The anticorrosion properties of pigments based on molybdates and tungstates surface-modified with conducting polymers

Antikorozní vlastnosti pigmentů na základě molybdenanů a wolframanů modifikovaných vodivými polymery

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The objective of this work was to examine the properties of molybdate or tungstate based pigments whose surface has been coated with a conductive polymer, viz. either polyaniline phosphate (PANI) or polypyrrole phosphate (PPY), if used as pigments in organic coating materials. The anticorrosion pigments were prepared by high-temperature solid-state synthesis from the respective oxides, carbonates. 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 accelerated corrosion test and by the linear polarisation method. Focus was on the anticorrosion properties of the paints depending on the pigment surface treatment, initial pigment composition, and pigment volume concentration (PVC) in the paint. The surface-treated pigment particles were expected to have a favourable effect on the anticorrosion and the mechanical properties of epoxy-ester resin based paints.

Cílem této práce bylo studium vlastností pigmentů se strukturou molybdenanů a wolframanů, jejichž povrch je pokryt vodivým polymerem polyanilin fosfátem (PANI), nebo polypyrrol fosfátem (PPY), které byly aplikovány v organických povlacích Tyto antikorozní pigmenty byly připraveny vysokoteplotní syntézou v pevné fázi z příslušných oxidů a uhličitanů. Kompozity (pigment/vodivý polymer) byly dispergovány v epoxyesterové pryskyřici rozpouštědlového typu a po získání nátěrového filmu, byly zjišťovány antikorozní vlastnosti pomocí zrychlené korozní a byla provedena lineární polarizace. Důraz byl kladen na antikorozní vlastnosti nátěrových hmot v závislosti na povrchové úpravy pigmentů vodivými polymery, počáteční pigmentové složení a objemová koncentrace pigmentu (OKP) v nátěru. Očekává se, že pigmentové částice s povrchovou úpravou by měly vykazovat pozitivní vliv na mechanické vlastnosti nátěru na bázi epoxyesterové pryskyřic.

INTRODUCTION

Paints designed to protect metals against corrosion always contain corrosion-inhibiting pigments that slow down the metal corrosion process through electrochemical and chemical reactions [1, 2]. Roughly 30 to 40 years ago, efforts started to be made to remove toxic materials from workplaces and the environment, including toxic substances serving as pigments in corrosion protection paints. Although less environmentally harmful, current new anticorrosion pigments are less efficient than the traditional anticorrosion pigments [3]. The potential of inorganic chemistry to offer suitable efficient non-toxic anticorrosion ingredients are currently virtually exhausted [4, 5]. Conceivable inorganic compounds are either little efficient (phosphates, silicates) or too expensive (modified (poly)phosphates, borates and, in particular, molybdates) [6, 7].

Conductive polymers start to be popular among organic corrosion inhibitors [8]. Examples of conductive polymers include polypyrrole and polyaniline, involving systems of conjugated double bonds with the presence of charge carriers making possible charge transfer along the chain [9]. Owing to their properties, conductive polymers induce passivation processes on steel surfaces, in which respect they are similar to the compounds containing heavy metals. This shows promise are regards the feasibility of using conductive polymers to replace, or reduce the use of, e.g., chromate-based corrosion inhibitors [10]. They may also find application as electrochemical, or electrically active, pigments to attain passivation of the surface of a corroding steel substrate [11, 12].

Composite particles consisting of an inorganic substance coated with a conductive polymer layer are advantageous ingredients of organic coating materials

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for active anticorrosion protection. Hence, they are pigment or filler particles that are provided with a layer of an active compound -an electrically conductive polymer. The core (chemically active pigment) should contribute the physical properties of the paint at the substrate metal–paint film interface, e.g. adhesion to the substrate, and ideally also provide additional active metal surface protection. In view of the specific properties of paint binders and of the various corrosion factors of the ambient environment, it is imperative to identify such a conductive modification type and volume concentration of the pigment/conductive polymer composite particles as do not affect adversely the stability of the film-forming component of the paint binder or the physical properties of the crosslinked polymeric coating material. The polymer must also retain its conductive form in order to continue to exert an anticorrosion protection effect [13-16].

Oxidic compounds of some metals, e.g. molybdenum and tungsten, themselves contribute to the anticorrosion effect of paints to which they are added as ingredients [17]. Molybdates and tungstates at low concentrations are good corrosion inhibitors for cold-rolled steel [18].

An interesting solution to the formulation of a composite anticorrosion pigment for paints consists in its combination with a conductive polymer [19, 20].

Molybdates and tungstates as well, whose surface has been modified with a conductive polymer may extend the range of anticorrosion pigments and become potential candidates for paints which are efficient in the anticorrosion protection of metals. And conversely, this may assist efforts to introduce conductive polymers into the industry as substances suitable for use in anticorrosion paints. In a pigment/conductive polymer composite system the amount of the conductive polymer is optimised, the pigment particle coverage by a conductive polymer layer is 50-60 % [21, 22]

In such a composite pigment, where both of the two components are efficient in anticorrosion protection -or where the combined effect of the two ingredients is even synergistic -a high anticorrosion efficiency of the pigmented paint may be achieved even at a low PVC. The molybdate or tungstate particles would be active at sites not coated with the PANI or polypyrrole phosphate (PPY) layer. Stability of the pigments owing to the oxide structure was one of the important factors that were taken into account when selecting specifically those pigments for surface treatment with the conducting polymers. Also advantageous are the facts that molybdates and tungstates are nontoxic [4] and that the anticorrosive capacity of pigments with molybdates or tungstates have already been demonstrated [17, 23].

