

1 **ANTI-KOROZÍ PIGMENTY NA BÁZI PEROVSKITŮ S POVRCHOVOU**
2 **ÚPRAVOU VODIVÝM POLYMEREM PPDA**

3 **ANTICORROSIVE PIGMENTS BASED OF PEROVSKITE WITH**
4 **A SURFACE LAYER CONDUCTIVE POLYMER PPDA**

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10
11 **Abstract**

12 The properties of protective organic coatings containing perovskites whose surface had been
13 modified with conductive polymers were investigated, with focus on their anticorrosion effect. The
14 perovskite type pigments (XYO_3 ; X = Ca, Sr, Y = Ti, Mn) were synthesized by high-temperature
15 solid-phase reaction, and their surface was modified with a conductive polymer, specifically
16 polyparaphenyldiamine phosphate (PPDA), by chemical oxidative polymerisation.

17 Conductive polymers are currently attracting considerable interest in a number of sectors,
18 among them the paint industry owing to their non-toxicity and high stability.

19 Paints consisting of a solvent-based epoxy-ester resin as the binder and the above-mentioned
20 perovskite/PPDA pigments were formulated and subjected to mechanical tests in order to assess the
21 effect of the composite pigment particles on the paints' mechanical resistance. Corrosion resistance of
22 the coatings was tested also evaluated in dependence on the type of particle surface treatment with the
23 conductive polymer, chemical composition of the pigment, and pigment volume concentration (PVC)
24 in simulated corrosive atmosphere.

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28 **Keywords:** perovskites, anticorrosion pigment, organic coating, conductive polymer, epoxy-ester
29 resin, paraphenyldiamine

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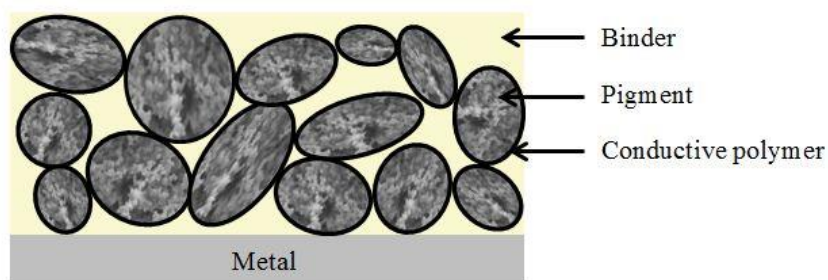
30 **Introduction**

31 The most famous method to protect the surfaces of metallic materials consists in coating
32 them with paints possessing anticorrosion properties [1, 2]. Paints designed to protect metals against
33 corrosion always contain corrosion-inhibiting pigments that slow down the metal corrosion process
34 through electrochemical and chemical reactions [3, 4]. Therefore, the possibility of developing
35 nontoxic pigments for anticorrosion pigments that would feature efficiency at the same or even better

36 level than the traditional toxic anticorrosion pigments is being explored. A number of papers have
 37 been devoted to protective coatings containing pigments based on oxides with the perovskite structure,
 38 which exhibit anticorrosion properties.

39 Chemically and electrochemically acting pigments encompass a wide range of substances of various
 40 chemical composition, mainly lead-containing compounds and chromate pigments, phosphate
 41 compounds, modified phosphates, and metal powder based pigments [5, 6].

