perovskites surface-modified with PANI and PPY

Pigment surface modification with PPY was beneficial in the inhibition of blistering both on the paint film surface and in the area of the cut in atmosphere with NaCl, observed also at higher pigment concentrations. Paint resistance to blistering was highest at PVC = 5% or up to 10%. Also beneficial was the pigment surface treatment with PPY in metal surface protection against corrosion, observed also at PVC > 10%.

The ability of the paint films containing pigments modified with PPY to inhibit corrosion of the substrate metal near the cut, also at higher PVC levels, can be explained in terms of a higher specific electric conductivity of the paint films containing PPY as compared to the paint films containing PANI, where this ability is lower. At the same time, this higher specific conductivity was not associated with a local loss of adhesion or with blistering. PPY was superior to PANI, also at PVC = 10%, and largely also at PVC = 15%. The highest anticorrosion efficiency at PVC = 10% was observed with the paints with the CaTiO₃/PPY and CaMnO₃/PPY systems (E_{NaCl} = 90 in either case).

Perovskites providing the best results in atmosphere with NaCl used as the cores for coating with the conductive polymers, particularly with PPY, were those with the Ca-Ti, Sr-Ti, and Ca-Mn combinations. This can be explained by the optimum combination of the specific electric conductivity of the pigments, their solubility in the wet aqueous environment, and the potential of the pigmented paint film adequate to hinder corrosion of the substrate metal. The results of the accelerated corrosion test in the atmosphere of the NaCl mist were supported by the linear polarization measurements.

The occurrence of blister was very low in the atmosphere with SO₂ and water condensation (in comparison with the atmosphere with the NaCl mist) when using the paints containing the composite pigments even at the higher pigment concentration levels. Conductive layer of PPY was superior to the layer of PANI also in this test; in fact, the PPY layer-perovskite carrier system was ideal as a corrosion inhibitor. The pigment particle treatment with PPY was beneficial particularly to corrosion inhibition on the substrate metal surface, up to the highest

PVC levels applied (PVC = 10–15%). Also beneficial was this treatment with respect to suppression of paint film blistering, and also across a wide range of PVC levels.

Corrosion of the substrate metal surface was also low across the whole PVC series in the atmosphere with SO_2 . This effect can be explained in terms of active electrochemical protection of the steel panel by the paint film containing the active form of the conducting polymer (**Figure 6**). The reason why the anticorrosion effect was higher in the atmosphere with SO_2 than in the atmosphere with NaCl lies in the fact that the former atmosphere is appreciably acid and the conducting polymers are more efficient in it, or the nonconductive forms of the composite pigments are maintained in/converted to the conductive forms. So, the electrochemical and chemical mechanisms of action of the pigments and conducting polymers can play their role [32, 33]. Therefore, the pigment surface modification with either of the conducting polymers resulted in more pronounced anticorrosion effects compared to the NaCl mist; also, the differences in the efficiencies of the paints between the different PVC levels of the composite pigments were less marked. The surface modification of the pigments with either of the two conducting polymers (PANI and PPY) was beneficial with respect to resistance against paint surface blistering (at any PVC) and also with respect to anticorrosion protection of the substrate metal.