The mechanism of action of the conductive PANI species at the metal/organic coating interface is shown in Fig. 1. Iron is directly oxidised to Fe^{3+} ions. (Passivating layers with Fe^{3+} are less soluble and hence more resistant

than passivating layers with Fe^{2+}). This direct oxidation is accelerated by the catalytic redox effect of PANI (ES = protonated emeraldine salt, LE = leucoemeraldine). The oxidising power of PANI is affected appreciably by the dopant type [24, 25]. The effect of PPY in the paint layer is explained likewise.
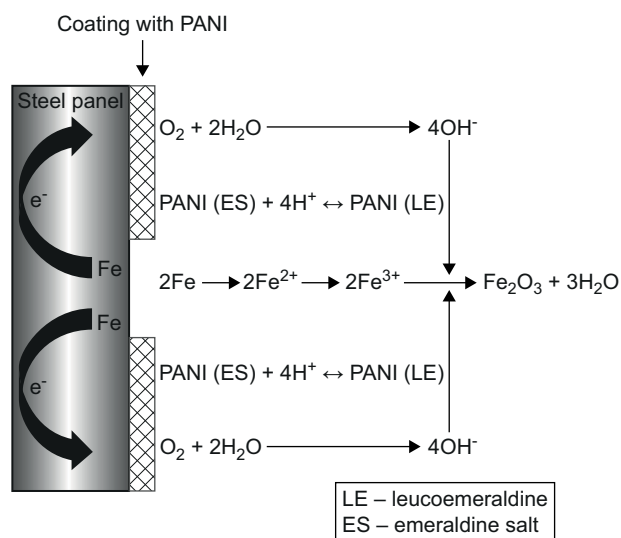

Fig. 1. Schematic of the iron passivation mechanism by means of a paint containing a pigment modified with PANI
Obr. 1. Schéma mechanismu pasivace železa pomocí nátěrového filmu obsahujícího PANI

EXPERIMENTAL

Pigment preparation procedure

The pigments were synthesized by solid-phase reaction, viz. by high-temperature calcination of the homogenized mixtures of the starting materials [26], by following the general principles of preparation of high-temperature inorganic pigments [27]. The stoichiometric molybdates and tungstates for the coating procedure with were prepared by calcination in a closed vessel at 750°C to 900°C and at 900°C to 1000°C, respectively. 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. 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 hours. The milled pigments were rinsed with water again and dried at 105°C in a laboratory electrical dryer.

The pigment particle shape obtained by scanning electron microscope (SEM) is shown in Fig. 2, demonstrating that regular particles or particle clusters were present. Description of the starting substances for synthesis of pigments is given in Tab. 1.

Tab. 1. The general characterization of of the starting substances / *Základní charakterizace výchozích pigmentů*

Pigment	Density (g cm^{-3})	Mean particle size (μm)	Molecular weight (g mol^{-1})
WO$_3$	4.69	12.4	231.84
MoO$_3$	7.16	10.5	143.91
α-Fe$_2$O$_3$	5.05	0.4	159.69
ZnO	2.75	0.6	81.39
SrCO$_3$	3.70	0.6	147.63

Laboratory preparation of pigments modified with a surface layer of polyaniline phosphate (PANI) and polypyrrole phosphate (PPY)

The pigment was suspended with monomer (aniline and pyrrole) solution in ortho-phosphoric acid and ammonium peroxydisulfate. The suspension was stirred for one hour during which monomer polymerized on the surface of the pigment particles. Next day the solids were filtered out and rinsed with phosphoric acid followed by acetone. The pigment particles coated were dried in air and then at 60 °C in a laboratory drier [28].

Determination of the physico-chemical 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, which is able to measure the distribution of particles sizes from 0.01 to 2000 μm. Particle size is represented by the diameter of the equivalent sphere, i.e. sphere whose laser radiation dispersion patterns are identical with those of the particle in question. The pigments' specific weight was determined by using a gas pycnometer. Linseed oil absorption was measured by the pestle-mortar method. The outcome, called the oil number (in g.100 g^{-1}), is a prerequisite for calculation of the CPVC and for the formulation of the paints [29, 30].

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

Formulation of the paints containing the pigments tested

Model solvent-based epoxy-ester resin-based paints were formulated for investigation of the pigments' anticorrosion properties. Description of binder: 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. The characteristic of the binder is showed in Tab. 2. The pigment volume concentration (PVC) 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. Co-octoate in a fraction of 0.3 wt.% was used as the siccative.

Preparation of samples for the testing of the anticorrosion properties

Test samples were prepared by applying the paint to steel panels (deep-drawn cold-rolled steel) 150 × 100 × × 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 magnetic thickness gauge fitted with ISO 2808 [31].

A total of 10 test panels were prepared for each paint. A thin cut 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.

Laboratory corrosion tests

Corrosion tests in artificial atmospheres – Salt spray tests : in this cyclic corrosion test the test panels were exposed to the mist of a 5% NaCl solution at 35°C (± 2°C) for 10 hours (1st cycle stage) and to condensing distilled water at 40°C (± 2°C) for 1 hour (2nd cycle stage), followed by drying at 23°C (± 2°C) for 1 hour (3rd cycle stage). The test encompassed 56 cycles, i.e. its total time was 1344 hours. The tests were conducted in a Liebisch S 400 salt chamber. The procedure was based on the ISO 9227 (ISO 9227:2012) standard.

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,

Tab. 2. The characteristic of binder resin / *Charakterizace pojiva*

Binder resin	Oil components (%)	Density (g cm⁻³)	Acid number (-)	Viscosity (Pa.s)	Flow time (s)
WorléeDur D 46	40	0.98	4	2.5 - 5.0	250

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). The results were converted to scores on a 100-0 scale, and a parameter called the protection efficiency of the paints was calculated by a mathematical relation in Eq. 1 [32].

$$E_{\text{NaCl}} = \frac{A + B + C + D}{4} \qquad (1)$$

A – degree of blistering in the paint film area, B – degree of blistering in the cut through the paint film, C – metal base corrosion, D – corrosion in the paint film cut.

Linear polarisation

The linear polarisation method is applied to corrosion monitoring. It is designed specifically for the determination of the polarisation resistance R_p and current density I_{cor}. Linear polarisation 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 polarisation curve in linear coordinates [33].

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. The paint films were exposed to the salt spray test solution for 24 hours, after which they were measured by the linear polarisation method. The polarisation region was from -10 mV/EOC to +10 mV/EOC at a rate of 0.166 mV/s [34].