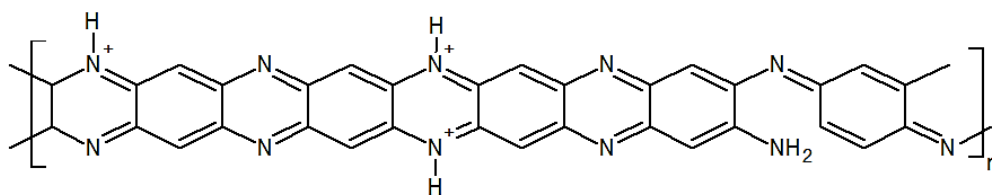
42 Conductive polymers start to be popular among organic corrosion inhibitors [7]. Examples of
 43 conductive polymers include polypyrrole and polyaniline (Fig. 1), involving systems of conjugated
 44 double bonds with the presence of charge carriers making possible charge transfer along the chain [8].
 45 Owing to their properties, conductive polymers induce passivation processes on steel surfaces, in
 46 which respect they are similar to the compounds containing heavy metals. This shows promise are
 47 regards the feasibility of using conductive polymers to replace, or reduce the use of, e.g., chromate-
 48 based corrosion inhibitors [9]. They may also find application as electrochemical, or electrically
 49 active, pigments to attain passivation of the surface of a corroding steel substrate [10, 11].



50

51 Figure 1. Pigments treated conductive polymers on the surface layer.

52 A new conductive polymer is polyphenylenediamine (PPDA), which can also be oxidized to
 53 the oligomer or polymer [12, 13]. Phenylenediamine contains two primary amino groups, serving to
 54 interconnect the monomers during the oxidative polymerization process. Ammonium peroxodisulphate
 55 is used as the oxidative reagent. The two amino groups can be included in a phenazine-like ladder
 56 structure if the oxidative reagent is present in appreciable concentrations [14, 15].
 57 Polyphenylenediamine is considerably less conductive than polyaniline but many properties are
 58 similar owing to the similarity of the structures (Fig. 2). Redox activity is one of such properties [16].



59

60 Figure 2. Idealized structure of poly(p-phenylenediamine) produced by the oxidation of both amine
 61 groups in p-phenylenediamine [15].

Experimental

62

63 *Laboratory preparation of pigments*

64 Perovskites with a generally isometric particle shape were synthesized to serve as the pigment
65 cores for coating with a conductive polymers and to be added to a binder to form anticorrosion paints.
66 Pigments possessing the simple perovskite structure: CaTiO_3 , SrTiO_3 , CaMnO_3 and SrMnO_3 , were
67 synthesized by calcination [17].

68 The anticorrosion pigment based on the zinc phosphate hydrate $\text{Zn}_3(\text{PO}_4)_2 \times \text{H}_2\text{O}$ (PVC = 15 %)
69 was also tested as a reference material allowing us to compare the results obtained with the pigments
70 synthesized by us with those obtained with a commercially available product.

71 *Pigment preparation procedure*

72 The pigments were synthesized by solid-phase reaction, viz. by high-temperature calcination
73 of the homogenized mixtures of the starting materials by following the general principles of
74 preparation of high-temperature inorganic pigments. The process of preparing the pigments consists of
75 4 operational steps: homogenization, calcination, washing with water and milling by wett process.
76 [17].

77 The surface of the pigments was modified by treatment with polyparaphenyldiamine
78 phosphate (PPDA). The anti-corrosion efficiency was evaluated both for the untreated pigments and
79 for the pigments with surfaces modified with PPDA.

80 *Preparation of the perovskites modified with a surface layer of polyparaphenyldiamine phosphate*

81 This is the oxidative polymerization of phenyldiamine, which is carried out under laboratory
82 conditions in the environment of phosphoric acid. Peroxydisulfate is the most commonly used oxidant
83 [18]. To this reaction was added to each of the synthetised perovskite [17].

84 *Determination of the physico-chemical properties of the perovskites with conductive polymer surface layers*

86 The pigments' specific weight was determined by using a AccuPyc II 1340, gas pycnometer
87 (Micromeritics, USA. Linseed oil absorption was measured by the pestle-mortar method. The
88 outcome, called the oil number (in $\text{g } 100 \text{ g}^{-1}$), is a prerequisite for calculation of the CPVC and for the
89 formulation of the paints Parameters are given as arithmetic averages within 10 measured values [19].

