EFFECT OF SURFACE TREATMENT OF PIGMENT PARTICLES WITH POLYPARAPHENYLENEDIAMINE PHOSPHATE ON THEIR CORROSION INHIBITING PROPERTIES IN ORGANIC COATINGS

Tereza HÁJKOVÁ[1a], Andréa KALENDOVÁ[a], Miroslav KOHL[a],
and Barbora ANTOŠOVÁ[b]
[a]Institute of Chemistry and Technology of Macromolecular Materials,
The University of Pardubice, CZ–532 10 Pardubice,
[b]Unipetrol výzkumně vzdělávací centrum, a.s., CZ–400 01 Ústí nad Labem

The main goal of this work was to investigate the corrosion inhibiting and physical properties of organic coatings containing pigments whose surface had been modified with a layer of a conductive polymer in comparison with the untreated pigments. Four perovskite-based pigments, viz. $CaTiO_3$, $SrTiO_3$, $CaMnO_3$ and $SrMnO_3$, were prepared by high-temperature calcination, and their surface modified with a layer of the conductive polymer poly(p-phenylenediamine). This modification was achieved by oxidative polymerisation. The physico-chemical properties of the pigments were examined by XRD, XRF, and SEM. The composite pigments were used in coatings (paints) based on a solvent-type epoxy-ester resin. The pigment volume concentration (PVC) in the

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[1] To whom correspondence should be addressed.

paints was 1 %, 5 %, 10 %, and 15 %. The paint films were subjected to physico-mechanical tests and accelerated corrosion tests; the respective results being correlated with the pigment type and concentration and with the surface modification with poly(p-phenylenediamine) as a conductive polymer. The anticorrosion and mechanical properties of the paints have been compared to those of a reference paint containing zinc phosphite hydrate, a proven and established anticorrosion pigment.

Introduction

Nearly all man-made materials undergo environmental degradation during a period of time. Although this applies not only to metals but also to polymers, ceramics, fabrics, and building materials, metal corrosion remains the most important corrosion type because it measures the losses due to this degradation that require costs over a billion dollars annually worldwide. This is why considerable efforts are made to understand and develop various strategies for protecting the materials against corrosion [1,2].

A number of organic coating types containing inorganic pigments as corrosion inhibitors are currently used to reliably protect metallic materials. Very efficient in this respect are chromium compounds. However, chromium(VI) is toxic, and so alternative compounds are being sought to replace this element. Roughly, three decades ago, new materials with immense potential applications were discovered represented by conductive polymers whose electric conductivity is so high that it approaches that one of some metals. A wide range of conductive polymers, such as polyaniline, polypyrrole, and poly(p-phenylenediamine), are among the most investigated polymers. Their electric conductivity distinguishes them from other polymers, which is due to the presence of conjugated double bond systems inside [6,7].

The use of compounds possessing the perovskite structure, as well as the general formula ABX_3, appears to be one of the promising approaches to the synthesis of anticorrosion pigments. Their very favourable properties as coating material ingredients include, in particular, physical and chemical stability, insolubility, and thermal stability [8].

Poly(p-phenylenediamine) (PPDA) can readily be prepared by chemical or electro-chemical oxidation of phenylenediamine. Its electric conductivity is several orders in magnitude lower than that of polyaniline, and so, it is sorted among non-conductors. Although conductivity is important, it is not the sole parameter for application of conductive polymers. Polymers derived from phenylenediamine have been studied to an increasing extent lately offering applications in biomedical branches, where aniline or its oligomers cannot be used because of their toxicity [9].

There exist three phenylenediamine isomers (Fig. 1) that are used as fundamental forms in the protonated state (see Fig. 2). The basic species are present in alkaline solutions, whereas the protonated species predominates in alkaline solutions; both species being pH dependent. This fact is important for practical applications because the oxidation process of the protonated species differs from that of the basic species [10].

Phenylenediamines possess two primary amino groups available for the oxidative connection of the monomers. If the oxidation agent concentration is to be adequately high, both amino groups can be included in a ladder structure (Fig. 3), which can be visualised by means of two intertwined polyaniline chains [11-13].
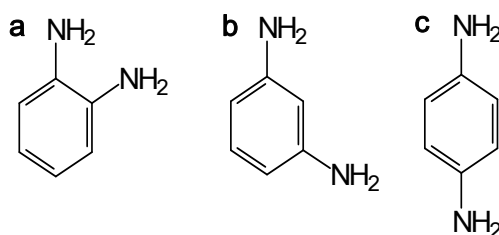

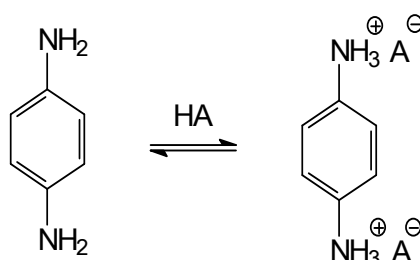Fig. 1 Phenylenediamine bases: (a) *ortho*, (b) *meta*, and (c) *para* isomer [14]

Fig. 2 Phenylenediamine bases form salts with acids (HA) as illustrated on poly(*p*-phenylenediamine) [14]
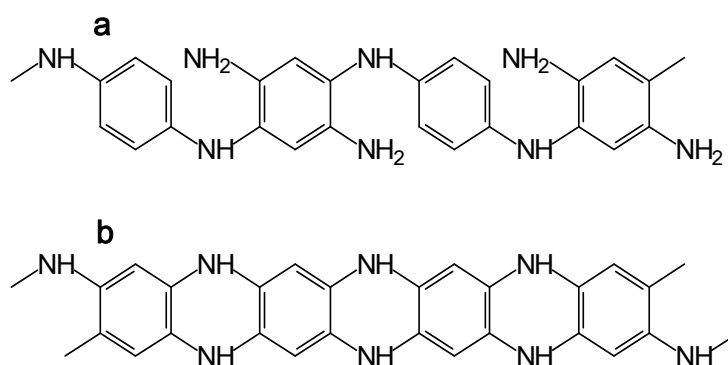

Fig. 3 Idealized structure of poly(*p*-phenylenediamine) produced by the oxidation of (a) one or (b) both amine groups in *p*-phenylenediamine [14]

Experimental

Laboratory Preparation of Pigments for Conductive Polymer Testing

The effect of the pigment surface treatment with polyparaphenyleendiamine phosphate (PPDA) on the anti-corrosion properties of organic coatings was tested with pigment particles differing in their structure and chemical composition. Pigments that are well suited for such a treatment with conductive PPDA were selected based on the previous work. Four pigments based on mixed oxides possessing the perovskite structure: $CaTiO_3$, $SrTiO_3$, $CaMnO_3$, and $SrMnO_3$, were synthesised in the laboratory for testing and investigating their anti-corrosion properties in the coating materials (paints) [15].

The anticorrosion pigment based on the zinc phosphate hydrate $Zn_3(PO_4)_2.H_2O$ (PVC = 15 %) was also tested as a reference material allowing us to compare the results obtained with the pigments synthesized with features typical for commercially available product.

Starting Substances for Synthesis of the Pigments

TiO_2 (titanium oxide, manufactured by Precheza a.s., Czech Republic, density 4.25 g cm^{-3}, M_r 79.88 g mol^{-1});
Mn_2O_3 (manganese (III) oxide, manufactured by Sigma–Aldrich Chemie, Germany, density 4.5 g cm^{-3}, M_r 157.87 g mol^{-1});
$CaCO_3$ (calcium carbonate, manufactured by Omya, GmbH, Austria, density 2.75 g cm^{-3}, M_r 100.09 g mol^{-1});
$SrCO_3$ (strontium carbonate, manufactured by Sigma–Aldrich Chemie, Germany, density 37 g cm^{-3}, M_r 147.63 g mol^{-1}).

Laboratory Synthesis of the Pigments

In general, perovskites can be described by the formula ABO_3, where the atom A is in the oxidation state 2+ and the atom B in the valency of 4+ [15]. Perovskites with a generally isometric particle shape [16, 17] were synthesized to serve as the pigment cores for coating with conductive polymers to be added to a binder in order to form the anticorrosion paints. Pigments possessing the simple perovskite structure: $CaTiO_3$, $SrTiO_3$, $CaMnO_3$ and $SrMnO_3$, were synthesized by solid-phase reaction, viz. by high-temperature calcination of homogenized mixtures of the starting materials by following the general principles of preparation of high-temperature inorganic pigments [18,19]. The process of preparing the pigments consists of four operational steps: (i) homogenization, (ii) calcination, (iii)

washing with water, and (iv) milling by wet process. The respective procedure was conducted in two stages: the pigments were first calcined at 1000 °C for two hours and then at 1 180 °C. Since the suitable size of the pigment particles is a very important factor, the calcination step was followed by wet milling in a Pulverisette 6 planetary ball mill (Netzsch, Germany); the rotation speed being 400 rpm and the process conducted for 4-5 h. Finally, the milled pigments were rinsed with water again and dried at 105 °C in a laboratory electrical dryer.

Preparation of Pigments with Conductive Polymer Surface Layers

The surface of the pigments (see Table I) was modified by treating with polyparaphenlen-diamine phosphate. The anticorrosion efficiency was evaluated both for the untreated pigments and for the pigments with surfaces modified with PPDA (Table II). The following pigments prepared in laboratory were coated with a layer of PPDA.