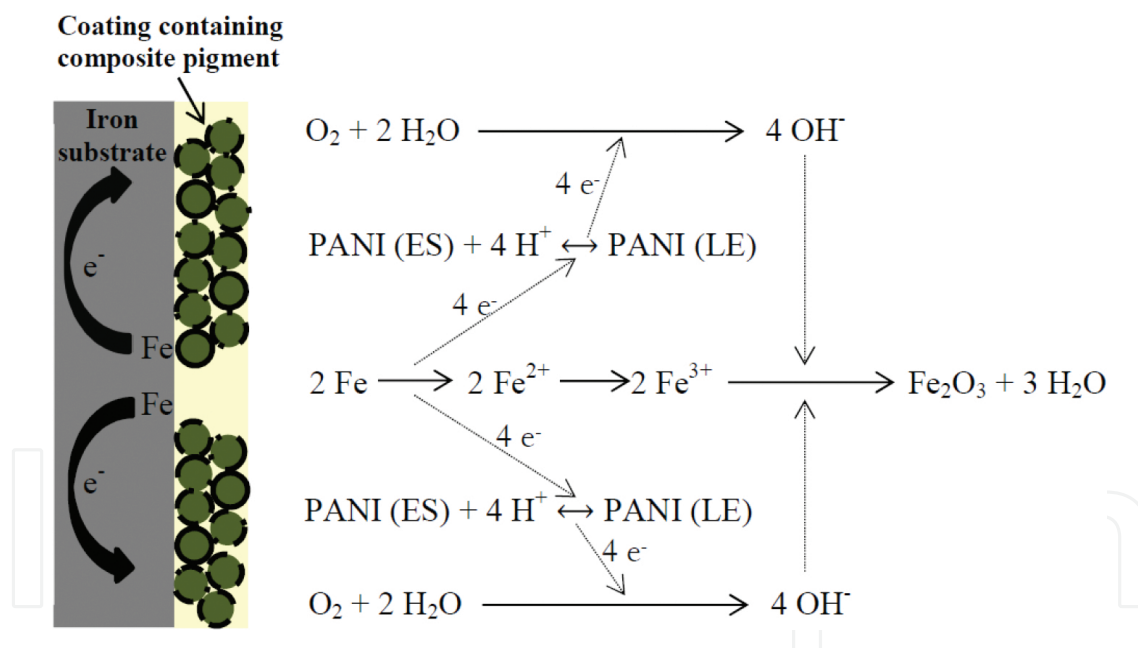


Figure 6. Mechanism of corrosion protection by polyaniline coating (PANI-LE = leucoemeraldine, PANI-ES = emeraldine salt).

2.6. Linear polarization

The parameters measured, that is, the spontaneous corrosion potential, polarization resistance, and corrosion rate, provide information about the paint films' corrosion resistance (**Table 9**). A paint containing zinc phosphate at PVC = 15% served as the reference material in the linear polarization measurements.

Pigment in the paint	PVC (%)	E_{corr} (mV)	I_{corr} (μA)	β_c (mV)	β_a (mV)	R_p (Ω)	v_{corr} (mm/year)
CaTiO ₃ /PANI	1	-431	7.10^{-4}	43.6	40.1	1.10^7	8.10^{-7}
	5	-382	2.10^{-4}	18.8	19.1	2.10^7	1.10^{-5}
	10	-463	4.10^{-3}	27.4	28.3	2.10^6	5.10^{-4}
	15	-468	8.10^{-3}	25.9	27.2	7.10^5	8.10^{-4}
SrTiO ₃ /PANI	1	-286	7.10^{-4}	16.4	19.1	5.10^7	8.10^{-7}
	5	-593	1.10^{-3}	22.6	19.3	4.10^6	1.10^{-5}
	10	-587	5.10^{-2}	31.6	31.7	1.10^5	5.10^{-4}
	15	-635	7.10^{-2}	32.7	29.8	1.10^5	8.10^{-4}
CaMnO ₃ /PANI	1	-687	9.10^{-5}	23.3	37.7	7.10^7	1.10^{-6}
	5	-558	7.10^{-3}	33.2	35.0	1.10^6	8.10^{-5}
	10	554	1.10^{-3}	12.4	11.6	2.10^6	1.10^{-5}
	15	-563	3.10^{-2}	36.5	35.0	2.10^5	4.10^{-4}
SrMnO ₃ /PANI	1	-585	3.10^{-3}	18.1	21.2	2.10^6	3.10^{-5}
	5	-551	4.10^{-3}	36.0	37.6	2.10^6	5.10^{-5}
	10	-590	2.10^{-2}	24.8	21.6	3.10^5	2.10^{-4}
	15	-651	6.10^{-3}	21.1	14.8	6.10^5	7.10^{-5}
CaTiO ₃ /PPY	1	-175	1.10^{-7}	27.2	26.6	5.10^{10}	1.10^{-11}
	5	-192	4.10^{-7}	7.8	6.2	3.10^9	5.10^{-9}
	10	-354	2.10^{-6}	35.9	34.9	4.10^9	2.10^{-8}
	15	-600	8.10^{-4}	35.3	38.6	1.10^7	9.10^{-6}
SrTiO ₃ /PPY	1	-556	7.10^{-8}	23.9	22.2	7.10^{10}	8.10^{-10}
	5	-553	5.10^{-8}	9.0	8.8	4.10^{10}	6.10^{-10}
	10	-544	4.10^{-4}	34.5	35.0	2.10^7	4.10^{-6}
	15	-521	3.10^{-4}	32.1	33.1	2.10^7	5.10^{-6}
CaMnO ₃ /PPY	1	-120	6.10^{-8}	17.8	15.3	4.10^{10}	7.10^{-10}
	5	-372	1.10^{-3}	36.4	24.3	6.10^6	1.10^{-5}
	10	-483	8.10^{-3}	33.0	31.0	7.10^5	9.10^{-5}
	15	-576	3.10^{-2}	28.7	29.8	2.10^5	4.10^{-4}
SrMnO ₃ /PPY	1	-574	6.10^{-6}	25.8	13.6	7.10^8	7.10^{-7}
	5	-500	2.10^{-6}	22.0	27.3	3.10^9	2.10^{-8}
	10	-492	2.10^{-3}	23.7	21.4	2.10^6	2.10^{-5}
	15	-509	4.10^{-4}	16.6	16.9	8.10^6	5.10^{-6}
Zn ₃ (PO ₄) ₃ ·xH ₂ O	15	-473	1.10^{-4}	17.0	16.1	3.10^7	1.10^{-6}
Nonpigmented film	0	42	2.10^{-3}	21.6	18.9	3.10^6	1.10^{-5}