90 *Formulation, preparation and testing of the paints*

91 Epoxy-ester resin-based paints were formulated for investigation of the pigments'
92 anticorrosion properties. Description of binder: a 60 % solution of a medium high molecular weight
93 epoxy resin esterified with a mixture of fatty acids of dehydrated ricin oil and soy oil, trade name
94 WorléeDur D 46, acid number 4, viscosity $2.5\text{--}5.0 \text{ Pa s}^{-1}$, flow time (DIN 53211-4200) 250 s, solvent
95 xylene. The pigment volume concentration (PVC) in the paints were invariably 1, 5, 10 %, and 15 %.

96 The PVC/CPVC ratio was adjusted in all the model paints to 0.50 by means of the anticorrosion-
97 neutral filler calcite CaCO_3 .

98 The paint films were applied to the substrates by means of an applicator for steel panels (Q-
99 panel, UK) 152 mm \times 102 mm \times 0.8 mm size. A total of 10 test panels were prepared for each paint. A
100 thin cut (groove), 10 cm long, which penetrated through the paint film and reached the substrate metal,
101 was made using a sharp blade. The samples on the test panels were allowed to dry under standard
102 conditions (temperature 20°C, relative humidity 50%) in a conditioned laboratory for 6 weeks. The dry
103 film thickness (DFT) was measured with a Minitest 110 magnetic thickness gauge fitted with a F16
104 type probe (Elektrophysik, Germany) in accordance with ISO 2808. A 7 mm long test cut was made
105 on the bottom of all steel panels for the corrosion tests.

106 *Cyclic corrosion test with salt mist and condensing moisture*

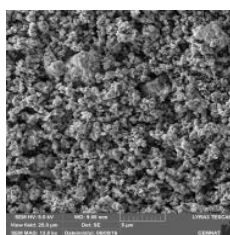
107 In the 24-hour cyclic corrosion test in the presence of *condensing water and SO_2* , the test
108 panels were exposed to condensing water containing SO_2 at 36°C \pm 2°C for 8 hours (1st cycle stage)
109 followed by drying at 23°C \pm 2°C (2nd cycle stage). This test encompassed 15 cycles, i.e. it took 1400
110 hours in total.

111

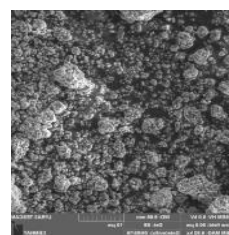
Results and discussion

112 *Structure and morphology of the composite pigment particles*

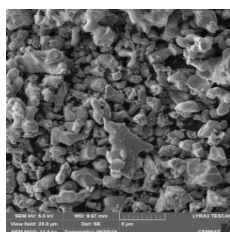
113 The pigment particle morphology is illustrated by scanning electron micrographs Figure 3 for
114 the perovskites and for the surface modified perovskites. The micrographs were taken in the secondary
115 electron imaging (SEI) mode. The composite pigments had a tendency to form clusters.



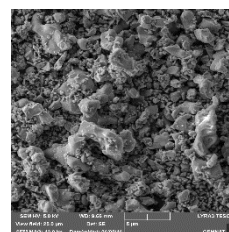
a)



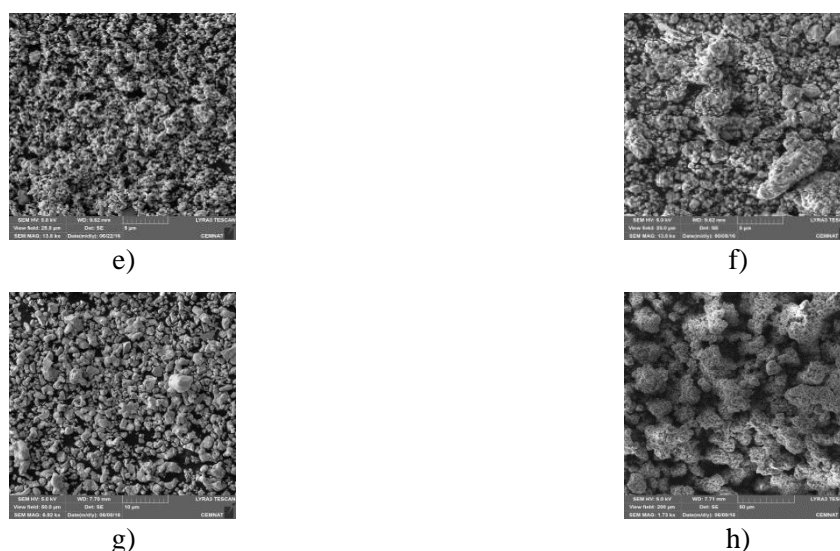
b)



