Theses of the Doctoral Dissertation

UNIVERSITY OF PARDUBICE

FACULTY OF CHEMICAL TECHNOLOGY

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Influence of Surface Treatment on the Selected Pigment Particles Properties by Conducting Polymers

Theses of the Doctoral Dissertation

Pardubice 2018

Study program: **Chemistry and Technology of Materials**

Study field: **Surface Engineering**

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Year of the defence: **2018**

References

HÁJKOVÁ, Tereza. *Influence of surface treatment on the properties of conducting polymers selected pigment particles.* Pardubice, 2018. 262 pages. Dissertation thesis (PhD.). University of Pardubice, Faculty of chemical technology, Institute of Chemistry and Technology of Macromolecular Materials. Supervisor: prof. Ing. Andréa Kalendová, Dr.

Abstract

The main goal of this work was to investigate the corrosion inhibiting and physical properties of organic coatings containing pigments whose surface has 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 was 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 paints was 1%, 5%, 10% and 15%. The paint films were subjected to physico-mechanical tests and accelerated corrosion tests. The test results were 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 were compared to those of a reference paint containing zinc phosphite hydrate, a proven and established anticorrosion pigment.

Abstrakt

Hlavním cílem této práce bylo posouzení korozních a fyzikálních vlastností organických nátěrových filmů obsahujících pigmenty, které byly povrchově upravené vodivým polymerem, ale i pigmenty bez povrchové úpravy.

Vysokoteplotní kalcinací byly připraveny čtyři pigmenty na bázi perovskitů (tj. $CaTiO_3$, $SrTiO_3$, $CaMnO_3$ a $SrMnO_3$) a jejich povrch byl modifikován vodivým polymerem polyparafenylendiaminem pomocí chemické reakce oxidativní polymerace. Fyzikálně-chemické vlastnosti byly zkoumány pomocí metod XRD, XRF a SEM.

Z takto připravených kompozitních pigmentů byl vytvořen nátěrový systém, u něhož byla jako pojivo použita expoxyesterová pryskyřice rozpouštědlového typu. Objemová koncentrace pigmentu (OKP) v nátěrovém systému byla zvolena na 1%, 5%, 10% a 15%. Nátěrové filmy byly podrobeny fyzikálně-mechanickým a zrychleným korozním zkouškám. Výsledky testů se lišily na základě zvoleného pigmentu, objemové koncentrace pigmentu i toho, zda byly či nebyly povrchově upraveny vodivým polymerem polyparafenylendiaminem.

Antikorozní i mechanické vlastnosti nátěrových filmů obsahující perovskity byly porovnávány s referenčním nátěrovým filmem obsahujícím zinkfosfát, který se běžně využívá jako průmyslový pigment.

Keywords

- Anticorrosive pigment
- Conductive polymer
- Organic coatings
- Anticorrosion protection
- Accelerated corrosion tests

Klíčová slova

- Antikorozní pigment
- Vodivý polymer
- Organické povlaky
- Antikorozní ochrana
- Zrychlené korozní zkoušky

Table of Contents

1 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 measures to make up for losses due to this degradation require costs over a billion dollars annually worldwide. This is why considerable efforts are made to understand and develop various strategies to protect 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. Roughly three decades ago, new materials with immense potential applications were discovered: they are conductive polymers, whose electric conductivity is so high that it approaches that of some metals. A wide range of conductive polymers, such as polyaniline (PANI), polypyrrole (PPY) and poly(p-phenylenediamine) (PPDA), have polyacetylene, polyaniline and polypyrrole are among the conductive polymers that are investigated most. Their electric conductivity distinguishes them from other polymers, which is due to the presence of conjugated double bond systems in them [6, 7].

The use of compounds possessing the perovskite structure, possessing 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 be readily prepared by chemical or electrochemical oxidation of phenylenediamine. Its electric conductivity is several orders of magnitude lower than that of polyaniline, and so it is classed among non-conductors. Although conductivity is important, it is not the sole parameter for application of conductive polymers [9].

Three phenylenediamine isomers (Figure 1) that are used as bases in the protonated form exist (Figure 2). The basic species is present in alkaline solutions, whereas the protonated species predominates in alkaline solutions. Both species are pH dependent. This fact is important for practical applications because the oxidation process of the protonated species is different from that of the basic species [10].