Table 9. Results of linear polarization measurements of the paints containing composite pigments, DFT = $60 \pm 10 \mu\text{m}$.

The nonpigmented coating, with a spontaneous corrosion potential of 42 mV, exhibited polarization resistance of $3 \times 10^6 \Omega$ and corrosion rate 1×10^{-5} mm/year. The reference paint with zinc phosphate at PVC = 15% exhibited a lower spontaneous corrosion potential, -473 mV, higher polarization resistance, $3 \times 10^7 \Omega$, and corrosion rate one order of magnitude lower, 1×10^{-6} mm/year. The two materials served as reference materials for the paint films containing the pigments that modified the conductive polymers: CaTiO_3 , SrTiO_3 , CaMnO_3 , SrMnO_3 , Ca_2ZnWO_6 , and $\text{Ca}_2\text{ZnMoO}_6$ at PVC = 1, 5, 10, and 15%.

The paint films with the $\text{CaTiO}_3/\text{PANI}$ system exhibited spontaneous corrosion potential increase (-382 to -468 mV) against the reference paint with zinc phosphate. In comparison with the nonpigmented coating, the corrosion rate of this paint was lower only at PVC = 15%, viz., $v_{\text{corr}} = 8 \times 10^{-7}$ and 1×10^{-5} mm/year, respectively. The paint films with the $\text{CaTiO}_3/\text{PPY}$ system at PVC = 1, 5, and 10% exhibited spontaneous corrosion potentials higher than the reference paint film with zinc phosphate, viz., -175 to -354 mV. The spontaneous corrosion potential was lower, -600 mV, only at PVC = 15%. The corrosion rate of the paint film at PVC = 1% was nearly one-half that of the above reference paint, viz., 1×10^{-11} mm/year. The paint films containing this pigment at PVC = 5 and 10% also exhibited appreciably lower corrosion rates, 5×10^{-9} and 2×10^{-8} mm/year, than the reference materials (nonpigmented coating and paint with zinc phosphate).

The paint films with $\text{SrTiO}_3/\text{PANI}$ exhibited increase in the spontaneous corrosion potential against that of the reference zinc phosphate paint at PVC = 1%, viz., -286 mV, whereas the reverse was true at PVC = 5, 10, and 15% (-635 to -587 mV). Also, the paint film with the pigment at PVC = 1% was the only one in the increasing PVC series to exhibit a corrosion rate lower (8×10^{-7} mm/year) than the corrosion rate of the two reference materials. The paint films with $\text{SrTiO}_3/\text{PPY}$ exhibited spontaneous corrosion potential decrease (-556 to -521 mV) compared to the reference paint film with zinc phosphate at any of the pigment concentrations used, and the corrosion rates at PVC = 1 and 5%, viz., 8×10^{-10} and 6×10^{-10} mm/year, respectively, were lower than the corrosion rate of the reference paint.