Comparison experiments

The anticorrosion pigment based on the zinc phosphate hydrate $Zn_3(PO_4)_2 \cdot xH_2O$ (PVC = 15 vol%) was also tested as a reference material allowing to compare the results obtained with the pigments-synthesized by with those obtained with a commercially available product. Paints containing only $CaCO_3$ at the same pigment volume concentrations as in the paints examined (PVC = 50%) and the coating material without any pigment served as reference materials in some tests, in the paint film pH measurements.

RESULTS

Composite pigment particle structure and morphology

Morphology of the particles of the pigments prior to surface treatment with the conductive polymers and of the composite pigments was observed by means of SEM. The pigment particle morphology is illustrated by scanning electron micrographs for the molybdates and tungstates in Fig. 2. The micrographs were taken in the secondary electron imaging (SEI) mode.

Corrosion tests

The size and frequency of blisters in the paint film were determined as per ASTM D 714-87 and ISO 4628/2 the fraction of substrate metal area affected by corrosion was determined as per ASTM D 610, the distance of propagation of corrosion in the cut was determined after removing the paint film as per ASTM D 1654-92, and the protection efficiency (E_{NaCl}) was calculated as described above [30].

The results of the corrosion test of the paints with the pigments in the environment of NaCl mist are given in Tabs 3-4. The results of the calculated protection efficiency of paints (E_{NaCl}).

Film blistering on the paint film in the atmosphere witthe salt spray test was few and dense degree for surface modified pigments with PANI (Tab. 3). Corrosion on the metal surface in the atmosphere with salt beneath the film, was from <0.01% to 33 % for pigments surface modified with PANI, and <0.03% to >50 % for pigments surface modified with PPY (Tab. 4). Film blistering on the paint film in the atmosphere in the salt spray test was few and medium dense degree for surface modified pigments with PPY.

Linear polarisation

The results of the electrochemical method of linear polarisation of the paint films are included in Tabs 3 and 4. The parameters measured include the spontaneous corrosion potential, polarisation resistance and corrosion rate of the films, providing information about the films' resistance to corrosion. The spontaneous corrosion potential (E_{cor}) of the films containing the pigments at PVC = 1-15 % lay within the region of -664 mV to

-218 mV for PPY as the conductive polymer and within the region of -571 mV to -18 mV for PANI as the conductive polymer. The polarisation resistance (R_p) for the paints with the pigments modified with PANI (PVC = 1 % to 15 %) lay within the region of 3×10^4 Ω to 7×10^8 Ω. The span was broader for the paints with the pigments modified with PPY, viz. from 9×10^3 Ω to 4×10^9 Ω. The corrosion rate (v_{cor}) was from 58×10^{-9} mm·year^{-1} to 28×10^{-4} mm·year^{-1} for the paint films containing the pigments modified with PANI (PVC = = 1 % to 15 %). Once again, the span was broader for the paint films containing the pigments modified with PPY, viz. from 10×10^{-10} mm.year^{-1} to 10×10^{-3} mm·year^{-1}.

DISCUSSION

Composite pigment structure, particle morphology

A total of 12 pigments with their surfaces modified with the conductive polymers PANI and PPY, respectively, were prepared for testing their properties in protective coatings. The particles of the initial inorganic pigments had a regular nodular shape (Fig. 2), which remained unchanged by the surface modification (Fig. 2). The pigments whose surface had been modified with the conductive polymers contained clusters of particles of the conductive polymers [29].

Results of the corrosion tests in artificial atmospheres - Salt spray tests

The results of the accelerated corrosion test with the paint films in the corrosion tests in artificial atmospheres - Salt spray tests are listed in Tabs 3 and 4. Occurrence of osmotic blisters on the paint film surface (i.e. paint film blistering) was higher at higher concentrations of the composite pigments. Among the reasons of this effect is the adverse effect of water-soluble substances due to the higher concentration of the composite pigment, appearing in the environment of the salt mist and increased humidity. As a result, the protective effect of the paint films decreased at higher pigment concentrations. As the barrier effect was diminished, the pigmented paint was less capable of preventing the formation of blisters. The results of this accelerated corrosion test were also in good agreement with the results of electrochemical measurements: the lower barrier efficiency exhibited by the paints with higher conductive polymer contents in the salt spray test was confirmed by the linear polarisation measurements.

The pigment particle modification with PANI was favourable especially as regards prevention of metal surface corrosion beneath the paint film up to PVC = 10 %.

Modification with PPY was inferior to the modification with PANI in this respect, the paint films were less capable of protecting the metal surface against corrosion, especially in the higher PVC range. This was due to the lower electric conductivity of PPY as compared to PANI. Pigment modification with a layer of PANI or PPY was also favourable with respect to corrosion protection near the cut, especially at PVC = 1-5 %.

The highest values of the calculated protection efficiency were obtained for paint films containing strontium molybdate modified with polyaniline phosphate (SrMoO$_4$/PANI) at PVC = 1 % (protection efficiency value E_{NaCl} = 89 %), followed by zinc molybdate modified with polypyrrole phosphate (ZnMoO$_4$/PPY) at PVC = 5 % (E_{NaCl} = 99 %). The two E_{NaCl} values exceeded substantially the protection efficiency of the reference material (E_{NaCl} = 61 %), thus demonstrating the pigment's ability to act as a corrosion inhibitor even at low concentrations [34].

The optimum concentrations of the composite pigments with respect to the protection efficiency were identified for all the systems. They lay within the range of PVC = 1-5 %.

The paint films containing strontium tungstate modified with polypyrrole phosphate (SrWO$_4$/PPY) were the only exception, exhibiting lower protection efficiencies than the reference standard at any PVC. This pigment contained more water-soluble substances and, in addition, included additional minority crystal phases affecting adversely the pigment's anticorrosion efficiency in the corrosion environment used.