c)



d)



116

117 Figure 3. Morphology of perovskite particles as observed by SEM: a) CaTiO_3 ; b) $\text{CaTiO}_3/\text{PPDA}$; c)
118 CaMnO_3 ; d) $\text{CaMnO}_3/\text{PPDA}$; e) SrTiO_3 ; f) $\text{SrTiO}_3/\text{PPDA}$; g) SrMnO_3 ; h) $\text{SrMnO}_3/\text{PPDA}$.

119 Corrosion tests

120 The size and frequency of blisters in the paint film were determined as per ASTM D 714-87,
121 the fraction of substrate metal area affected by corrosion was determined as per ASTM D 610, the
122 distance of propagation of corrosion in the cut was determined after removing the paint film as per
123 ASTM D 1654-92, and the overall anticorrosion efficiency (E_{SO_2}) was calculated as described above
124 [20].

125 Table 1. Results of accelerated corrosion tests of the paints containing composite pigments in mist of a
126 salt electrolyte (exposure 1400 hours, film thickness = $100 \pm 10 \mu\text{m}$).

Pigment	PVC/ %	Blistering		Corrosion		Anticorrosion efficiency $E_{\text{SO}_2}/\%$
		In a cut/dg	Metal base/dg	In the cut/mm	Metal base/%	
CaTiO_3	1	8MD	-	0-0,5	0,1	83
	5	8M	-	0-0,5	0,03	89
	10	8M	-	0-0,5	0,03	89
	15	8M	-	0-0,5	0,03	89
SrTiO_3	1	8F	-	0-0,5	0,1	93
	5	8F	-	0-0,5	0,03	94
	10	8F	-	0-0,5	0,1	93
	15	8F	-	0-0,5	0,1	93
CaMnO_3	1	6M	-	0-0,5	0,1	87
	5	6MD	-	0,5-1	0,03	80

	10	8MD	-	0,5-1	0,3	80
	15	8MD	-	0,5-1	0,03	82
SrMnO ₃	1	8MD	-	0-0,5	0,03	84
	5	8MD	-	0,5-1	0,1	81
	10	8M	-	0-0,5	1	85
	15	8F	-	0-0,5	0,1	93
CaTiO ₃ /PPDA	1	8M	-	0,5-1	0,1	86
	5	8F	-	0-0,5	1	90
	10	-	-	0-0,5	0,3	98
	15	-	-	0-0,5	0,1	99
SrTiO ₃ /PPDA	1	8M	-	0,5-1	-	86
	5	-	-	0-0,5	0,3	98
	10	-	-	0-0,5	0,03	99
	15	-	-	0-0,5	0,03	99
CaMnO ₃ /PPDA	1	8F	-	0-0,5	1	90
	5	8F	-	0,5-1	3	85
	10	8F	-	0-0,5	1	90
	15	-	-	0-0,5	3	93
SrMnO ₃ /PPDA	1	-	-	0-0,5	-	99
	5	-	-	0-0,5	3	93
	10	8M	-	0,5-1	3	80
	15	8M	-	0-0,5	0,1	88
Zn ₃ (PO ₄) ₃ ×H ₂ O	15	2M	8M	4.0–5.0	10	59
Non-pigm. film	-	-	-	0.5–1.0	>50	73