All of the paint films with the $\text{CaMnO}_3/\text{PANI}$ and $\text{SrMnO}_3/\text{PANI}$ systems exhibited spontaneous corrosion potential decrease against the reference paint with zinc phosphate; only the paint film with $\text{CaMnO}_3/\text{PANI}$ at PVC = 1% exhibited a corrosion rate at the same level as the reference paint film, viz., 1×10^{-6} mm/year. All of the paint films with the $\text{CaMnO}_3/\text{PPY}$ and $\text{SrMnO}_3/\text{PPY}$ systems also exhibited spontaneous corrosion potential decrease against the reference paint with zinc phosphate (-576 to -483 mV), except for the paint films with $\text{CaMnO}_3/\text{PPY}$ at PVC = 1 and 5%, where the spontaneous corrosion potential values were higher (-120 and -372 mV, respectively). The paint films with $\text{CaMnO}_3/\text{PPY}$ at PVC = 1% exhibited a lower corrosion rate than the reference paint with zinc phosphate, viz., 7×10^{-10} mm/year, and the same was true of the paints with $\text{SrMnO}_3/\text{PPY}$ at PVC = 1 and 5% (7×10^{-7} and 2×10^{-8} mm/year, respectively).

2.6.1. Conclusion from measurements of linear polarization

Perovskites with PPY layer appeared to be superior to perovskites with PANI layer, also in the linear polarization measurements, and lower concentrations of the pigments coated with PPY

were more efficient than high concentrations. Paint films with the following composite pigments exhibited better resistance and lower corrosion rates than the reference paint with the zinc phosphate pigment: CaTiO₃/PPY at PVC = 1 and 5% (1×10^{-11} and 5×10^{-9} mm/year, respectively); SrTiO₃/PPY at PVC = 1 and 5% (8×10^{-10} and 6×10^{-10} mm/year, respectively); CaMnO₃/PPY at PVC = 1% (7×10^{-10} mm/year); SrMnO₃/PPY at PVC = 1 and 5% (7×10^{-7} and 2×10^{-8} mm/year, respectively); CaTiO₃/PANI at PVC = 1 (8×10^{-7} mm/year); and SrTiO₃/PANI at PVC = 1% (8×10^{-7} mm/year).

3. Conclusion

This study was devoted to the anticorrosion and adhesive-barrier properties of paint films containing perovskite pigments whose surface had been modified with polyaniline phosphate or polypyrrole phosphate. The findings from the tests can be summarized as follows:

1. PPY as the conductive polymer for pigment particle surface modification was found superior to PANI with respect to the corrosion-inhibiting efficiency of the composite pigments. It is an advantage that a low PVC in the epoxy-ester resin based paint is adequate to attain a high anticorrosion efficiency. The pigments with PPY exhibited more favorable physicochemical properties (water-soluble content, pH of the extracts, etc.), which did not detract from the binder's barrier efficiency. For some of the pigments, their optimum concentration in the paints was as low as PVC = 1%, which is beneficial also from the financial aspect.
2. The highest anticorrosion efficiency in the environment with a neutral NaCl mist was exhibited by paint films containing the Ca–Ti or Ca–Mn perovskites, specifically CaTiO₃/PPY and CaMnO₃/PPY, both at PVC = 1 and 5%. The same pigments, plus the Sr–Ti and Ca–Mn perovskites, were also most efficient in the environment with SO₂. All of the paint films attained high anticorrosion efficiencies in the SO₂ environment. Outstanding results were obtained with the paint films containing pigments coated with a layer of PANI, in particular, SrTiO₃/PANI at PVC = 5 and 10%. PPY was found superior to PANI in the environment with the NaCl mist, while the differences between the two conductive polymers were not that marked in the environment with SO₂, and both polymers can be used with advantage. A 1% PVC will be sufficient to attain a high anticorrosion efficiency with the pigments described above.
3. Corrosion in the cut diminished with increasing pigment concentration in the paint (particularly in the atmosphere with SO₂), irrespective of the conductive polymer coating the perovskite core. This result is in line with the catalytic passivation mechanism in the paint film damage area. Steel surface corrosion beneath the paint film was low up to high pigment concentrations, which was facilitated by the anodic protection mechanism [31, 32], in which the composite pigments containing metal oxides are assumed to be able to form a protective layer on the metal surface, thereby protecting the metal against corrosion.

4. The most efficient paints, based on the linear polarization measurements and the accelerated corrosion test in the neutral salt mist atmosphere, were those containing the CaTiO_3 /PPY composite pigment and the SrTiO_3 /PPY composite pigment.
5. All of the paints with the pigments modified with the conductive polymers exhibited good physicomaterial resistance levels—to the extent that the paints are applicable to surfaces exposed to mechanical stresses.
6. The surface-modified pigments are promising from several aspects, particularly owing to their high anticorrosion efficiency compared to that of the reference paint, low pigment concentration in the paints adequate to attain a high anticorrosion effect, and their environmental harmlessness. The results obtained suggest that the pigments deserve further research.

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