The optimum concentrations with respect to the anticorrosion efficiency of the paint films (E_{NaCl}) were as follows: ZnMoO$_4$/PANI: PVC = 1 % (E_{NaCl} = 76); SrMoO$_4$/PANI: PVC = 1 % (E_{NaCl} = 89); Fe$_2$(MoO$_4$)$_3$/PANI: PVC = 10 % (E_{NaCl} = 76); ZnWO$_4$/PANI: PVC = = 1 % (E_{NaCl} = 80); SrWO$_4$/PANI: PVC = 10 % (E_{NaCl} = 75); Fe$_2$WO$_6$/PANI: PVC = 1 % (E_{NaCl} = 84); ZnMoO$_4$/PPY: PVC = 5 % (E_{NaCl} = 99); SrMoO$_4$/PPY: PVC = = 1 % (E_{NaCl} = 88); Fe$_2$(MoO$_4$)$_3$/PPY: PVC = 1 % (E_{NaCl} = = 66); ZnWO$_4$/PPY: PVC = 5 % (E_{NaCl} = 77); SrWO$_4$/PPY: PVC = 5 % (E_{NaCl} = 60); and Fe$_2$WO$_6$/PPY PVC = = 5 % (E_{NaCl} = 79). The optimum PVC was 1% or 5% for the majority of pigments.

The findings from the 1344-hour exposure of the steel panels coated with the paint films to the neutral salt mist atmosphere can be summarised as follows:

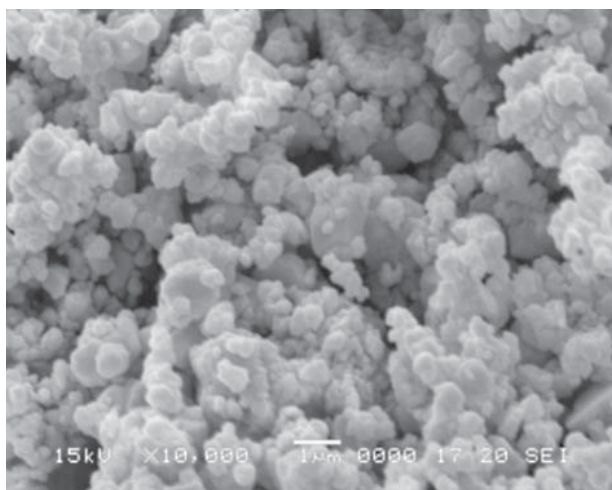- Paints providing high protection against corrosion of the substrate metal (corroded metal surface fraction up to 0.01-0.03 %) contained the following composite pigments: SrMoO$_4$/PANI, PVC = 1 % (corroded area 0.01 %) > ZnMoO$_4$/PANI, PVC = 1 % (corroded area 0,03 %), Fe$_2$(MoO$_4$)$_3$/PPY, PVC = 1 % (corroded area 0.03 %), ZnMoO$_4$/PPY, PVC = 5 % (corroded area 0.03 %);
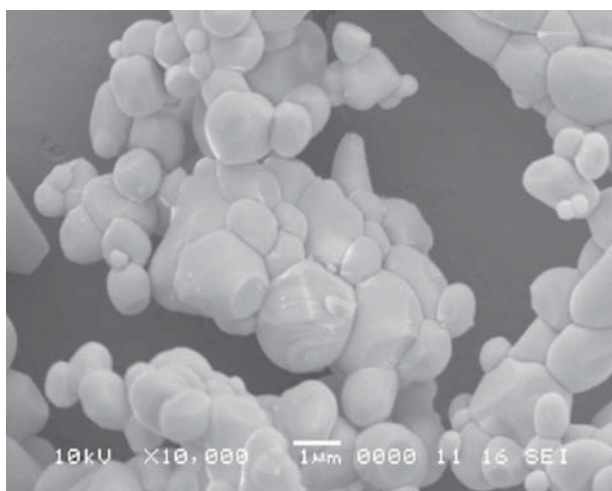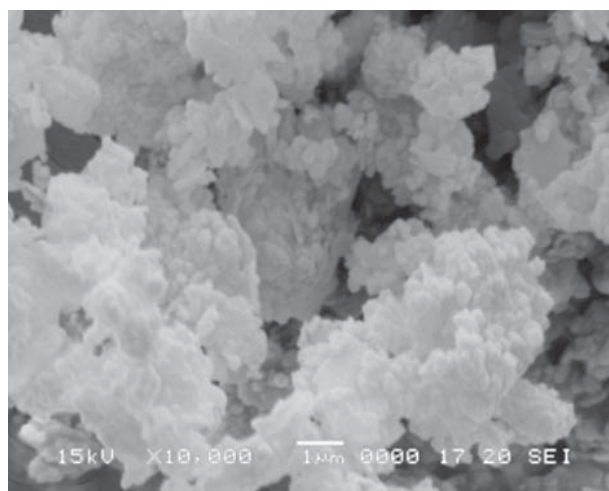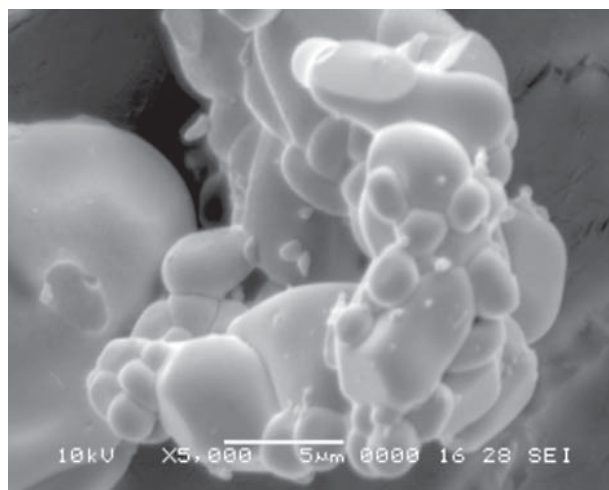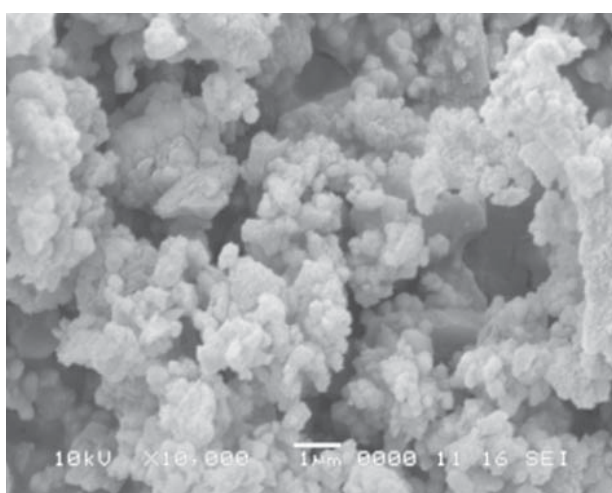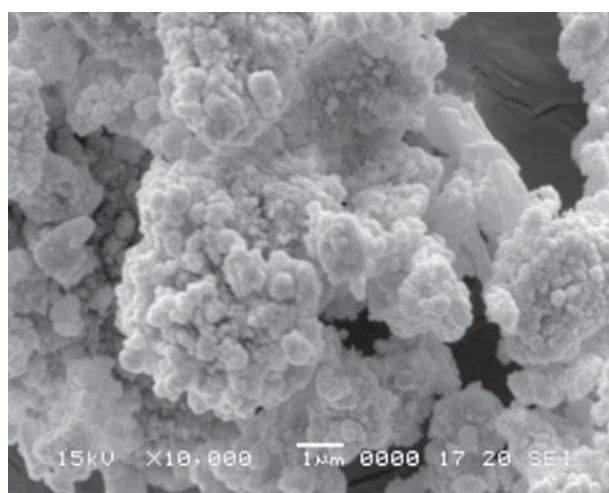
Fig. 2. SEM photographs
Obr. 2. SEM fotografie