Phenylenediamines possess 2 primary amino groups available for oxidative connection of the monomers. If the oxidation agent concentration is adequately high, both amino groups can be included in a ladder structure (Figure 3). The ladder structure can be visualised by means of two intertwined polyaniline chains [11-13].
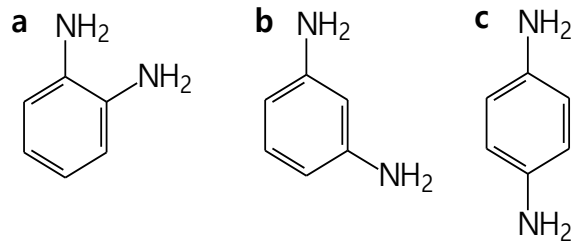
Figure 1: Phenylenediamine bases: (a) *ortho*, (b) *meta*, and (c) *para* isomer [14].
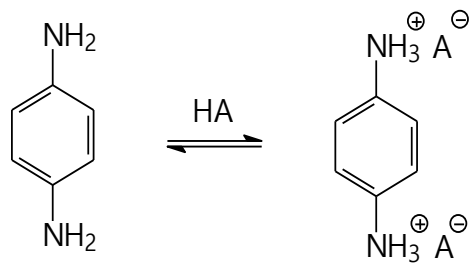
Figure 2: Phenylenediamine bases form salts with acids (HA) as illustrated on poly(*p*-phenylenediamine) [14].
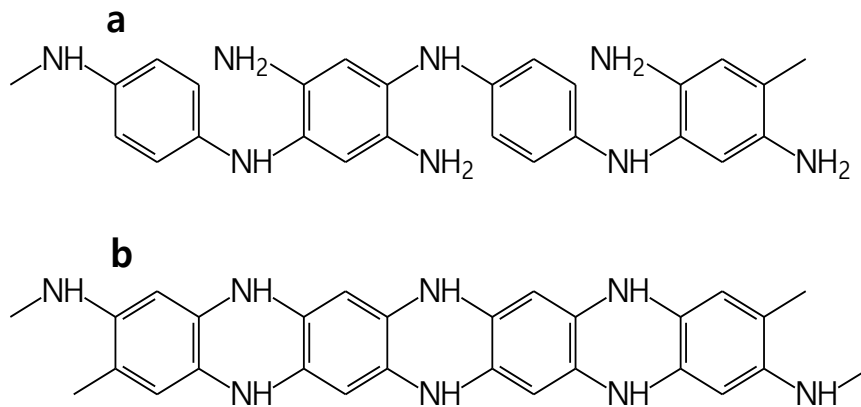
Figure 3: Idealized structure of poly(*p*-phenylenediamine) produced by the oxidation of (a) one or (b) both amine groups in *p*-phenylenediamine [14].

2 The aim of the thesis

The aim of this work was to assess the effect of pigment surface modification with conductive polymer on the corrosion-inhibiting capacity of the coating materials. Pigment surface modification with a thin layer of a conductive polymer was achieved by a process called oxidation polymerisation. The pigment volume concentration was PVC = 1%, 5%, 10% and 15%. The untreated pigments and the modified pigments were added to an epoxyester resin. The paint films applied to steel substrates were subjected to resistance testing by physicomechanical and corrosion tests.

The overall anti-corrosion efficiency of the paints was tested by exposure to corrosion in standardised simulated laboratory conditions and by the chemical resistance test. In many cases, this treatment enhanced the anti-corrosion efficiency of the paint films significantly.

Assessment of the paint film's resistance to mechanical damage revealed good physicomechanical resistance of paint films with pigments modified with the conductive polymer; paints containing PPDA alone exhibited very good properties as well. This provides evidence that the paints can be applied to surfaces that are subject to mechanical stress.

In the future we could try to use another conductive polymers. It will be better applicated coating in wider range of pigment volume concentration (PVC).

3 Experimental

3.1 Laboratory preparation of pigments for conductive polymer testing

The effect of pigment surface treatment with polyparaphenylenediamine phosphate (PPDA) on the anti-corrosion properties of organic coatings, was tested on pigment particles that differ in their structure, chemical composition. Pigments that are well suited for treatment with conductive PPDA were selected based on 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 for investigating their anti-corrosion properties in coating materials (paints) [15].