Table I   Results of XRF analysis of the untreated pigments (the data are in weight per cent; elements present at concentrations lower than 0.01% are omitted)

Parameter wt. %	$CaTiO_3$	$SrTiO_3$	$CaMnO_3$	$SrMnO_3$
Al_2O_3	2.2	2.4	2.0	1.7
SiO_2	0.4	0.1	0.2	0.2
CaO	41.8	-	45.5	-
MnO	-	-	52.3	56.3
TiO_2	55.6	42.3	-	-
SrO	-	55.2	-	41.8

Table II   Results of XRF analysis of the treated pigments (the data are in weight per cent; elements present at concentrations lower than 0.01% omitted)

Parameter wt. %	$CaTiO_3$ PPDA	$SrTiO_3$ PPDA	$CaMnO_3$ PPDA	$SrMnO_3$ PPDA
Al_2O_3	2.8	2.2	1.4	2.6
P_2O_5	4.1	4.3	4.8	5.1
SO_3	3.7	7.9	3.9	4.0
CaO	27.4	-	40.9	-
TiO_2	62.0	44.1	-	-
SrO	-	41.5	-	38.7
MnO	-	-	49.0	49.6

Laboratory Preparation of Pigments Modified with a Surface Layer of Polyparaphenylene-diamine Phosphate (PPDA)

The pigment (20 g) was suspended in 500 ml of 10.81 g *p*-phenylenediamine solution in 0.4 M *ortho*-phosphoric acid and 500 ml of 0.5 M ammonium persulfate [20], also in 0.4 M *ortho*-phosphoric acid, was added to initiate the polymerisation process of *p*-phenylene-diamine at room temperature. The suspension was stirred for one hour during which the *p*-phenylenediamine polymerised on the surface of the pigment particles. The following day, the solids were filtered out and rinsed with 0.2 M phosphoric acid and afterwards with acetone [15]. The pigment particles coated with the PPDA overlayer were dried up in the air and then at 60 ˚C in a laboratory dryer. The composite particles contained about 10 wt.% PPDA.

Structure and Morphology of the Composite Pigment Particles

The pigment particle morphology is illustrated by imaging with scanning electron micrographs (SEM) [15] for the perovskites and for the surface modified perovskites. The micrographs were taken in the secondary electron imaging (SEI) mode. As found out, the composite pigments had a tendency to form clusters.

Characterisation of the Composite Pigments Untreated and Treated Conductive Polymer

A total of four perovskite type pigments untreated and treated PPDA were prepared and analysed by X-ray fluorescence (XRF) using a Philips PW 1404 X-ray spectrometer equipped with a Rh-cathode, in conjunction with UniQuant software enabling one to determine up to 74 elements (from fluorine to uranium) semiquantitatively (with a error of ±10 % rel.). X-ray diffraction spectra (XRD) of the synthetised perovskites were measured with an X'Pert PRO MPD 1880 X-ray diffractometer (PANanalytical, The Netherlands); the diffraction data being evaluated by means of the X'Pert programs (X´Pert HighScore Plus Software version 2.1b and X'Pert Industry Software version 1.1 g), the phases identified *via* the data from the ICCD 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 [21].

Determination of the pH of Aqueous Extracts Pigments and Loose Paint Films

The pH values of aqueous extracts were measured in accordance with ISO 789-9; namely, pH of pigments (pH_p) and of loose paint films (pH_f). For loose paint films a pigment volume concentration of PVC = 1 % and 15 % were chosen. Suspensions (10 wt. %) of the pigments in redistilled water were prepared and their pH measured periodically until constant levels were observed, which had happened within 28 days. After that period of time, the suspensions were filtered off and the final pH of the filtrate [15] recorded. A WTW pH 320 Set-2 multiprocessor pH-meter with a glass measuring electrode (both WTW Wissenschaftliche Werkstätten, Germany) were used.

Electric Conductivity of Aqueous Extracts Pigments and Loose Paint Films

Electric conductivity of aqueous extracts pigments (χ_p) and loose paint films (χ_f) were measured in accordance with ISO787-14. The specific electric conductivity of the aqueous suspensions were monitored conductometrically with a Handylab LF1 conductometer (Schott–Geräte GmbH, Germany) in combination with a measuring Pt-cell; the proper measurements being performed in 10% pigment suspensions in redistilled water [15,22]. The samples were measured for 28 days until the conductivity levels remained nearly constant. Subsequently, the suspension was filtered off and the final conductivity of the filtrate measured.

Determination of Corrosion-Induced Steel Weight Loss

This test measured the weight losses in steel panels submerged in liquid systems causing metal corrosion (ČSN 67 3004). The liquids were aqueous filtrates (referred to as extracts) of 10% suspensions of the powdered pigments and aqueous extracts of 10% suspensions of the cut pieces of the coating films containing the pigments tested. The suspensions were filtered only after their pH and the specific electric conductivity had attained constant levels [22]. The steel panels to be submerged in the extracts were weighed with a precision of $\pm\,0.001$ g and their dimensions (20 mm × 50 mm × 0.5 mm) were measured with a precision of $\pm\,0.01$ mm. The steel panel exposure time was 28 days. The corrosion losses per unit surface area, Pp [g cm^{-2}] (where the subscripts p refer to the suspensions of the pigments), were calculated by using Eq. (1)

$$P_p = 10^4 \frac{m - m_1}{2S} \tag{1}$$

where: P_p – corrosion losses per unit surface area, g cm^{-2}

m – weight of the steel panel before exposure, g
m_1 – weight of the steel panel after exposure, g
S – steel panel area, cm^2

Determination Concentrations of Substances Soluble in Cold and in Hot Water

The fraction of substances extractable into distilled water at 20 °C (W_{20}) and at 100°C (W_{100}) was determined gravimetrically by the procedure described in ČSN EN ISO 787-3, i.e., by gravimetric determination (in %) of substances dissolved in distilled water at laboratory temperature and at the boil [15,22].

Pull-off Test

The pull-off test was performed on a steel panel into which a steel target (20 mm in diameter) was fixed with a two-component adhesive (methyl methacrylate/dibenzoyl peroxide 10 : 1) and loaded with a 1000 g mass left to act for ≥ 2 hours. The pull-off test was performed on a COMTEST®OP3P instrument (the Czech Republic) at 800 kPa s^{-1} by applying a limiting force of 15 kN [23]. This test was performed after removing the paint films from the cyclic corrosion test in the atmosphere with condensing water after 270 days.

Cross-cut Test as per ISO 2409

A special cutting instrument (Cross-cut tester; Byk Gardner GmbH, Germany) with a blade spacing of 2 mm was used to cut the film into square pieces of 2 mm × 2 mm in size. The lattice pattern was evaluated through a score on the 0-5 scale. In this case, a glass substrate was used to measure the paint adhesion by cross-cut test.

Glass was selected because of a very smooth surface, owing to which the desired conditions are accomplished for the paint films [22] and the various paints exhibiting larger differences. This test was performed after removing the paint films from the cyclic corrosion assay in the atmosphere with condensing water after 270 days.

Corrosion-Inhibiting Efficiency of the Pigments

By comparing with untreated pigments, the corrosion-inhibiting properties of the pigments with a surface layer of conductive polymer (pigment/PPDA) were

examined by applying the coating materials on the organic binder. Furthermore, the paint films with the pigment/PPDA systems were compared with the results obtained using an industrial pigment based on modified aluminium zinc phosphate [21]. To do so, a grand total of four pigment/PPDA modified systems and four untreated pigments were tested including the PDA powders and the non-pigmented coating materials tested in the reference experiments.

Organic Coating Formulations Containing the Pigments and Preparation of Test Samples of the Paint Films

All the coating materials were model formulations, containing no additional fillers nor additives that might affect notably the efficiency of the individual formulations. The pigment volume concentration (PVC) was invariably kept constant at 1 %, 5 %, 10 % a 15 %. The critical pigment volume concentration (CPVC) — an important parameter in the formulation of coating materials — was calculated from the density, determined with a Micromeritics Autopycnometer 1320 (Micromeritics Instrument Corp., USA) and from linseed absorption by the pigment (oil consumption) [15].

The PVC/CPVC (critical pigment volume concentration) 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 vol. %, whereby the constant total concentration of powder fractions in the dry paint film was assured, while varying only the amount of the composite pigment in the mixture. The paints were prepared by dispersing the powders in the liquid binder in a pearl mill (model Dispermat CV; WMA GETZMANN Verfahrenstechnik, Germany). Cobalt-octoate in a fraction of 0.3 wt. % was used as the siccative. Epoxy-ester resin-based paints were formulated for investigation of the anticorrosion properties. In this case, the composition of the binder can be described as follows: a 60% solution of medium molecular weight epoxy resin esterified with a mixture of fatty acids of dehydrated ricin oil and WorléeDur D 46 soybean oil [21], acid number: 4, viscosity: 2.5-5.0 Pa s^{-1}, flow time: (DIN 53211-4200) 250 s, in xylene.

The paint films on steel panels (Q-panel, UK) with dimensions of 152×102×0.8 mm were prepared by means of an applicator for the corrosion tests. The samples on steel panels with dimensions of 152×75×0.8 mm were prepared for the physicomechanical resistance tests and samples on glass panels with dimensions of 150×100×10 mm for the adhesion test. Paint films were prepared on a polyethylene sheet, which was removed when dry, cut into 1×1-mm pieces and used for the preparation of 10 wt.% aqueous suspensions of the free films, which that were treated in the same way as the powder samples for pH measurement [15] and for the corrosion loss determination. The samples were

allowed to dry and conditioned on the test panels at normal conditions (air-conditioned laboratory, 20 °C, 50% RH) for six weeks. The dry film thickness (DFT) was measured with a Minitest 110 magnetic thickness gauge combined with an F16 type probe (Elektrophysik, Germany) in accordance with ISO 2808 [23]. A 7-mm-long test cut was made on the bottom of all steel panels for completing the corrosion tests.