- Paints providing high protection against corrosion propagation near the cut, 0-1 mm from the cut, contained the following composite pigments: $ZnMoO_4$/PPY, PVC = 5 % (corrosion spread to 0-0.5 mm) > $SrMoO_4$/PPY, PVC = 10% (corrosion spread to 0.50-1.0 mm) ~ $SrMoO_4$/PANI, PVC = 1 % (corrosion spread to 0.5-1 mm) ~ Fe_2WO_6/PANI, PVC = 5 and 10 % (corrosion spread to 0.5-1 mm);

- Paints exhibiting high resistance against film surface blistering (i.e. no blisters) contained the following composite pigments: $SrMoO_4$/PANI, PVC = 1 % (no blisters) ~ $ZnMoO_4$/PANI, PVC = 10 %, 15 % (no blisters) ~ Fe_2WO_6/PANI, PVC = 1 % (no blisters) ~ $SrWO_4$/PANI, PVC = 15 % (no blisters) ~ $ZnMoO_4$/PPY PVC = 5 % (no blisters) ~ $SrMoO_4$/PPY, PVC = 1 % (no blisters), $ZnWO_4$/PPY, PVC = 5 %, 15 %, (no blisters) ~ Fe_2WO_6/PPY, PVC = 5 %, 15 % (no blisters);

- Paints that were efficient in corrosion protection (E_{NaCl} >76) at a pigment concentration as low as PVC = 1 % contained the following composite pigments: $SrMoO_4$/PANI (E_{NaCl} = 89) > $SrMoO_4$/PPY (E_{NaCl} = 88) > Fe_2WO_6/PANI (E_{NaCl} = 84) > $ZnWO_4$/PANI (E_{NaCl} = 80) > $ZnMoO_4$/PANI (E_{NaCl} = 76);

- For all of the pigments in the salt mist atmosphere, pigment particle modification with polyaniline phosphate (PANI) was superior (more efficient or better balanced) to modification with polypyrrole phosphate (PPY) with respect to the anticorrosion properties;

Tab. 3. Results of accelerated corrosion tests of the paints containing molybdates and tungstates modified with PANI in the salt spray test (exposure 1344 hours, DFT = 100 ±10 μm) / *Výsledky zrychlené korozní zkoušky nátěrů s obsahem molybdenanů a wolframanů s povrchovou úpravou PANI v atmosféře s obsahem solné mlhy (expozice 1344 hodin, DFT = 100 ±10mm)*

Pigment	PVC (%)	Paint evaluation		Substrate metal evaluation		Protection efficiency E_{NaCl}
		Degree of blistering ASTM D 714-87 / ISO 4628/2		Corrosion in the cut ASTM D 1654-92	Surface corrosion ASTM D 610-85	
		Near the cut	Film surface	(mm)	(%)	
ZnMoO₄ / PANI	1	4M / 3(S4)	6F / 2(S3)	1.0 – 1.5	0.03	76
	5	4M / 3(S4)	8F / 2(S2)	1.5 – 2.0	0.3	75
	10	– / 0	4M / 3(S4)	3.0 – 3.5	1	73
	15	– / 0	2MD / 4(S5)	2.0 – 2.5	16	60
SrMoO₄ / PANI	1	– / 0	4F / 2(S4)	0.5 – 1.0	0.01	89
	5	4F / 2(S4)	6F / 2(S3)	1.0 – 1.5	1	78
	10	2F / 2(S5)	6F / 2(S3)	1.5 – 2.0	0.3	78
	15	4M / 3(S4)	– / 0	1.5 – 2.0	10	73
Fe₂(MoO₄)₃ / PANI	1	4MD / 4(S4)	6M / 3(S3)	2.0 – 2.5	0.1	63
	5	4M / 3(S4)	2M / 3(S5)	2.5 – 3.0	0.1	65
	10	2F / 2(S5)	4F / 2(S4)	2.0 – 2.5	0.1	76
	15	8F / 2(S2)	4MD / 4(S4)	1.5 – 2.0	33	53
ZnWO₄ / PANI	1	4F / 2(S4)	4F / 2(S4)	1.0 – 1.5	0.1	80
	5	2F / 2(S5)	4F / 2(S4)	2.0 – 2.5	10	66
	10	6M / 3(S3)	6M / 3(S3)	1.5 – 2.0	10	63
	15	6F / 2(S3)	4D / 5(S4)	2.0 – 2.5	33	50
SrWO₄ / PANI	1	4M / 3(S4)	2M / 3(S5)	2.5 – 3.0	0.1	65
	5	2F / 2(S5)	4M / 3(S4)	2.5 – 3.0	1	66
	10	4F / 2(S4)	4F / 2(S4)	2.5 – 3.0	0.3	75
	15	– / 0	4MD / 4(S4)	2.5 – 3.0	10	65
Fe₂WO₆ / PANI	1	– / 0	4F / 2(S4)	2.0 – 2.5	0.3	84
	5	6MD / 4(S3)	4M / 3(S4)	0.5 – 1.0	0.3	66
	10	2F / 2(S5)	6MD / 4(S3)	0.5 – 1.0	0.3	70
	15	6D / 5(S3)	6D / 5(S3)	1.0 – 1.5	50	29
Zn₃(PO₄)₃·xH₂O	15	2M / 3(S5)	8M / 3(S2)	2.0 – 2.5	3	61
Non pigmented film	–	6M / 3(S3)	– / 0	1.5 – 2.0	50	60