The anticorrosion pigment based on the zinc phosphate hydrate $Zn_3(PO_4)_2.xH_2O$ (PVC = 15 %) was also tested as a reference material allowing us to compare the results obtained with the pigments synthesized by us with those obtained with a commercially available product.

3.2 Laboratory synthesis of the pigments

Perovskites can be described generally by the formula ABO_3 where atom A is in the oxidation state 2+ and atom B is in the oxidation state 4+ [15].

Perovskites with a generally isometric particle shape [16, 17] were synthesized to serve as the pigment cores for coating with a conductive polymers and to be added to a binder to form 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 the 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 4 operational steps: homogenization, calcination, washing with water and milling by wet process.

3.3 Preparation of pigments with conductive polymer surface layers

The surface of the pigments was modified by treatment with polyparaphenlenediamine phosphate. The anti-corrosion efficiency was evaluated both for the untreated pigments and for the pigments with surfaces modified with PPDA. The following pigments prepared in the laboratory were coated with a layer of PPDA.

3.4 Laboratory preparation of pigments modified with a surface layer of polyparaphenylenediamine 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 peroxydisulfate [20], also in 0,4 M *ortho*-phosphoric acid, was added to initiate the *p*-phenylenediamine polymerisation process 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 followed by acetone [15]. The pigment particles coated with the PPDA overlayer were dried in air and then at 60 °C in a laboratory dryer. The composite particles contained about 10 wt.% PPDA.

3.5 Structure and morphology of the composite pigment particles

The pigment particle morphology is illustrated by 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. The composite pigments had a tendency to form clusters.

3.6 Characterisation of the composite pigments untreated and treated conductive polymer

A total of 4 perovskite type pigments untreated and treated PPDA were prepared and subjected to X-ray fluorescence (XRF) analysis on a Philips PW 1404 X-ray spectrometer equipped with a Rh cathode, in conjunction with UniQuant software enabling 74 elements (from fluorine to uranium) semiquantitatively determined (10 % relative error). X-ray diffraction spectra (XRD) of the synthetised perovskites were measured on an X'Pert PRO MPD 1880 X-ray diffractometer [21].

3.7 Determination of the pH levels of aqueous extracts pigments and loose paint films

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

3.8 Electric conductivity of aqueous extracts pigments and loose paint films

Electric conductivity of aqueous extracts pigments (χ_p) and loose paint films (χ_f) was measured in accordance with ISO 787-14. The specific electric conductivity of the aqueous suspensions were measured conductometrically with a Handylab LF1 conductometer (Schott–Geräte GmbH, Germany) in combination with a measuring Pt cell. The measurements were 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 was measured.

3.9 Determination of corrosion-induced steel weight loss

This test measured weight losses in steel panels submerged in liquid systems causing metal corrosion (ČSN EN ISO 12944-2). 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 specific electric conductivity had attained constant levels [22]. The steel panels to be submerged in the extracts were weighed with a precision of ± 0,001 g and their dimensions (20 mm × 50 mm × 0,5 mm) were measured with a precision of ± 0,01 mm. The steel panel exposure time was 28 days.

3.10 Determination concentrations of substances soluble in cold water 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 dissolving in distilled water at laboratory temperature and at the boil [15, 22].

3.11 Corrosion-inhibiting efficiency of the pigments

The corrosion inhibiting properties of the pigments with a surface layer of conductive polymer (pigment/PPDA) in comparison with those of the untreated pigments were examined following the application of 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]. A total of 4 pigment/PPDA modified systems and 4 untreated pigments were tested. In addition, PPDA powders and the non-pigmented coating materials were tested in reference experiments.

3.12 Organic coating formulations containing the pigments and preparation of test samples of the paint films

All coating materials were model formulations, i.e., they contained no additional fillers or additives that might affect appreciably the formulations' efficiency. The pigment volume concentration (PVC) was invariably 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 instrument (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 0,30 by means of the anticorrosion-neutral filler calcite, $CaCO_3$. The total pigment plus filler concentration in the paint film was 30 vol%, whereby a constant total concentration of the powder fractions in the dry paint film was assured, while varying only the proportion of the composite pigment. The paints were prepared by dispersing the powders in the liquid binder in a pearl mill Dispermat CV (WMA GETZMANN GmbH 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 anticorrosion properties. Description of binder: a 60 % solution of a medium molecular weight epoxy resin esterified with a mixture of fatty acids of dehydrated ricin oil and soybean oil WorléeDur D 46 [21], acid number 4, viscosity 2,5–5,0 Pa/s, flow time (DIN 53211-4200) 250 s, in xylene.