127

128 *Corrosion test in the atmosphere with SO₂*

129 The paints were exposed to a corrosion test in the atmosphere with SO₂ (Tab. 1) for 1400
 130 hours. Modification with a surface layer conductive polymer improved the paints' overall anti-
 131 corrosion efficiency. Modification of particles of the perovskite SrTiO₃ with PPDA (SrTiO₃/PPDA)
 132 gave rise to a form that exhibited an anti-corrosion efficiency that was higher than that of untreated
 133 perovskite (SrTiO₃). The highest anticorrosion efficiency was found with SrTiO₃/PPDA, where the
 134 overall anticorrosion efficiency score was 99 (PVC = 10% and 15%).

135 Perovskite itself possesses a relatively low electric conductivity, which was increased to an
 136 optimum level for use in paints by modification with PPDA.

137 The highest anticorrosion efficiency was found with SrTiO₃/PPDA, where the overall
138 anticorrosion efficiency score was 99 (PVC = 10% and 15%).

139 The overall conclusions from the exposure of the paints to an atmosphere with SO₂ are as
140 follows:

- 141 • Paints with conductive polymer PPDA reduced the rate of the corrosion phenomena occurring
142 in the steel substrate surface.
- 143 • The anti-corrosion efficiencies of paints with pigments modified with the conductive polymers
144 were higher than those of the respective paints with the untreated pigment.
- 145 • The highest corrosion resistance showed pigment CaTiO₃/PPDA.
- 146 • The anti-corrosion efficiencies of paints decreased in the following order:
147 SrTiO₃/PPDA > CaTiO₃/ PPDA > SrTiO₃ > CaMnO₃/PPDA > SrMnO₃/ PPDA > CaTiO₃ >
148 SrMnO₃ > CaMnO₃

149 *Anticorrosion effect of perovskites and conductive polymers in a paint layer*

150 In recent years, application of conductive polymer coatings such as PPDA on ferrous and non-
151 ferrous alloys against corrosion has received much attention [21, 22]. In addition to applying the
152 physical barrier, which is the protection mechanism of most coatings, the conductive polymers are
153 capable to anodic protection of metal surface by the healing their oxidative properties and accelerating
154 the formation of stable metal oxides on the surface of the substrate [23, 24]. In other words, the ability
155 of the conducting polymer to oxidize the substrate metals allows potential of metals to be shifted to the
156 passive state, in which the metals are protected by the passive oxide formed beneath the conducting
157 polymer. The application of the conducting polymer coating to the corrosion protection of steels was
158 reviewed by Tallman et al. (2002).

159 Where the pigment particle is not modified with a conductive polymer layer, the anticorrosion
160 protection role is played by the inorganic pigment itself.

161

161 **Conclusions**

162 PPDA as the conductive polymer for pigment particle surface modification was found superior
163 to the corrosion-inhibiting efficiency of the composite pigments. It is an advantage that a low pigment
164 volume concentration in the epoxy-ester resin based paint is adequate to attain a high anticorrosion
165 efficiency. For some of the pigments, their optimum concentration in the paints was as high as PVC =
166 10 % and 15 %, which is beneficial also from the financial aspect.

167 When exposed to the atmosphere with SO₂, the paint films exhibited an anticorrosion effect
168 particularly at high PVC levels (10% and 15%).

169 All of the paint films exhibited a high anticorrosion resistance in this chamber; excellent results were
170 obtained with the paints containing PPDA. Specifically, they were paints containing SrTiO₃/PPDA at
171 PVC = 10% and 15%, where the overall anticorrosion efficiency score was 99%.

172 The surface modified pigments are promising from several aspects, particularly owing to their
173 high anticorrosion efficiency compared to that of the reference paint, low pigment concentration in the
174 paints adequate to attain a high anticorrosion effect, and their environmental harmlessness. The results
175 obtained suggest that the pigments deserve further research.

176 **Acknowledgment**

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