- Molybdates as the pigment cores are superior (more efficient/effective) to tungstates with respect to the anticorrosion properties in the salt mist atmosphere;

- Efficient paint films attaining a better protection efficiency than the reference paint, i.e. $E_{NaCl} > 61$, contained the following composite pigments at the following concentrations: $Fe_2(MoO_4)_3$/PANI, PVC = 1%, 5% and 10%; $SrMoO_4$/PANI, PVC = 1%, 5%, 10% and 15%; $ZnMoO_4$/PANI, PVC = 1%, 5% and 10 %; $Fe_2(MoO_4)_3$/PPY, PVC = 1%; $SrMoO_4$/PPY, PVC = 1%; $ZnMoO_4$/PPY, PVC = 1% and 5%; Fe_2WO_6/PANI, PVC = 1%, 5% and 10%; $SrWO_4$/PANI, PVC = 1%, 5%, 10% and 15%; $ZnWO_4$/PPY, PVC = 1%, 5% and 10%; Fe_2WO_6/PPY, PVC = 1%, 5% and 10%; $ZnWO_4$/PPY, PVC = 1%, 5% and 10%;

- The paint containing the composite pigment at PVC = 15% that exhibited anticorrosion efficiency better than or comparable to that of the reference material, i.e. paint with zinc phosphate also at PVC = 15% (E = 61), was the paint containing $ZnMoO_4$/PANI (E_{NaCl} = 60).

Linear polarisation

The parameters investigated, i.e. spontaneous corrosion potential, polarisation resistance and corrosion rate, provide information about the paint films' resistance to corrosion (Tabs 5-6). The measurements with the composite pigments were completed with measurements with two reference materials, viz. the coating material with zinc phosphate at PVC = 15 % and the non-pigmented coating material.

The non-pigmented coating material, with 42 mV spontaneous corrosion potential, attained a polarisation resistance of 3×10^6 Ω and corrosion rate

Tab. 4. Results of accelerated corrosion tests of the paints containing molybdates and tungstates modified with PANI in the salt spray test (exposure 1344 hours, DFT = 100 ±10 µm) / *Výsledky zrychlené korozní zkoušky nátěrů s obsahem molybdenanů a wolframanů s povrchovou úpravou PPY v atmosféře s obsahem solné mlhy (expozice 1344 hodin, DFT = 100 ±10mm)*

Pigment	PVC (%)	Paint evaluation		Substrate metal evaluation		Protection efficiency E_{NaCl}
		Degree of blistering ASTM D 714-87 / ISO 4628/2		Corrosion in the cut ASTM D 1654-92	Surface corrosion ASTM D 610-85	
		Near the cut	Film surface	(mm)	(%)	
$ZnMoO_4$ / PPY	1	4F / 2(S4)	6F / 2(S3)	1.0 – 1.5	0.1	81
	5	– / 0	– / 0	0.0 – 0.5	0.03	99
	10	4F / 2(S4)	4M / 3(S4)	1.0 – 1.5	50	51
	15	8M	4MD / 4(S4)	2.0 – 2.5	10	55
$SrMoO_4$ / PPY	1	– / 0	6F / 2(S3)	1.0 – 1.5	0.1	88
	5	2M / 3(S5)	6M / 3(S3)	2.5 – 3.0	3	60
	10	8F / 2(S2)	6M / 3(S3)	0.5 – 1.0	50	56
	15	2F / 2(S5)	6M / 3(S3)	1.0 – 1.5	> 50	51
$Fe_2(MoO_4)_3$ / PPY	1	2M / 3(S5)	8MD / 4(S2)	1.0 – 1.5	0.03	66
	5	2M / 3(S5)	6MD / 4(S3)	2.0 – 2.5	1	59
	10	2M / 3(S5)	6MD / 4(S3)	2.5 – 3.0	1	58
	15	6F / 2(S3)	6MD / 4(S3)	2.5 – 3.0	> 50	45
$ZnWO_4$ / PPY	1	6F / 2(S3)	4M / 3(S4)	2.0 – 2.5	0.3	72
	5	- / 0	4M / 3(S4)	1.5 – 2.0	1	77
	10	2M / 3(S5)	4F / 2(S4)	2.0 – 2.5	3	65
	15	– / 0	6MD / 4(S3)	1.0 – 1.5	50	55
$SrWO_4$ / PPY	1	2MD / 4(S5)	8M / 3(S2)	2.5 – 3.0	10	54
	5	2M / 3(S5)	6MD / 4(S3)	2.0 – 2.5	0.3	60
	10	4MD / 4(S4)	2MD / 4(S5)	2.5 – 3.0	16	40
	15	2F / 2(S5)	4MD / 4(S4)	2.5 – 3.0	> 50	41
Fe_2WO_6 / PPY	1	6F / 2(S3)	4M / 3(S4)	2.0 – 2.5	0.3	73
	5	– / 0	4M / 3(S4)	1.0 – 1.5	1	79
	10	2M / 3(S5)	4F / 2(S4)	1.5 – 2.0	3	66
	15	– / 0	6MD / 4(S3)	1.0 – 1.5	> 50	55