3.13 Laboratory corrosion test

The cyclic corrosion test in an atmosphere with condensing water was performed in line with ČSN 03 8131. 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 following 6480 hours' exposure.

The cyclic corrosion test in a NaCl solution spray environment [15] was derived from ČSN EN ISO 9227. The paint films were exposed to the mist of a 5% NaCl solution at

35 °C for 10 hours (1st cycle stage), followed by 1 hour of water condensation at 40 °C (2nd cycle stage) and 1 hour of drying at 23 °C (3rd cycle stage). The outcome was evaluated following 1440 hours' exposure.

3.14 Corrosion test outcome evaluation

The following parameters were evaluated to assess the corrosion effects in the tests: site and frequency of occurrence of blisters on the paint film, degree of corrosion of the metallic substrate surface and degree of corrosion of the substrate near the cut [21]. Methods as per ASTM D 714-87, ASTM D 610-85, and ASTM D 1654-92 were used. The corrosion effects were rated on a 100–0 scale. The total anti-corrosion efficiency was obtained based on the arithmetic mean of the degree of corrosion of the metallic substrate, 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 Equation 1:

$$E = \frac{A + B + C + D}{4} \tag{1}$$

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.

3.15 Linear polarisation

The linear polarisation method was applied to corrosion monitoring. 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 accommodating the reference saturated calomel electrode, platinum counter-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.

A 1 cm^2 area of the working electrode in the measuring cell was exposed to a 1 M NaCl solution. The cell was connected to a potentiostat/galvanostat (VSP-300/France). The paint films were exposed to the NaCl solution for 24 hours, after which they were measured by the linear polarisation method. The polarisation region was from -10 mV/E_{OC} to +10 mV/E_{OC} at a rate of 0,166 mV/s [25].

3.16 Comparison experiments

The anticorrosion pigment based on the zinc phosphate hydrate (called Heucophose) $Zn_3(PO_4)_2.xH_2O$ (PVC = 15 vol. %) was also tested as a reference material allowing us to compare the results obtained with the pigments synthesized by us with a commercial product. Films of the coating materials free from any pigment were also used in some tests, in the linear polarisation measurements.

4 Results and Discussion

4.1 Pigment specification and structural analysis results

Four perovskite type pigments were prepared and a fraction of each was subjected to surface treatment with the conductive polymer, PPDA. Both the treated and untreated pigments were examined by X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis to elucidate their structure and composition. ABO_3 structure 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; $CaMnO_3$ contained the $CaMnO_3$ crystal phase; and $SrMnO_3$ contained the $SrMnO_3$ crystal phase [26].

The composite pigments contained the amorphous conductive polymer moiety and the crystalline inorganic core moiety. All of the treated pigments also contained some amount of sulphate. The results of the analysis gave evidence that the pigments had been prepared as intended and were consistent with previous studies [21, 27].

The XRF results: the pigments contained small amounts (1,7%-2,4%) of Al_2O_3 and trace amounts of SiO_2 (0,1%-0,4%) from the wearing corundum balls in the ball mill. Both impurity types are neutral and will in no way affect the chemical properties of the anticorrosion pigments. The results of the XRF analysis of the surface-treated pigments are, that they contained the appropriate oxides (TiO_2, MnO, SrO, CaO) plus small amounts of compounds from the surface treatment, i.e. P_2O_5 (4,1%-5,1%) and SO_3 (3,7%-7,9%).

4.2 Physico-chemical properties of the pigments

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

The densities of the modified pigments lay within the range of 2,07 to 3,28 g/cm^3, which is narrower than the range of densities of the initial untreated pigments, 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, which 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 34% to 53% for the modified pigments and 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 the starting pigments (Table 1).