Laboratory Corrosion Test

The cyclic corrosion test in the atmosphere with condensing water was performed in a series with EN ISO 6270. The samples were exposed to condensed water at 40 °C for 12 hours and dried at 23 °C for 12 hours. The outcome was evaluated after the exposure for 270 days.

The cyclic corrosion test in a NaCl solution spray environment [15] was arranged according to the ISO 7253 norm. The paint films were exposed to the aerosol of a 5% NaCl solution at 35 °C for ten hours (1st cycle stage), followed by one hour of water condensation at 40 °C (2nd cycle stage) and one hour of drying at 23 °C (3rd cycle stage). The outcome was evaluated after 60 days.

Corrosion Test Outcome Evaluation

The following parameters were evaluated to assess the corrosion effects in the tests: (i) site and frequency of occurrence of blisters on the paint film, (ii) the degree of corrosion of the metallic substrate surface and (iii) the degree of corrosion of the substrate near the cut [21]. Methods as per ASTM D 714-87, ASTM D 610, and ASTM D 1654-92 were used. The corrosion effects were rated using a 0-100 scale. The total anti-corrosion efficiency was obtained based on the arithmetic mean of the degree of corrosion of the metallic substrate, the degree of blister formation on the paint film surface and the degree of corrosion of the metallic substrate near the cut. In other words, the total anti-corrosion efficiency E [24] from the corrosion tests (E_{H2O}, E_{NaCl}) was calculated by using Eq. (2)

$$E = \frac{A + B + C + D}{4} \tag{2}$$

where: A is the degree of blistering in the cut,
B is the degree of blistering in the paint film area,
C is the substrate metal corrosion,
D is corrosion in the paint film cut.

Linear Polarisation

The linear polarisation method was applied to monitor the corrosion. It is designed specifically for the determination of the polarisation resistance, R_p, and current density, I_{corr}. Linear polarisation was measured in a cell incorporating the reference saturated calomel electrode, platinum counter-electrode and the working electrode chosen according to the sample. The method is based on the fact that a linear segment near the corrosion potential occurs on the I-E polarisation curve within linear coordinates. A 1 cm^2 area of the working electrode in the measuring cell was exposed to a 1 M NaCl solution; the cell being connected to a potentiostat/ galvanostat (model VSP-300; France). The paint films were exposed to the NaCl solution for 24 hours and then measured by the linear polarisation method. The polarisation range was from –10 mV/E_{OC} to +10 mV/E_{OC} at a scan rate of 0.166 mV s^{-1} [25].

Comparison Experiments

The anticorrosion pigment based on the zinc phosphate hydrate, $Zn_3(PO_4)_2.H_2O$ (PVC = 15 vol . %) was also tested as a reference material allowing us to compare the results obtained with those for the pigments synthesized from a commercial product. Films of the coating materials free from any pigment were also used in some tests, e.g., in the linear polarisation measurements described in the previous paragraph.

Results and Discussion

Pigment Particle Morphology

Morphology of the composite pigments was examined by SEM in combination with a SEI detector. The SEM images feature the particle shapes (see Fig. 4). In contrast to the untreated pigments with a regular particle shape in the photographs, the pigments whose surface had been treated with PPDA formed the distinct aggregates [26].

Pigment Specification and Results of Structural Analysis

Four perovskite type pigments were prepared and a fraction of each subjected to surface treatment with the conductive polymer, PPDA. Both treated and untreated pigments were examined by X-ray diffraction (XRD) and X-ray fluorescence
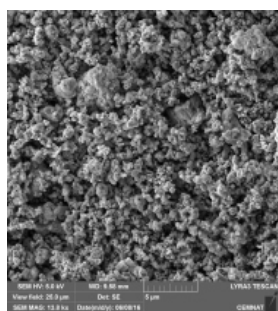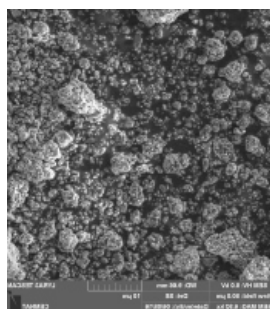
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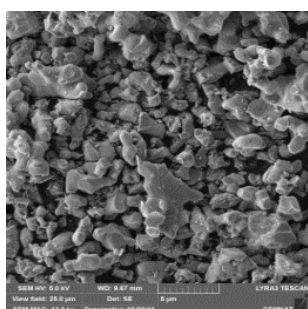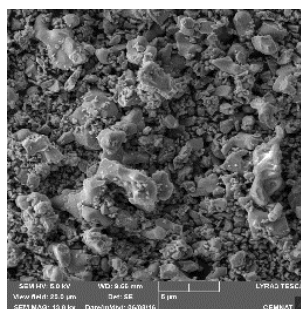
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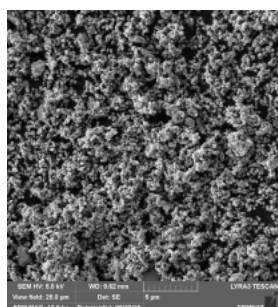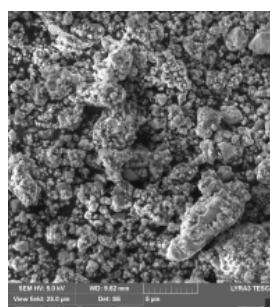
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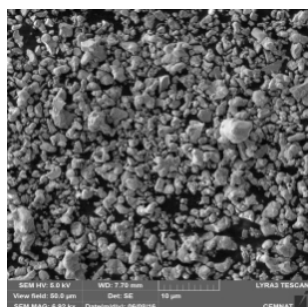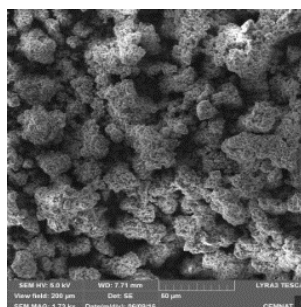
g)   h)

Fig. 4 Morphology of perovskite particles *via* SEM imaging: a) $CaTiO_3$; b) $CaTiO_3$/PPDA; c) $CaMnO_3$; d) $CaMnO_3$/PPDA; e) $SrTiO_3$; f) $SrTiO_3$/PPDA; g) $SrMnO_3$; h) $SrMnO_3$/PPDA

(XRF) analysis to elucidate their structure and composition. The former method gave evidence that the required ABO_3 structure (Fig. 4) had been achieved for most of the pigments, although traces of the starting substances were also present. The $CaTiO_3$ pigment contained the major $CaTiO_3$ crystal phase and a small amount of rutile (TiO_2) and $Ca(OH)_2$; $SrTiO_3$ contained the $SrTiO_3$ crystal phase; similarly as $CaMnO_3$ and $SrMnO_3$.