12×10^{-6} mm·year^{-1}. With the paint film pigmented with zinc phosphate at PVC = 15 %, the spontaneous corrosion potential (E_{cor}) decreased (compared to the non-pigmented coating) to –473 mV and the polarisation resistance was higher, $R_p = 3 \times 10^7$ Ω. Corrosion rate was one order of magnitude lower, viz. $v_{cor} = 12 \times 10^{-7}$ mm·year^{-1}. This paint served as reference for the paint films with the following pigments whose surface had been modified with the conductive polymers: Fe$_2$(MoO$_4$)$_3$, Fe$_2$WO$_6$, SrMoO$_4$, SrWO$_4$, ZnMoO$_4$ and ZnWO$_4$ at PVC = 1 %, 5 %, 10 % and 15 %.

The paint films containing the molybdate pigments modified with polyaniline phosphate exhibited a higher spontaneous corrosion potential than the paint film with zinc phosphate. All paint films containing those pigments at PVC = 1 %, 5 % and 10 % attained a lower reduced corrosion rate than both the non-pigmented coating material and the paint film with zinc phosphate.

The paint films containing the molybdate pigments modified with polypyrrole phosphate exhibited spontaneous corrosion potentials within the range of E_{cor} = = -385 mV to -572 mV of the spontaneous corrosion potential of the paint film pigmented with zinc phosphate (E_{cor} = ±100mV). The paint films containing ZnMoO$_4$/ /PPY at PVC = 1% and 5 % attained a corrosion rate 2 orders of magnitude lower ($v_{cor} = 23 \times 10^{-9}$ mm·year^{-1}), and the paint film containing Fe$_2$(MoO$_4$)$_3$/PPY at PVC = = 1%, even 3 orders of magnitude lower ($v_{cor} = 10 \times 10^{-10}$ mm·year^{-1}) than the paint film with zinc phosphate. As to the remaining films containing the molybdate pigments modified with polypyrrole phosphate, the corrosion rate was comparable to or higher than that of the paint film with zinc phosphate.

The paint films containing the tungstate pigments modified with polyaniline phosphate exhibited spontaneous corrosion potentials within the range of the spon-

Tab. 5. Results of linear polarisation measurements of the paints containing pigments modified with PANI, DFT = 50 ± 10 μm / *Vyhodnocení měření lineární polarizace nátěrů s obsahem pigmentů povrchově upravených PANI, DFT = 50 ± 10 μm*

Pigment in the paint	PVC (%)	E$_{cor}$ (mV)	I$_{cor}$ (μA)	β$_a$ (mV)	β$_c$ (mV)	R$_p$ (Ω)	v$_{cor}$ (mm year^{-1})
ZnMoO$_4$ / PANI	1	-106	0.2×10^{-4}	21.6	16.4	2×10^8	24×10^{-8}
	5	-140	0.1×10^{-4}	22.1	17.2	2×10^8	36×10^{-8}
	10	-127	0.5×10^{-4}	24.6	22.3	1×10^8	52×10^{-8}
	15	-179	0.6×10^{-2}	30.2	29.0	1×10^6	70×10^{-8}
SrMoO$_4$ / PANI	1	-42	0.5×10^{-5}	18.5	15.2	7×10^8	58×10^{-9}
	5	-18	0.1×10^{-3}	24.1	20.5	3×10^7	16×10^{-8}
	10	-427	0.6×10^{-4}	18.6	18.3	6×10^7	74×10^{-8}
	15	-374	0.6×10^{-2}	28.0	25.6	10×10^5	70×10^{-6}
Fe$_2$(MoO$_4$)$_3$ / PANI	1	-41	0.1×10^{-3}	22.6	23.3	4×10^6	12×10^{-7}
	5	-86	0.4×10^{-4}	27.1	23.2	1×10^8	45×10^{-8}
	10	-29	0.2×10^{-3}	22.6	19.8	3×10^7	18×10^{-7}
	15	-456	0.6×10^{-2}	27.0	26.3	9×10^5	70×10^{-6}
ZnWO$_4$ / PANI	1	-420	0.6×10^{-2}	28.2	29.1	1×10^5	71×10^{-6}
	5	-571	0.6×10^{-1}	26.2	29.9	9×10^4	74×10^{-5}
	10	-509	0.3×10^{-1}	30.6	34.1	2×10^5	38×10^{-5}
	15	-571	0.2×10^{-1}	16.0	16.4	5×10^5	27×10^{-5}
SrWO$_4$ / PANI	1	-454	0.3×10^{-4}	14.5	11.8	7×10^7	37×10^{-8}
	5	-506	0.6×10^{-2}	34.8	46.0	2×10^6	70×10^{-6}
	10	-547	0.2×10^{-1}	39.9	42.7	5×10^5	22×10^{-5}
	15	-510	0.4×10^{-1}	23.6	27.4	1×10^5	45×10^{-5}
Fe$_2$WO$_6$ / PANI	1	-471	0.2×10^{-3}	17.0	15.8	2×10^7	18×10^{-7}
	5	-463	0.3×10^{-3}	19.1	16.3	1×10^7	36×10^{-7}
	10	-385	0.8×10^{-3}	16.4	17.2	4×10^6	96×10^{-7}
	15	-538	0.2×10^{-1}	30.3	32.4	3×10^4	28×10^{-4}
Zn$_3$(PO$_4$)$_3$·xH$_2$O	15	-473	0.1×10^{-3}	17.0	16.1	3×10^7	12×10^{-7}
Non pigmented film	0	42	0.2×10^{-2}	21.6	18.9	3×10^6	12×10^{-6}

taneous corrosion potential of the paint film with zinc phosphate (± 100 mV). The paint film with SrWO$_4$/ / PANI at PVC = 1 % attained a corrosion rate one order of magnitude lower that the paint film with zinc phosphate. The corrosion rates of the paint films with iron(III) tungstate Fe$_2$WO$_6$/PANI at PVC = 1 %, 5 % and 10 % were at the same order of magnitude as the corrosion rate of zinc phosphate. The remaining paint films with the tungstate pigments treated with polyaniline phosphate exhibited corrosion rates comparable to or higher than the corrosion rate of the paint film with zinc phosphate.