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 given volume is lower than the entered values of D (4,3). The mean particle size (D 4,3) of the perovskites treated with PPDA was 12,89 – 13,71 μm, in contrast to that of the initial pigments which was mere 0,83 – 3,92 μm. Hence, the mean particle size increased multiply on coating the surface with the PPDA layer. This is borne out by the SEM photographs, exhibiting formation of clusters of the pigment/PPDA systems.

4.3 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 1. The pH is a quantity providing information on the properties of the pigments governed by the presence of acid or alkaline components. The 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. This effect was observed for all of the pigments tested. The extracts of the untreated pigments containing alkaline earth cations, i.e. Ca and Sr, exhibited pH even higher than 9, thus approaching the steel passivation region. The pH levels of the free paint films (pH_f) were measured for pigment volume concentrations (PVC) 1% and 15%. Unlike the extracts of the pigment powders, the extracts of the paint films did not exhibit a shift to the acid 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 development 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 1: Physico-chemical properties of the pigments

Pigment	[a]pH_p [-]	[*]W_{20} [%]	[*]W_{100} [%]	[b] χ_p [µS/cm]
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	1996
SrTiO$_3$/PPDA	3,79	6,43	7,29	1282
CaMnO$_3$/PPDA	3,05	7,02	7,32	1891
SrMnO$_3$/PPDA	3,13	9,53	9,60	1086

[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 5 measured values.*

4.4 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 (χ_p) of the perovskites modified with PPDA measured the 28th day of the experiment lay within the region from 1086 to 1996 µS/cm, compared to the values for the untreated perovskites (Table 1), which were from 82 to 128 µS/cm. In other words, the pigment surface modification with poly(p-phenylenediamine) increased the specific electric conductivity considerably, more than by an order of magnitude. The perovskites with no surface modification did not affect the specific electric conductivity appreciably, 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 (χ_f) increased with increasing conductive polymer content, i.e. from PVC = 1% to PVC = 15% (Table 2).

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

Table 2: Specific electric conductivity of aqueous extracts of loose paint films containing the composite pigments

Pigment	PVC [%]	pH_f [-]	χ_f [µS/cm]	Δm_{21} [g]	P_p [g/cm]
CaTiO₃	1	7,13	0,35	0,018	15,89
	15	7,01	0,24	0,020	17,27
SrTiO₃	1	7,07	0,56	0,022	18,61
	15	6,97	0,61	0,023	19,23
CaMnO₃	1	7,13	0,70	0,017	14,33
	15	7,25	0,41	0,019	16,47
SrMnO₃	1	7,24	0,89	0,028	23,06
	15	7,36	0,56	0,021	19,95
CaTiO₃/PPDA	1	7,49	0,39	0,017	14,05
	15	7,24	0,70	0,024	20,06
SrTiO₃/PPDA	1	7,52	0,41	0,024	20,04
	15	7,38	0,88	0,018	15,21
CaMnO₃/PPDA	1	7,68	0,11	0,013	10,25
	15	7,36	1,74	0,014	10,99
SrMnO₃/PPDA	1	7,63	0,47	0,021	17,97
	15	7,38	0,94	0,015	12,07
Heucophos	15	3,70	0,23	0,023	19,51
CaCO₃	-	8,47	0,18	0,025	21,13

[*] *Conductivity was measured with an accuracy ± 0,5%.*

4.5 Water-soluble substance content in water

The amount of water-soluble substances provides information on substances extractable from the pigment into the aqueous environment. 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 1. 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 the cold and hot water-soluble contents were higher for the pigments modified with poly(*p*-phenylenediamine) than for the untreated pigments. The hot-water-soluble contents were expected to be higher (more substances are dissolved) than the cold-

water-soluble contents [21], and this was really observed but the values did not differ substantially.

The lowest amounts of substances soluble in cold water and in hot water were observed for calcium permanganate, $CaMnO_3$, viz. $W_{20} = 0,80\%$ and $W_{100} = 0,84\%$, while the highest values were observed for strontium permanganate 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 appreciably between the untreated and treated pigment – the differences 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 modified with the conductive polymer or not. 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 attests to deprotonation of the conductive polymer layers in the former pigments. A high water-soluble content is indicative of a 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 governing the electrochemical inhibition of corrosion.

4.6 Corrosion loss of steel panels coated with the paints

Investigation of the anticorrosion properties of pigments requires a comprehensive view upon the relation between the anticorrosion pigment, the binder and the substrate. This may be facilitated by information gained by determining the weight loss of steel panels [22] submerged in aqueous extracts (filtrates) of the pigments.