The results of XRD analysis of the pigments treated with PPDA are shown in Fig. 5. The composite pigments contained the amorphous conductive polymer moiety and the crystalline inorganic core. All of that treated pigments also contained some amount of sulphate. The $CaTiO_3$/PPDA pigment contained $CaTiO_3$ as the major crystal phase and a small fraction of $CaSO_4.2H_2O$ and rutile (TiO_2). The $SrTiO_3$/PPDA crystal phase included $SrTiO_3$ and $SrSO_4$. The $CaMnO_3$/PPDA
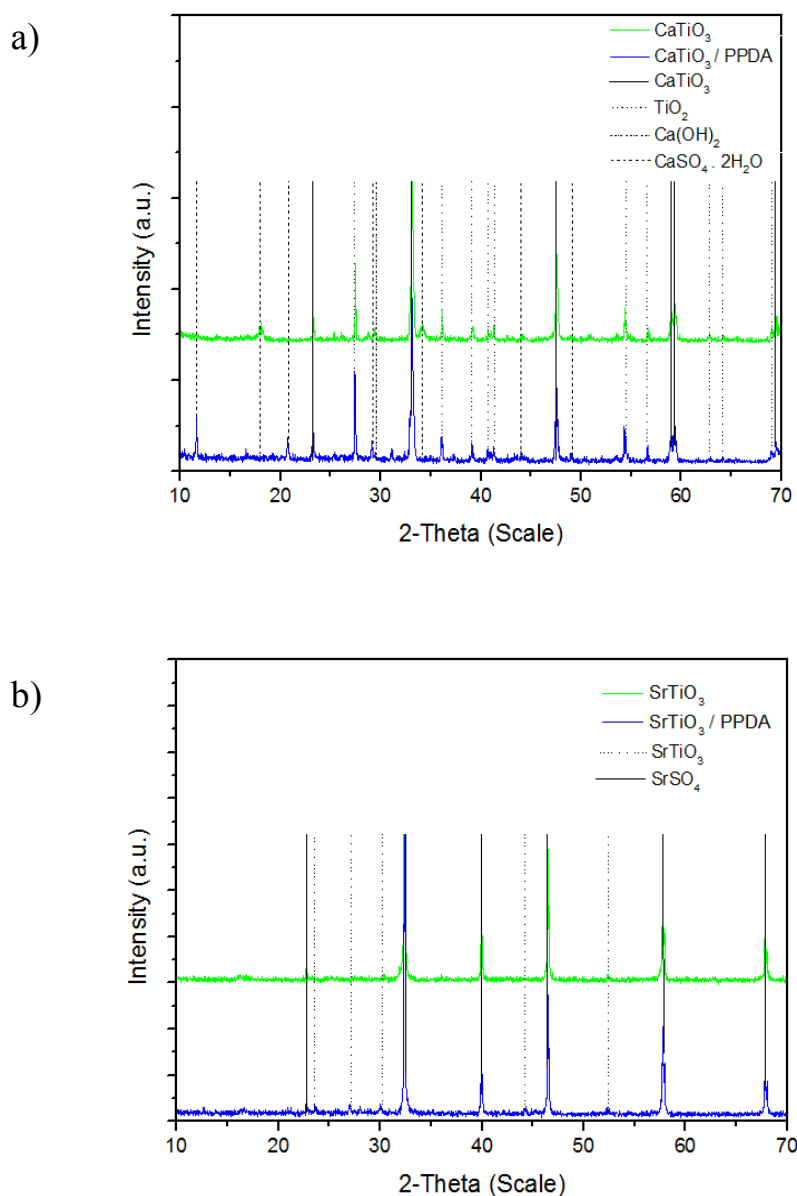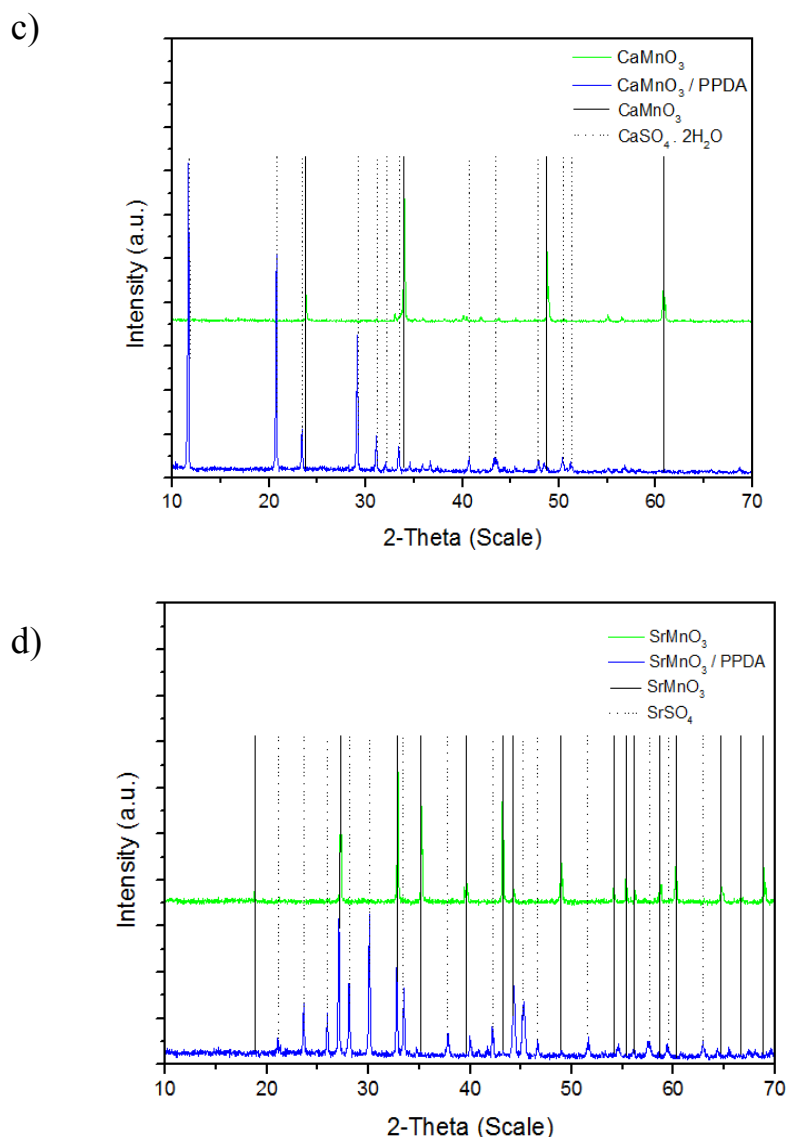
Fig. 5   Difractograms of synthetised composite pigments: a – CaTiO$_3$; b – SrTiO$_3$; c – CaMnO$_3$; d – SrMnO$_3$

pigment contained CaMnO$_3$ as the major crystal phase and a small amount of CaSO$_4$.2H$_2$O; SrMnO$_3$/PPDA pigment containing SrMnO$_3$ and SrSO$_4$. The results of the analysis gave evidence that the pigments had been prepared as intended and being consistent with the previous studies [21,27].

The XRF results are presented in Table I. The pigments contained small amounts of Al$_2$O$_3$ (1.7-2.4 %) and traces of SiO$_2$ (0.1-0.4 %) from the wearing corundum balls in the mill. Both impurity types are of inert character and will not affect the chemical properties of the anticorrosion pigments in any way. As for chemical properties the anticorrosion pigments, the results of XRF analysis of the surface-treated pigments are listed in Table II. They contained the appropriate oxides (TiO$_2$, MnO, SrO, CaO) plus small amounts of compounds from the surface treatment, i.e. P$_2$O$_5$ (4.1-5.1 %) and SO$_3$ (3.7-7.9 %). The precise compositions of the untreated and treated pigments are listed in Tables I and II.

Physicochemical Properties of the Pigments

The physico-chemical properties of the pigments, including density, oil number, critical pigment volume concentration (CPVC) and particle size distribution, are listed in Table III for the untreated pigments and for those modified with the conductive polymer [28].

The densities of the modified pigments lay in the range from 2.07 to 3.28 g cm^{-3}, which is narrower than the range of densities of the initial untreated pigments, from 4.12 to 5.05 g cm^{-3}. The former densities were lower than the latter due to the presence of the conductive polymer layer; the density of the PPDA powder itself being 1.69 g cm^{-3} [22].

The oil consumption levels that are generally dependent on the particle size and shape, or more specifically, on the specific surface area, were higher for the modified pigments (32 to 55 g per 100 g of the pigment) than for the starting pigments (20 to 29 g per 100 g of the pigment) due to the presence of the porous conductive polymer layer on the inorganic core surface. As for the critical pigment volume concentrations, they were from 34 % to 53 % for the modified pigments and from 42% to 50% for the untreated pigments. Hence, surface treatment of the pigments with PPDA gave rise to composite pigments possessing higher oil numbers and lower densities than those for the starting pigments (Table III).

The particle size distribution is characterised by the $D(0.5)$, $D(0.9)$ and $D(0.1)$ values, demonstrating that the size of 50 %, 90 % or 10 % particles in the respective volume is lower than the entered values of $D(4.3)$. The mean particle size ($D4.3$) of the perovskites treated with PPDA was 12.89-13.71 µm, in contrast to that of the initial pigments being merely 0.83-3.92 µm. Hence, the mean particle size increased multiply on the surface coating with the PPDA layer. This is also featured by the SEM photographs, exhibiting the formation of clusters of the pigment/PPDA systems.

pH of Aqueous Extracts of the Pigments and of Free Paint Films

The pH values of extracts of the pigment powders (pH$_p$) are listed in Table IV, where pH is a quantity unit providing the information on the properties of pigments governed by the presence of acidic or alkaline components. The pH values of the untreated pigments lay in the alkaline region, namely from 8.93 to 10.60, whereas the pH values of the pigments coated with the conductive polymer layer varied from 2.87 to 3.79. In other words, surface treatment of the pigments with the conductive polymer brought about a large pH shift from the alkaline region to the appreciably acidic region. This can be explained in terms of deprotonation of the PPDA phosphate salts in the aqueous solution; the same effect being observed for all the pigments tested. The extracts of the untreated

pigments containing alkaline earth cations, i.e. Ca^{2+} and Sr^{2+}, exhibited pH even higher than 9, thus approaching the region for steel passivation.

Table III Physicochemical properties of the powdered pigments

Pigment	Density[*] g cm^{-3}	Oil consumption[*] g 100 g^{-1} pigment	CPVC %	Particle size, µm Per cent fraction below the specific size			
				D(0.1)	D(0.5)	D(0.9)	D(4.3)
CaTiO$_3$	4.12	29	44	0.07	0.17	2.53	0.83
SrTiO$_3$	4.84	26	42	0.07	0.18	2.67	0.86
CaMnO$_3$	4.28	21	50	1.07	2.55	6.48	3.92
SrMnO$_3$	5.05	20	48	0.53	2.22	6.49	2.96
CaTiO$_3$/PPDA	2.99	32	49	2.02	8.14	31.37	13.62
SrTiO$_3$/PPDA	3.28	55	34	1.94	9.98	30.45	12.89
CaMnO$_3$/PPDA	2.07	40	53	1.34	9.21	29.98	13.01
SrMnO$_3$/PPDA	3.20	43	40	2.11	10.74	31.81	13.71
Zn$_3$(PO$_4$)$_3$.H$_2$O	3.28	34	45	0.13	4.78	9.96	5.34
CaO$_3$	2.72	14	70	0.20	5.60	9.99	6.14

[*]Parameters are given as arithmetic averages within 10 measured values

The pH levels of the free paint films (pH_f) were measured for pigment volume concentrations (PVC) 1 % and 15 %. In contrast to the powdered pigment extracts, the paint film extracts did not exhibit any clear-cut pH difference between the untreated and the modified pigments — the ranges were from pH 6.97 to pH 7.36 for paint films with the untreated pigments and from pH 7.24 to pH 7.68 for paint films with the pigments modified with the conductive polymer. The reference paint film containing zinc phosphate provided acidic extracts, pH 3.7. The pH of the extract of the paint film containing calcite at PVC = 50 % was slightly alkaline, pH 8.47. Unlike the extracts of the pigment powders, the extracts of the paint films did not exhibit a shift to the acidic region on pigment surface modification. This was due to the presence of calcite, serving as the filler in the paint. This fact is favourable with respect to the reduction of corrosion progress on the substrate metal surface.

In the neutral pH region, phosphates are not very well soluble and the barrier effect predominates. The solubility increases at lower pH and the pigments become equally or more efficient than chromates. This effect would be undesirable.