The paint films containing the tungstate pigments modified with polypyrrole phosphate also exhibited spontaneous corrosion potentials within the range of the spontaneous corrosion potential of the paint film with zinc phosphate (± 100 mV). Corrosion rates comparable to the corrosion rate of this reference paint film were attained by the paint films containing Fe$_2$WO$_6$/PPY at PVC = 10 % and SrWO$_4$/PPY at PVC = 1 % and 5 %. The remaining paint films with the tungstate pigments

treated with polypyrrole phosphate exhibited corrosion rates comparable to or higher than the corrosion rate of the paint film with zinc phosphate.

CONCLUSION

This work was devoted to the anticorrosion and adhesion-barrier properties of paint films containing molybdates and tungstates whose surface had been modified with polyaniline phosphate or polypyrrole phosphate. The pigment volume concentrations (PVC) were 1%, 5%, 10% and 15% and the best of them with respect to the anticorrosion properties was sought.

Overall, polyaniline phosphate (PANI) as the modifying conductive polymer appeared to be superior to polypyrrole phosphate (PPY) with respect to the corrosion-inhibiting efficiency of the composite pigments. From the same aspect, the molybdates appeared to be superior to the tungstates. It is an advantage of the

Tab. 6. Results of linear polarisation measurements of the paints containing pigments modified with PPY. DFT = 50 ± 10 μm / *Vyhodnocení měření lineární polarizace nátěrů s obsahem pigmentů povrchově upravených PPY, DFT = 50 ± 10 μm*

Pigment in the paint	PVC (%)	E$_{cor}$ (mV)	I$_{cor}$ (μA)	β$_a$ (mV)	β$_c$ (mV)	R$_p$ (Ω)	v$_{cor}$ (mm year^{-1})
ZnMoO4/PPY	1	-464	0.2×10^{-5}	10.4	8.3	4×10^9	23×10^{-9}
	5	-540	0.2×10^{-5}	31.4	29.2	3×10^9	23×10^{-9}
	10	-543	0.8×10^{-1}	36.6	38.2	1.10^6	88×10^{-6}
	15	-553	0.3×10^{-2}	26.0	20.6	1×10^6	35×10^{-6}
SrMoO4/ PPY	1	-512	0.5×10^{-2}	23.0	25.1	2×10^6	28×10^{-6}
	5	-539	0.4×10^{-2}	24.0	26.6	1×10^6	46×10^{-6}
	10	-570	0.2×10^{-1}	11.9	14.1	1×10^6	21×10^{-6}
	15	-529	0.2×10^{-2}	21.2	23.7	3×10^6	24×10^{-6}
Fe2(MoO4)3/PPY	1	-560	0.3×10^{-6}	13.7	7.4	7×10^7	10×10^{-10}
	5	-440	0.8×10^{-5}	13.3	9.7	3×10^8	93×10^{-6}
	10	-385	0.3×10^{-2}	16.9	16.0	1×10^6	35×10^{-6}
	15	-572	0.9×10^{-1}	30.5	41.2	9×10^3	10×10^{-3}
ZnWO4/PPY	1	-525	0.8×10^{-2}	35.3	33.3	9×10^5	93×10^{-6}
	5	-538	0.6×10^{-2}	26.9	24.4	9×10^5	70×10^{-6}
	10	-382	0.3×10^{-1}	23.1	26.3	2×10^4	37×10^{-4}
	15	-557	0.3×10^{-1}	21.1	16.8	1×10^4	36×10^{-4}
SrWO4/PPY	1	-554	0.6×10^{-3}	15.4	18.8	7×10^6	64×10^{-7}
	5	-536	0.6×10^{-3}	17.5	18.7	7×10^6	65×10^{-7}
	10	-566	$0.2v10^{-1}$	21.3	25.5	2×10^4	26×10^{-4}
	15	-664	0.6×10^{-1}	29.2	48.2	1×10^4	71×10^{-4}
Fe2WO6/PPY	1	-517	0.4×10^{-1}	34.9	35.4	2×10^5	43×10^{-5}
	5	-218	0.4×10^{-2}	32.1	36.1	2×10^6	39×10^{-6}
	10	-492	0.2×10^{-3}	29.0	22.3	3×10^7	22×10^{-7}
	15	-498	0.4×10^{-1}	28.7	27.0	1×10^5	48×10^{-5}

surface-modified pigments that a low PVC is sufficient to attain a high anticorrosion efficiency of the epoxy-ester resin based paints. For some pigments (e.g. $SrMoO_4$/PANI), PVC = 1% is the optimum level, which is advantageous from the financial aspect as well.

Based on the results of the linear polarisation measurements and of the accelerated corrosion test in the condensation chamber with salt mist, the best paint was that containing strontium molybdate whose surface had been modified with PANI ($SrMoO_4$ / PANI) at PVC = 1 % and 5%. Presumably, anodic protection of the steel substrate played a major role. This paint provided outstanding results in the other tests as well, its total mechanical resistance attained high values.

With respect to linear polarisation, the molybdate pigments were superior to the tungstate pigments, and PANI as the modifying conductive polymer appeared to be superior to PPY. Really, paint films containing molybdate pigments modified with PANI (PVC = 1%, 5% and 10%) exhibited corrosion rates lower than or comparable to the corrosion rate observed with the reference paint with zinc phosphate, in contrast to the paint films containing the tungstate pigments modified with PPY, which exhibited corrosion rates higher than the corrosion rate of the reference paint.

The pigments studied are promising owing to their properties: high efficiency compared to the reference pigment; low effective concentration in the paint; and environmental friendliness. They deserve continuation of the present research.

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