For the untreated pigments, the mean corrosion losses of the steel panels were from 14,33 to 23,06 g/cm^3. They were 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 $SrMnO_3$ pigment, viz. 23,06 g/cm^3 at PVC = 1%.

For the pigments modified with PPDA, the corrosion losses were very similar. A marked difference was observed for the $CaMnO_3$/PPDA pigment at PVC = 1%, where the losses 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 better than the remaining paints examined.

4.7 Corrosion following coated steel panel exposure in a chamber with condensed water vapour atmosphere

The aim of the 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 and to calculate the overall anticorrosion efficiency score.

The steel panels coated with the paints tested were exposed in the chamber with condensed water vapour for 6480 hours. The results are listed in Table 3.

Table 3: Results of accelerated corrosion tests of the paints containing composite in an atmosphere with condensing water (exposure 6480 hours, DFT = 100 ±10μm)

Pigment	PVC [%]	Paint assessment		Substrate metal assessment		Calculated anticor. efficiency E_{H2O}
		Degree of blistering		Corrosion in the cut [mm]	Surface corrosion [%]	
		In a cut	Metal base			
CaTiO$_3$	1	4M	4M	0-0,5	0,03	79
	5	4F	4F	0-0,5	0	84
	10	-	-	0-0,5	0	99
	15	8M	8MD	0-0,5	0,03	74
SrTiO$_3$	1	8F	8F	0-0,5	0	89
	5	-	-	0-0,5	0	99
	10	-	-	0-0,5	0	99
	15	-	-	0-0,5	0	99
CaMnO$_3$	1	-	-	0	0	100
	5	-	8F	0	0	95
	10	-	-	0-0,5	0,03	99
	15	-	8M	0	0,03	90
SrMnO$_3$	1	4M	4D	0-0,5	1	60
	5	4M	4D	0-0,5	3	58
	10	4M	4D	0	50	41
	15	4MD	4MD	0	1	60
CaTiO$_3$/PPDA	1	4F	-	0-0,5	0,3	90
	5	6F	6M	0-0,5	3	75
	10	8F	8F	0-0,5	16	75
	15	8F	8M	0-0,5	33	65
SrTiO$_3$/PPDA	1	8F	-	0-0,5	0,03	94
	5	-	-	0-0,5	0,3	98
	10	-	-	0	3	94
	15	-	-	0	10	91
CaMnO$_3$/PPDA	1	-	-	0-0,5	0,3	98
	5	-	-	0-0,5	1	95
	10	-	-	0-0,5	3	93
	15	-	-	0-0,5	10	90
SrMnO$_3$/PPDA	1	4F	4F	0-0,5	0,03	84
	5	-	-	0-0,5	0,03	99
	10	-	-	0-0,5	3	93
	15	4F	4M	0-0,5	50	55
Heucophose	15	2M	8M	0-0,5	3	59
Non-pigm. film	-	8F	8F	0-0,5	0	89

Osmotic blisters were formed both on the paint film area and in the artificial cut made through the film. The corrosion in the cut through films containing the untreated pigments was largely medium extent, scored as 8F-4MD; the same score was assigned to corrosion beneath the paint film area. Where the pigments modified with the conductive polymer PPDA were used, blisters were rarely present in the cut, scored 4F-8F, and small to medium blisters, scored 8F-4M, were present on the paint film area.

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 increasing PVC. This can be explained in terms of reduction of the organic film's 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 score was highest for the pigments $SrTiO_3$ and $CaMnO_3$, both untreated and modified with the conductive polymer. The score values all lay within the range of 91–100. The lowest anticorrosion efficiency, on the contrary, was found for $SrMnO_3$, also both untreated and modified, although it was somewhat better – exhibiting a lower occurrence of blisters both on the paint film surface and in the cut – with the pigment modified with PPDA than with the untreated substance.

4.8 Corrosion following coated steel panel exposure in a salt fog chamber

The steel panels coated with the paints tested were exposed in the salt fog chamber for 1440 hours. The results are listed in Table 4.