Table IV Physico-chemical properties of the pigments

Pigment / coating	^{a}pH$_p$	W_{20} %	W_{100} %	$^b\chi_p$ µS cm^{-1}
CaTiO$_3$	10.60	1.24	2.04	128
SrTiO$_3$	10.05	0.96	1.04	96
CaMnO$_3$	9.90	0.80	0.84	101
SrMnO$_3$	8.93	1.60	1.33	82
CaTiO$_3$ / PPDA	2.87	6.69	8.29	1 996
SrTiO$_3$ / PPDA	3.79	6.43	7.29	1 282
CaMnO$_3$ / PPDA	3.05	7.02	7.32	1 891
SrMnO$_3$ / PPDA	3.13	9.53	9.60	1 086

^{a} pH was measured with an accuracy ± 0.01. ^{b}Conductivity was measured with an accuracy ± 0.5 %, *Parameters are given as arithmetic averages within 10 measured values

Specific Conductivities of the Aqueous extracts of the Pigments and of Free paint films

A certain specific electric conductivity of the anticorrosion pigments is necessary for passivation of the substrate metal beneath the paint film. The observed specific electric conductivities (c_p) of the perovskites modified with PPDA measured the 28th day of the experiment lay within the region from 1 086 to 1 996 µS cm^{-1}, compared to the values for the untreated perovskites (Table IV), which varied from 82 to 128 µS cm^{-1}. In other words, the pigment surface modification with poly(p-phenylenediamine) increased the specific electric conductivity considerably, more than by one order of magnitude. The perovskites with no surface modification did not affect the specific electric conductivity, satisfactorily while the conductive polymer layer had a pronounced effect on the specific electric conductivity.

The specific electric conductivity of extracts of the free paint films (c_f) increased with a higher ratio of PVC in the conductive polymer content, from 1% to 15% (see Table V). The specific electric conductivity of the paint film containing the untreated pigment at PVC = 1 % was affected by the calcite presence, actually approaching the level of the paint film containing solely calcite (0.18 µS cm^{-1}). The specific electric conductivities of the paint films with the untreated perovskites were from 0.35 to 0.89 mS cm^{-1} at PVC = 1 %, to decrease to 0.24-0.61 mS cm^{-1} at PVC = 15 %. When the pigments modified with PPDA were used, specific electric conductivities of the paint films increased in an

interval of 0.11-0.87 mS cm^{-1} at PVC = 1 % and of 0.70-2.02 mS cm^{-1} at PVC = 15 %.

The increase in the specific electric conductivity of the paint film extracts on transition from the untreated pigments into the pigments modified with PPDA was due to the presence of the free charge carriers on the poly(*p*-phenylenediamine) chain, providing the charge transfer along the chain. The positive charge at this chain is compensated by the negatively charged anion of the acid molecule used for protonation; specifically, *o*-phosphoric acid, and of the phosphate anion derived from. A partial deprotonation of the conductive polymer layers takes place in the aqueous environment [22].

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

Pigment	PVC %	pH$_f$	χ_f μS cm^{-1}	Δm_{21} g	P_p g cm^{-3}
CaTiO$_3$	1	7.13	0.35	0.018	15.89
	15	7.01	0.24	0.020	17.27
SrTiO$_3$	1	7.07	0.56	0.022	18.61
	15	6.97	0.61	0.023	19.23
CaMnO$_3$	1	7.13	0.70	0.017	14.33
	15	7.25	0.41	0.019	16.47
SrMnO$_3$	1	7.24	0.89	0.028	23.06
	15	7.36	0.56	0.021	19.95
CaTiO$_3$/PPDA	1	7.49	0.39	0.017	14.05
	15	7.24	0.70	0.024	20.06
SrTiO$_3$/PPDA	1	7.52	0.41	0.024	20.04
	15	7.38	0.88	0.018	15.21
CaMnO$_3$/PPDA	1	7.68	0.11	0.013	10.25
	15	7.36	1.74	0.014	10.99
SrMnO$_3$/PPDA	1	7.63	0.47	0.021	17.97
	15	7.38	0.94	0.015	12.07
Zn$_3$(PO$_4$)$_2$.H$_2$O	15	3.70	0.23	0.023	19.51
CaCO$_3$	-	8.47	0.18	0.025	21.13

*Conductivity was measured with an accuracy ±0.5 %

Water-soluble Substance Content in Water

The amount of water-soluble substances provides information on substances extractable from the pigment into the aqueous phase. The stability of the binder and of the crosslinked paint film is affected adversely if the water-soluble content is too high. The amounts of substances soluble in cold water (W_{20}) and in hot water (W_{100}) are listed in Table IV. The identification of substances that dissolve in water and are washed out of the pigment allows us to assess the behaviour of the pigment in the coating film, e.g. in high humidity/moisture environments.

Both cold and hot water-soluble contents were higher for the pigments modified with poly(p-phenylenediamine) than those for the untreated pigments. The hot-water-soluble contents were expected to be higher (more substances being dissolved) than the cold-water-soluble contents [21], which was really observed but the values did not differ substantially.

The lowest amounts of substances soluble in cold and hot water were observed for calcium manganite, $CaMnO_3$, viz. $W_{20} = 0.80$ % and $W_{100} = 0.84$ %, while the highest values were observed for strontium manganite modified the PPDA, viz. $W_{20} = 9.53$ %, $W_{100} = 9.60$ %, due to the presence of the soluble $SrSO_4$ as a by-phase. The W_{20} and W_{100} levels are related with the amounts of by-phases in the surface-modified pigments, such as $SrSO_4$. The water-soluble contents did not largely differ between the untreated and treated pigment – the nuances found were in the order of units per cent. The hot-water-soluble contents were higher than the cold-water-soluble contents for all pigments, irrespective of whether or not being modified with the conductive polymer. The highest water-soluble contents were $W_{20} = 1.24$ % and $W_{100} = 2.04$ % for the untreated pigments and $W_{20} = 9.53$ % and $W_{100} = 9.60$ % for the pigments modified with PPDA.

The multiply higher water-soluble contents for the modified pigments compared to the untreated pigments reveal the deprotonation of the conductive polymer layers in the former pigments. A high water-soluble content can then be indicated *via* potentially increased occurrence of osmotic blisters on the paint films [22]. Since the pigments synthesized were applied in paint systems, their solubility should not be regarded as the sole parameter enabling the electrochemical inhibition of corrosion.

Corrosion Loss of Steel Panels Coated with the Paints

Investigation of the anticorrosion properties of pigments requires a comprehensive view at the relation between the anticorrosion pigment, the binder, and the substrate. This may be facilitated by information gained from the weight loss of steel panels [22] submerged in aqueous extracts (filtrates) of the pigments. The weight losses measured in two weeks of leaching are listed in Table V.

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For the untreated pigments, the mean corrosion losses of the steel panels were from 14.33 to 23.06 g cm^{-3}. They were found lowest for the CaMnO$_3$ pigment, viz. 14.05 and 16.47 g cm^{-3}, at PVC = 1 % and 15 %, respectively, and highest for the SrMnO$_3$, viz. 23.06 g cm^{-3} at PVC = 1 %.

For the pigments modified with PPDA, the losses due to corrosion were very similar. A marked difference was observed for the CaMnO$_3$/PPDA pigment at PVC = 1 %, where the corresponding values were as low as 10.25 and 10.99 g cm^{-3} at PVC = 1% and 15%, respectively. The next very low corrosion loss, viz. 12.07 g cm^{-3}, was observed for the SrMnO$_3$/PPDA pigment at PVC = 15 %. Hence, such paints can be expected to protect the steel substrate from the effect of humidity/moisture more effectively than the remaining paints examined.

Paint Film Adhesion to the Substrate as Determined by the Cross-cut Method

In this method, the paint film is cut crosswise providing a lattice, where the coating condition degree is visually scored. Double-layered films were prepared and exposed to a simulated atmosphere with condensed water for 270 days prior to test, serving to score the paint film resistance to separation from the substrate after cutting the film through onto the steel panel with a (carpet) cutting knife This determination was affected markedly by the paint film corrosion, as shown in Table VI along with the paint film adhesion data. The tests demonstrated that a smooth cut without damaging the film was obtained at sites free from blisters (substrate steel corrosion); see Fig. 6. This concerned the films containing the following untreated pigments: CaTiO$_3$ at PVC = 10 %, SrTiO$_3$ at PVC = 10 and 15 %, and CaMnO$_3$ at PVC = 1, 5, 10, and 15 %. As to the films with pigments modified with PPDA, no damage was observed for the following pigments: CaTiO$_3$/PPDA at PVC = 1 %; CaMnO$_3$/ PPDA at PVC = 1, 5, 10, and 15 %; and SrMnO$_3$/PPDA at PVC = 1 and 5 %. Also, no damage was observed with the non-pigmented epoxy-ester resin coating.

Where corrosion took place on the steel panel beneath the whole paint film area / the paint film exhibited blisters, cutting the film through to the steel panel surface revealed a loss of adhesion. The paint film damage degree was usually low, scored "1" on the scale chosen. The film that was damaged most during the cross-cut test contained the SrMnO$_3$ and its damage was scored "3" at PVC = 5, 10, and 15 %, and "5" at PVC = 15 %. In the last case, adhesion was lost nearly over the entire area, in direct relation to the ample occurrence of blisters on the paint film surface (4MD), as well as inside the cut (4MD).