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 were used, the blisters in the cut were scored 2F-2MD, the blisters on the film surface, 2F-6MD. Corrosion in the test cut was observed for all paints containing the untreated pigment, and it was less pronounced if the paint contained the modified pigments. This bears out the concept of catalytic passivation (Figure 4) at the metal/coating interface. So, 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%.

Weak corrosion, comparable between the untreated and treated pigments, was observed on the metal panels after stripping down the paint films. It was between 0,01-16%, except for the pigment $CaTiO_3$/PPDA at PVC 15%, where the extent of corrosion on the steel panel surface reached 33%.

The overall anticorrosion efficiency scores for the paints with the untreated pigments were higher at higher pigment concentrations, PVC = 10% and 15%, whereas the reverse was true of the paints with the pigments modified with the conductive polymer, where the results were more favourable at PVC = 1% and 5%. The highest overall anticorrosion efficiency score on 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%.

It can be concluded from the comparison between the untreated and the surface-modified perovskites that the pigment surface modification brought about reduction in

the numbers of blisters both on the paint film surface and in the test cut. This also applies to corrosion in the cut.

Generally, 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, was lower, Also, corrosion in the paint film cut was lower, supporting the concept of steel panel passivation at the interface with the paint film containing the conductive polymer.
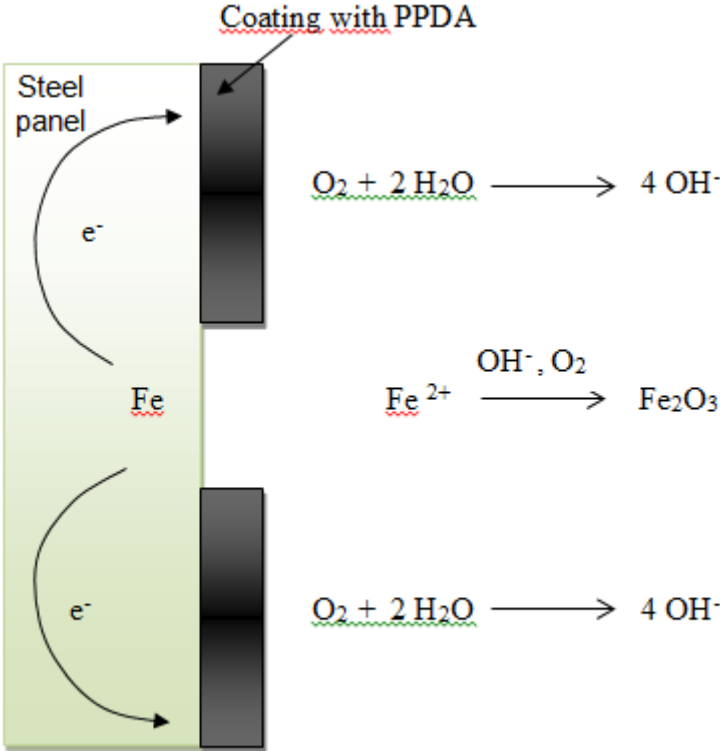

Figure 4: Schematic of the iron passivation mechanism by means of a paint containing a pigment modified with PPDA

Table 4: Results of accelerated corrosion tests of the paints containing composite pigments in a NaCl solution spray environment (exposure 1440 hours, film thickness = 95 ± 10 μm)

Pigment	PVC [%]	Paint assessment		Substrate metal assessment		Calculated anticor. efficiency E_{NaCl}
		Degree of blistering		Corrosion in the cut [mm]	Surface corrosion [%]	
		In a cut	Metal base			
CaTiO₃	1	2F	8M	1-1,5	16	62
	5	-	-	0-0,5	10	90
	10	-	-	0-0,5	10	90
	15	2F	-	0,5-1	0,3	86
SrTiO₃	1	2M	4M	0,5-1	0,01	70
	5	4F	4MD	0-0,5	10	65
	10	2F	-	0-0,5	0,01	90
	15	2F	-	0,5-1	0,3	86
CaMnO₃	1	2MD	6M	0,5-1	10	55
	5	4MD	4M	0,5-1	10	58
	10	4MD	4M	0,5-1	1	63
	15	4F	-	0,5-1	16	75
SrMnO₃	1	2MD	6M	0-0,5	10	58
	5	2MD	4M	0-0,5	16	52
	10	2MD	4M	0,5-1	1	61
	15	2F	-	0-0,5	0,01	90
CaTiO₃/ PPDA	1	-	2F	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	0-0,5	1	88
	10	-	-	0-0,5	3	92
	15	-	6F	0	3	88
CaMnO₃/ PPDA	1	-	8M	0,5-1	10	78
	5	-	4F	1-1,5	16	74
	10	-	-	0,5-1	3	90
	15	-	6M	0	0,3	88
SrMnO₃/ PPDA	1	6F	-	0	0,1	92
	5	2F	4F	0,5-1	3	74
	10	2F	2MD	2-3	16	50
	15	2MD	2MD	0-0,5	16	48
Heucophos	15	2M	8M	2,0 - 2,5	3	61
Non-pigm. film	-	6M	-	1,5 - 2,0	50	60