Table VI Results of accelerated corrosion tests of the paints containing a composite in an atmosphere with condensing water (exposure 270 days, DFT = 100 ±10mm)

Pigment	PVC %	Paint assessment		Substrate metal assessment		Calculated anticorrosion efficiency E_{H2O}	σ_{max} Pa s^{-1}	Cross-cut test as ISO 2409
		Degree of blistering ASTM D 714-87		Corrosion in the cut ASTM D 1654-92 mm	Surface corrosion ASTM D 610-85 %			
		In a cut	Metal base					
CaTiO$_3$	1	4M	4M	0-0.5	0.03	79	258.9	2
	5	4F	4F	0-0.5	0	84	352.4	2
	10	-	-	0-0.5	0	99	476.6	0
	15	8M	8MD	0-0.5	0.03	74	127.6	1
SrTiO$_3$	1	8F	8F	0-0.5	0	89	307.3	1
	5	-	-	0-0.5	0	99	481.5	1
	10	-	-	0-0.5	0	99	486.1	0
	15	-	-	0-0.5	0	99	491.6	0
CaMnO$_3$	1	-	-	0	0	100	553.5	0
	5	-	8F	0	0	95	437.6	0
	10	-	-	0-0.5	0.03	99	492.8	0
	15	-	8M	0	0.03	90	372.7	0
SrMnO$_3$	1	4M	4D	0-0.5	1	60	75.1	5
	5	4M	4D	0-0.5	3	58	69.8	3
	10	4M	4D	0	50	41	49.8	3
	15	4M	4MD	0	1	60	53.7	3
CaTiO$_3$/ PPDA	1	4F	-	0-0.5	0.3	90	458.9	0
	5	6F	6M	0-0.5	3	75	157.2	1
	10	8F	8F	0-0.5	16	75	224.8	1
	15	8F	8M	0-0.5	33	65	204.1	1
SrTiO$_3$/ PPDA	1	8F	-	0-0.5	0.03	94	444.1	1
	5	-	-	0-0.5	0.3	98	471.1	1
	10	-	-	0	3	94	444.3	1
	15	-	-	0	10	91	384.1	1

Table VI — continued

Pigment	PVC %	Paint assessment		Substrate metal assessment		Calculated anticorrosion efficiency E_{H2O}	σ_{max} Pa s^{-1}	Cross-cut test as ISO 2409
		Degree of blistering ASTM D 714-87		Corrosion in the cut ASTM D 1654-92 mm	Surface corrosion ASTM D 610-85 %			
		In a cut	Metal base					
CaMnO$_3$/ PPDA	1	-	-	0-0.5	0.3	98	504.6	0
	5	-	-	0-0.5	1	95	433.3	0
	10	-	-	0-0.5	3	93	413.7	0
	15	-	-	0-0.5	10	90	373.7	0
SrMnO$_3$/ PPDA	1	4F	4F	0-0.5	0.03	84	356.1	0
	5	-	-	0-0.5	0.03	99	485.2	0
	10	-	-	0-0.5	3	93	415.5	1
	15	4F	4M	0-0.5	50	55	95.7	1
Zn$_3$(PO$_4$)$_3$. H$_2$O	15	2M	8M	0-0.5	3	59	155.9	1
Non/pigm. film	-	8F	8F			89	387.2	1
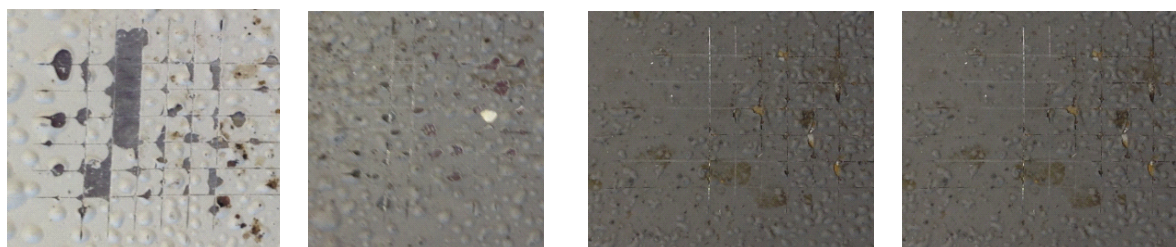
SrMnO$_3$, PVC = 1 %   SrMnO$_3$, PVC = 5 %   SrMnO$_3$, PVC = 10 %   SrMnO$_3$, PVC = 15 %

Fig. 6   Adhesion test-grid picture after cutting the film to the substrate steel panel

Paint Film Pull-off Test

The pull-off test data are summarised in Table VI. The test was performed by exposing the painted steel panels to a simulated atmosphere with condensed water for 270 days. Where the paint films exhibited no blisters / no corrosion evident beneath the films; the maximum pull-off force being about 500 Pa s^{-1}. Such corrosion effects were absent for paint films containing these untreated pigments:

CaMnO$_3$ at PVC = 1 and 10 % (F_{max} = 553.5 and 492.8 Pa s^{-1}, respectively); SrTiO$_3$ at PVC = 5, 10, and 15 % (F_{max} = 481.5, 486.1, and 491.6 Pa s^{-1}, respectively); CaTiO$_3$ at PVC = 10 % (F_{max} = 476.6 Pa s^{-1}), and for paint films containing the following pigments modified with PPDA: CaMnO$_3$/PPDA at PVC = 1, 5, and 10% (F_{max} = 504.6, 433.3, and 413.7 Pa s^{-1}, respectively); SrMnO$_3$/PPDA at PVC = 5 and 10 % (F_{max} = 485.2 and F$_{max}$ = 415.5 Pa s^{-1}, respectively); SrTiO$_3$/PPDA at PVC = 1, 5 and 10 % (F_{max} = 444.1, 471.1 Pa s^{-1} and 444.3 Pa s^{-1}, respectively); and SrTiO$_3$/PPDA at PVC = 1% (F_{max} = 458.9 Pa s^{-1}).

The maximum force required to pull off the paint film was lower if blisters appear on the paint film or corrosion occurs on the substrate surface even to a small extent. This force was lowest, 49.8-75.1 Pa s^{-1}, for the paint with SrMnO$_3$ at PVC = 1, 5 and 10 %, where the film exhibited (Fig. 7) blisters scored 4D. At PVC = 15 %, the blisters were scored 4MD and the maximum pull-off strength was mere 53.7 Pa s^{-1}. With two pigments, the area affected by corrosion beneath the paint film exceeded 50%, which was also mirrored by the low pull-off strength. They were SrMnO$_3$ at PVC = 10 %, with F_{max} = 49.8 Pa s^{-1}, and SrMnO$_3$/PPDA at PVC = 15 %, providing F_{max} = 96.7 Pa s^{-1}.

Generally, the higher the paint film anticorrosion efficiency the higher the pull-off strength. The pull-off strength was lowest in cases, where blisters (Fig. 7) were present on the paint film and the steel substrate corroded appreciably beneath the film.

SrMnO$_3$, PVC = 1 %   SrMnO$_3$, PVC = 5 %   SrMnO$_3$, PVC = 10 %   SrMnO$_3$, PVC = 15 %
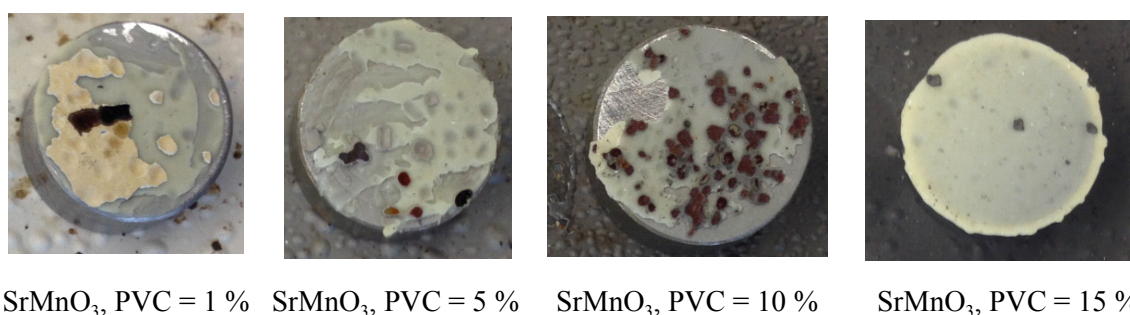
Fig. 7   Pull-off test - photo targets after the separation of the paint film

Corrosion Following Coated Steel Panel Exposure in a Chamber with Condensed Water Vapour Atmosphere

The aim of these tests was to evaluate the efficiency of paint films in protection against corrosion of the substrate metal near the cut in the paint film and across the whole area when calculating the overall anticorrosion efficiency.

The steel panels coated with the paints tested were exposed in the chamber with condensed water vapour for 270 days. The results are summarised in Table VI.

Osmotic blisters were formed both on the paint film area and in the artificial cut made through the film. The corrosion in the cut of the films containing untreated pigments was largely of medium extent, scored as 8F-4MD; the same score being assigned to corrosion beneath the paint film area. Where the pigments modified with the conductive polymer PPDA were used, the corresponding blisters were rarely present in the cut, scored as 4F-8F, small or medium blisters, scored as 8F-4M, could be found on the paint film area. Among the untreated pigments, $SrTiO_3$ provided the most favourable results — blisters scored 8F both on the paint film area and in the cut at PVC = 1 %, whereas no blistering was observed at PVC = 5, 10, and 15 %. Also efficient was $CaMnO_3$, with no signs of blistering at PVC = 1 and 10 %, with blisters scored 8F and 8M on the paint film area at PVC = 5 and 15 %, respectively. Films with the pigments $CaTiO_3$ and $SrMnO_3$ exhibited blistering both on the paint film area and in the cut, where the case of $CaTiO_3$ at PVC = 10 % was an exception, exhibiting no blisters. The thickness of corrosion layer beneath the paint film was 0-0.5 mm almost in all cases. No corrosion ("size zero") in the cut was observed only with $CaMnO_3$ at PVC = 1, 5, and 15 %, $SrMnO_3$ at PVC = 10 and 15 %; and $SrTiO_3$/ PPDA at PVC = 10 and 15 %. Corrosion on the steel panel surface was typically very low, 0-3 %; except the pigments $SrTiO_3$/PPDA at PVC = 10% and $CaMnO_3$/PPDA at PVC = 15 %, where corrosion in the cut reached a degree of 10 %; $CaTiO_3$/PPDA at PVC = 10 %, degree of 16 %; $CaTiO_3$/PPDA at PVC = 15 %, with degree of 33 %, and $SrMnO_3$ at PVC = 10 % and $SrMnO_3$/PPDA at PVC = 10 %, where reaching up to 50 %.

For some of the organic coatings containing the pigments modified with a surface layer of PPDA at PVC >10 %, corrosion on the steel panel surface increases and more blisters are observed on the paint film surface with the increasing PVC (ratio). This can be explained in terms of reduction of the organic film *via* the barrier effect with a higher amount of the conductive polymer in the formula.

A lower barrier effect implies a higher organic coating permeability for the aggressive medium and hence, easier attack on the substrate. This fact has also been observed within previous studies examining the anticorrosion efficiency of the conductive polymer [25,26].

The calculated total anticorrosion efficiency was highest for the pigments $SrTiO_3$ and $CaMnO_3$, both untreated and modified with the conductive polymer. The score values of all have laid within the range of 91-100 %; the lowest anticorrosion efficiency being found for $SrMnO_3$ — also, for both untreated and modified forms — although this parameter was somewhat better and exhibiting a lower occurrence of blisters on the paint film surface and in the cut; this applying rather for the pigment modified with PPDA than that with untreated substance.

Corrosion Following Coated Steel Panel Exposure in a Salt-Fog Chamber

The aim of this series of tests was to evaluate the efficiency of paint films in protection against corrosion of the substrate metal near a cut in the paint film and across the whole area, occurrence of blisters in the cut and on the paint film area, and to calculate the overall anticorrosion efficiency.

The steel panels coated with the paints tested were exposed in the salt-fog chamber for 60 days. The results are listed in Table VII. As seen, nearly all paint films containing the untreated pigments exhibited blisters both on the metal/film interface in the cut and on the paint film surface, scored 2F-6MD and 2F-6MD, respectively. Where the pigments modified with the conductive polymer had been used, the blisters in the cut were scored 2F-2MD, the blisters on the film surface then 2F-6MD. Corrosion in the test cut was observed for all paints containing the untreated pigment, and the whole effect was less pronounced if the paint had contained the modified pigments. This indicates the mechanism of catalytic passivation at the metal/coating interface (Fig. 8). Thus, no corrosion at all was observed in the cut for the paints containing the pigments $CaTiO_3$/PPDA at PVC = 5, 10, and 15 %; $SrTiO_3$/PPDA at PVC = 15 %; $CaMnO_3$/PPDA at PVC = 15 %; and $SrMnO_3$/ PPDA at PVC = 1 %.

A weak corrosion, comparable between the untreated and treated pigments, was observed on the metal panels after stripping down the paint films, the respective degree being 0.01-16 %, except for the pigment $CaTiO_3$/PPDA at PVC 15%, where the extent of corrosion on the steel panel surface reached up to 33 %.

The overall anticorrosion efficiency scores for the paints with the untreated pigments were higher with the increasing pigment concentrations, PVC = 10 and 15 %. And the overall anticorrosion efficiency scores for the pigments modified with the conductive polymer were higher with the decreasing pigment concentrations, PVC = 1 and 5 %. The highest anticorrosion efficiency score within the 0-100 scale, viz. 92, was obtained for the paints containing $SrTiO_3$/PPDA at PVC 1 and 10 %, and $SrMnO_3$/PPDA at PVC 1 %. To compare untreated and the surface-modified perovskites, it can be concluded that the pigment surface modification has led to the reduced numbers of blisters on the paint film surface and those in the test cut. The same statement also applies to corrosion in the cut.

Generally, the surface treatment of the pigments with the conductive polymer PPDA improved the anticorrosion properties of the paints if pigments were present at low concentrations, PVC = 1 and 5 %; the occurrence of osmotic blisters, both on the paint film surface and in the cut, being lower. Also, corrosion in the paint film cut was lower, supporting the concept of steel panel passivation at the interface with the paint film and the conductive polymer.

Table VII Results of accelerated corrosion tests of the paints containing composite pigments in a NaCl solution spray environment (exposure 60 days, film thickness = 95 ± 10 mm)

Pigment	PVC %	Paint assessment		Substrate metal assessment		Calculated anticorrosion efficiency E_{H2O}
		Degree of blistering ASTM D 714-87		Corrosion in the cut ASTM D 1654-92 mm	Surface corrosion ASTM D 610-85 %	
		In a cut	Metal base			
CaTiO₃	1	2F	8M	1.0-1.5	16	62
	5	-	-	0.0-0.5	10	90
	10	-	-	0.0-0.5	10	90
	15	2F	-	0.5-1.0	0.3	86
SrTiO₃	1	2M	4M	0.5-1.0	0	70
	5	4F	4MD	0.0-0.5	10	65
	10	2F	-	0.0-0.5	0.01	90
	15	2F	-	0.5-1.0	0.3	86
CaMnO₃	1	2MD	6M	0.5-1.0	10	55
	5	4MD	4M	0.5-1.0	10	58
	10	4MD	4M	0.5-1.0	1	63
	15	4F	-	0.5-1.0	16	75
SrMnO₃	1	2MD	6M	0.0-0.5	10	58
	5	2MD	4M	0.0-0.5	16	52
	10	2MD	4M	0.5-1.0	1	61
	15	2F	-	0.0-0.5	0.01	90
CaTiO₃/ PPDA	1	-	2F	0.0-0.5	0.3	89
	5	6F	6M	0	1	60
	10	6MD	6MD	0	16	53
	15	6MD	6MD	0	33	48
SrTiO₃/ PPDA	1	6F	-	0	0.1	92
	5	-	4F	0.0-0.5	1	88
	10	-	-	0.0-0.5	3	92
	15	-	6F	0	3	88

Table VII — continued

| Pigment | PVC % | Paint assessment | | Substrate metal assessment | | Calculated anticorrosion efficiency E_{H2O} |
| | | Degree of blistering ASTM D 714-87 | | Corrosion in the cut ASTM D 1654-92 mm | Surface corrosion ASTM D 610-85 % | |
		In a cut	Metal base			
CaMnO$_3$/PPDA	1	-	8M	0.5-1.0	10	78
	5	-	4F	1.0-1.5	16	74
	10	-	-	0.5-1.0	3	90
	15	-	6M	0	0.3	88
SrMnO$_3$/PPDA	1	6F	-	0	0.1	92
	5	2F	4F	0.5-1.0	3	74
	10	2F	2MD	2.0-3.0	16	50
	15	2MD	2MD	0.0-0.5	16	48
Zn$_3$(PO$_4$)$_3$.H$_2$O	15	2M	8M	2.0-2.5	3	61
Non/pigm. film	-	6M	-	1.5-2.0	50	60

Potentiodynamic Polarisation

The results of the electrochemical examination by the linear polarisation method are listed in Table VIII. The aim of the measurements was to determine the spontaneous corrosion potential, polarisation resistance, and corrosion rates for the organic coatings studied. It was expected that these parameters would provide information on the resistance of organic coatings towards corrosion.

For the non-pigmented organic coating, the polarisation resistance at the spontaneous corrosion potential 42 mV was 3.0×10^6 Ω, the corrosion rate was 1.0×10^{-3} mm year^{-1}. The organic coating containing the ZP-10 pigment at PVC = 15 %, serving as a reference sample, exhibited spontaneous corrosion potential decrease to –473 mV, while the polarisation resistance attained 7.0×10^4 Ω and the corrosion rate, 9.8×10^{-4} mm year^{-1}. The spontaneous corrosion potential of the organic coatings tested laid within the range from –285 to –667 mV vs. ref. electrode. The surface treatment of the CaTiO$_3$ pigment with PPDA appeared to be beneficial at PVC = 1 % — the corrosion rate decreased from 9.1×10^{-3} (CaTiO$_3$) to 1.2×10^{-5} (CaTiO$_3$/PPDA) and the polarisation resistance improved appreciably. The surface treatment of the SrTiO$_3$ pigment was beneficial within the

whole PVC range (1-15 %), most markedly at PVC = 1 and 5 %, at which corrosion rate decrease by 1 to 2 orders of magnitude was observed while the polarisation resistance increased by 2-3 orders of magnitude. Surface treatment of $CaMnO_3$ was beneficial at PVC = 1 and 5 %; the corrosion rate being lowest among all the organic coatings tested. The corrosion rate was 1.9×10^{-8} and 1.3×10^{-8} mm year^{-1} at PVC = 1 and 5 %, respectively, and the polarisation resistance also increased substantially – from three to five orders of magnitude. The surface treatment of $SrMnO_3$ was beneficial at PVC = 1 %: the corrosion rate decreased by one order of magnitude and the polarisation resistance increased by two orders of magnitude.
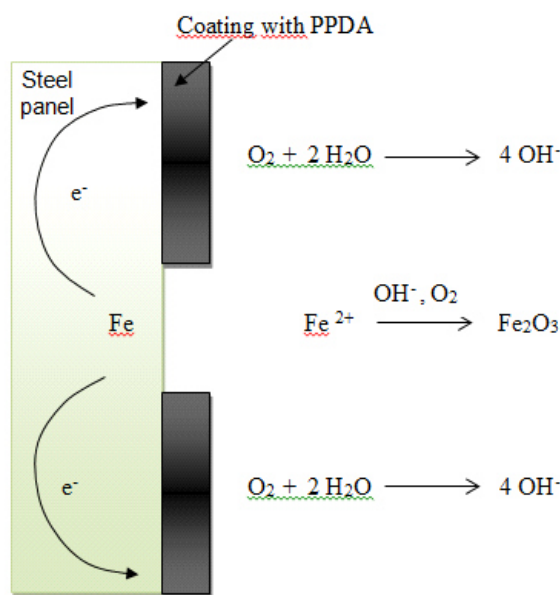
Fig. 8   Schematic view of the iron passivation mechanism by means of a paint containing a pigment modified with PPDA