4.9 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 much attention [29, 30]. In addition to applying the physical barrier, which is the protection mechanism of most coatings, the conductive polymers are capable to anodic protection of metal surface by the healing 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 passive state, in which the metals are protected by the passive oxide formed beneath the conducting polymer. The application of the conducting polymer coating to the corrosion protection of steels was reviewed by Tallman et al. (2002).

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

4.10 Potentiodynamic polarisation

The results of the electrochemical examination by the linear polarisation method are listed in Table 5. The aim of the measurements was to determine the spontaneous corrosion potential, polarisation resistance and corrosion rates for the organic coatings studied. The parameters provide information on the organic coating resistance to corrosion.

For the non-pigmented organic coating, the polarisation resistance at the spontaneous corrosion potential 42 mV was 30×10^5 Ω, the corrosion rate was 10×10^{-4} mm/year. The surface treatment of the $CaTiO_3$ pigment with PPDA appeared to be beneficial at PVC = 1% – the corrosion rate decreased from 91×10^{-4} ($CaTiO_3$) to 12×10^{-6} ($CaTiO_3$/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 was lowest among all of the organic coatings tested. The corrosion rate was 19×10^{-9} and 13×10^{-9} mm/year at PVC = 1% and 5%, respectively, and the polarisation resistance also increased substantially – by 3 to 5 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.

Table 5: 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]
CaTiO$_3$	1	-523	8×10^{-1}	44,0	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	36,0	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	17,0	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}	36,0	37,2	22×10^{6}	12×10^{-6}
	5	-546	8×10^{-1}	42,0	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}
SrTiO$_3$/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}
CaMnO$_3$/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}
SrMnO$_3$/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}
Heucophose	15	-473	1×10^{-4}	17,0	16,1	70×10^{3}	98×10^{-5}
Non-pigm. film	0	42	2×10^{-3}	21,6	18,9	30×10^{5}	10×10^{-4}

5 Conclusions

The objective of the synthesis was to obtain pigments imparting the paint system a high anticorrosion efficiency. This is affected by a number of factors, such as pigment particle morphology, acid-base properties and others. They can, for instance, change the pH of the aqueous phase sorbed in the paint film, they affect the pH of the aqueous medium while the corrosive substances diffuse through the coating, produce protective layers by reaction with the OH^- ions at the cathodic sites and create a passivating film by redox reactions with the Fe^{2+} ions. Targeted selection of the cations in the perovskite pigment structure can be used to guide the pigments' properties, 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 to the region where the metal does not corrode, i.e. to the passive state. It is true that the pigments whose surface has been modified with the conductive polymer, poly(*p*-phenylenediamine), are acidic, this, however, is very important for preserving their conductivity and so 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 aim of the pigment surface modification with poly(*p*-phenylenediamine) was to improve the paint's anticorrosion efficiency.

The corrosion tests in the simulated atmosphere with condensed water gave evidence that the surface treatment with the conductive polymer helps 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.

The corrosion tests in simulated salt fog atmosphere 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 lower when the modified pigments were used: this concerns, 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 attests to good electrochemical inhibition in the salt fog atmosphere. This accelerated corrosion test has shown that the paints' anticorrosion efficiency decreases if the pigment volume concentration is 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 steel surfaces against corrosion. The binder system that was used in this work – a solvent-based epoxy-ester resin – exhibited outstanding adhesion to the substrate and low diffusion permeability at the film thicknesses applied and proved to be well usable in combination with the pigments studied.

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