Anticorrosion Effect of Perovskites and PPDA in a Paint Layer

In recent years, application of conductive polymer coatings such as PPDA on ferrous and non-ferrous alloys against corrosion has received considerable attention [29,30]. In addition to applying the physical barrier, which is the protection mechanism for most of coatings, the conductive polymers are capable of anodical protection of metal surface by the suppressing their oxidative properties and accelerating the formation of stable metal oxides on the surface of the substrate [31,32]. In other words, the ability of the conducting polymer to oxidize the substrate metals allows potential of metals to be shifted to the passivation state, in which the metals are protected by the newly formed oxides occuring beneath the conducting polymer. Where the pigment particle is not modified with a conductive polymer layer, the anticorrosion protection can be

accomplished *via* the inorganic pigment itself.

The application of the conducting polymer coating in the corrosion protection of steels was reviewed by Tallman *et al.* [32].

Table VIII   Results of linear polarisation measurements of the paints containing composite pigments (DFT = 60 ± 10 μm)

Pigment in the paint	PVC %	E_{corr} mV	I_{corr} μA	β_c mV	β_a mV	R_p Ω	v_{corr} mm year^{-1}
CaTiO$_3$	1	−523	8×10^{-1}	44	39.8	11×10^{3}	91×10^{-4}
	5	−640	2×10^{-2}	35.2	36.3	37×10^{4}	24×10^{-5}
	10	−518	7×10^{-2}	31.9	37.4	10×10^{4}	81×10^{-5}
	15	−481	2×10^{-4}	39.4	35.7	39×10^{6}	24×10^{-7}
SrTiO$_3$	1	−496	6×10^{-2}	38.8	36	12×10^{4}	74×10^{-5}
	5	−401	6×10^{-3}	32.1	30.8	13×10^{5}	71×10^{-6}
	10	−625	4×10^{-6}	12.1	17	52×10^{7}	51×10^{-7}
	15	−636	5×10^{-6}	11.7	15.4	58×10^{7}	58×10^{-7}
CaMnO$_3$	1	−285	8×10^{-1}	36.4	34.2	90×10^{2}	88×10^{-4}
	5	−465	6×10^{-2}	37.6	37.6	12×10^{4}	71×10^{-5}
	10	−598	9×10^{-6}	24.1	18.2	59×10^{7}	11×10^{-9}
	15	−519	1×10^{-5}	26.9	13.5	38×10^{7}	13×10^{-8}
SrMnO$_3$	1	−412	3×10^{-4}	31.6	33.8	15×10^{5}	34×10^{-6}
	5	−618	4×10^{-6}	12.8	14.1	48×10^{7}	45×10^{-7}
	10	−615	3×10^{-6}	12.5	13.9	42×10^{7}	42×10^{-7}
	15	−623	5×10^{-6}	12.2	13.1	41×10^{7}	46×10^{-7}
CaTiO$_3$/PPDA	1	−667	1×10^{-3}	36	37.2	22×10^{6}	12×10^{-6}
	5	−546	8×10^{-1}	42	38.1	22×10^{3}	71×10^{-4}
	10	−526	7×10^{-1}	41.1	40.1	11×10^{2}	72×10^{-2}
	15	−518	7×10^{-1}	42.3	40.9	10×10^{2}	70×10^{-1}

Table VIII – continued

Pigment in the paint	PVC %	E_{corr} mV	I_{corr} µA	β_c mV	β_a mV	R_p Ω	v_{corr} mm year^{-1}
SrTiO₃/PPDA	1	−601	1×10^{-6}	11.1	13.9	45×10^{7}	46×10^{-7}
	5	−614	2×10^{-6}	11.8	14.8	48×10^{7}	50×10^{-7}
	10	−351	3×10^{-4}	17.1	23.5	15×10^{6}	34×10^{-7}
	15	−363	4×10^{-4}	17.1	22.8	14×10^{6}	36×10^{-7}
CaMnO₃/PPDA	1	−618	8×10^{-6}	21.8	15.9	69×10^{7}	19×10^{-9}
	5	−600	8×10^{-6}	22.1	16.1	70×10^{7}	13×10^{-9}
	10	−468	6×10^{-2}	36.3	36.1	11×10^{4}	83×10^{-5}
	15	−299	1×10^{-1}	36.8	35.9	10×10^{3}	92×10^{-4}
SrMnO₃/PPDA	1	−618	4×10^{-6}	12.8	14.1	48×10^{7}	45×10^{-7}
	5	−418	3×10^{-4}	32.8	34.2	14×10^{5}	36×10^{-6}
	10	−319	1×10^{-1}	32.2	38.8	59×10^{2}	14×10^{-3}
	15	−588	9×10^{-2}	40.8	41.8	98×10^{3}	10×10^{-4}
Zn₃(PO₄)₂.H₂O	15	−473	1×10^{-4}	17	16.1	70×10^{3}	98×10^{-5}
Non-pigmented film	0	42	2×10^{-3}	21.6	18.9	30×10^{5}	10×10^{-4}

Conclusion

The objective of this work was to assess the anticorrosion properties of paint films containing perovskite-based pigments and to compare the systems with untreated pigments and systems with those where the pigment surfaces had been modified with the conductive polymer poly(*p*-phenylenediamine) (PPDA) by chemical oxidative polymerisation. Although possessing different structures, the pigments were all supposed to possess good anticorrosion properties. The pigment volume concentrations (PVC) applied were 1, 5, 10, and 15 %. The paint systems were based on a solvent-type epoxy-ester resin. To investigate their anticorrosion properties, the paints were applied in steel panels as the subjects for corrosion tests. In the tests, the epoxy-ester resin itself and a system with the commercial ZP10 $Zn_3(PO_4)_2$ anticorrosion pigment served as the reference configuration.

The objective of the synthesis was to obtain pigments ensuring a high anticorrosion efficiency. This is affected by a number of factors, such as the morphology of pigment particle, acid-base properties and others. They can, for

instance, change the pH of the aqueous phase sorbed in the paint film, affect the pH of the aqueous medium while the corrosive substances diffuse through the coating, or produce the protective layers by reaction with the OH^- ions at the cathodic sites by forming a passivation film via redox reactions with the Fe^{2+} ions. A target selection of the cations in the perovskite pigment structure can be used to control the properties of pigments, particularly those affecting the corrosion-inhibiting behaviour of the pigment in the paint system. The perovskites, with their basic nature, can shift the pH of the aqueous layer present on the substrate metal beneath the paint film towards the region where the metal does not corrode, i.e. towards its passivation state. It is true that the pigments whose surface has been modified with the conductive polymer, poly(*p*-phenylenediamine) are acidic, which is, however, very important for preserving their conductivity and thus for maintaining their anticorrosion properties. In fact, the action mechanism of this conductive polymer is not fully understood yet but it is interpreted in terms of the same mechanism as that acting in polyaniline.

The total anticorrosion efficiency of the paints was tested by exposing steel panels coated with the paints to simulated corrosive atmospheres in the test chambers. The anticorrosion properties of paints containing the untreated pigments and pigments modified with the conductive polymer were compared. The aim of the pigment surface modification with poly(*p*-phenylenediamine) was to improve the paint's anticorrosion efficiency. The fact that conductive polymers have generally possessed a larger pore size somewhat supports the effect of water absorption. This might result in the formation of blisters in the paint film, which will be investigated in more detail in our forthcoming studies.

The corrosion tests in the simulated atmosphere with condensed water has given evidence that the surface treatment with the conductive polymer helps to improve the overall anticorrosion efficiency, exhibiting a lower occurrence of blisters both on the paint film surface and in the artificial cut through the film. This conclusion is also supported by the results of the cross-cut test and the pull-off test following exposure to this atmosphere for 6480 hours which are also more favourable for the paints with the pigments modified with the conductive polymer. The corrosion tests in simulated salt-fog atmosphere have demonstrated improvement of the anticorrosion properties at low pigment volume concentrations; specifically, at PVC = 1 % for all the modified pigments and at PVC = 5 % for some of them, compared to the untreated pigments. Overall, the corrosion effects were found lower when the modified pigments had been used: this concerned, in particular, the extent of blistering both on the paint film surface and in the cut through the film, as well as the corrosion in the cut. All this has shown good electrochemical inhibition in the salt-fog atmosphere, accelerating the corrosion test and revealing that the paints anticorrosion efficiency decreases if the pigment volume concentration increased above 10 %. The results of the accelerated corrosion test are in good agreement with those of the electrochemical

measurement. Also, the results regarding corrosion in the test cut are consistent with the catalytic passivation mechanism (picture on the metal/coating interface). In conclusion, the results of the anticorrosion efficiency tests give evidence that the perovskite based pigments whose surface has been modified with a layer of poly(*p*-phenylenediamine) can be used in paints to protect the steel surface against corrosion. The binder system used in this work — a solvent-based epoxy-ester resin — exhibited an outstanding adhesion towards the substrate and low diffusion permeability for the respective films, proving to be well applicable in combination with the pigments studied.

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