Study on the properties of new anti-corrosion pigments containing Mg²⁺ cation in epoxy ester resin-based coatings

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The aim of the work was to study the protective properties of epoxy ester coatings containing newly synthesized organic pigments based on azo compounds in dependence of their chemical composition and concentration. For applications in anti-corrosion coatings, organic pigments containing the Mg²⁺ cation with expected anti-corrosion properties have been newly synthesized and their effect on epoxy ester coatings' physicochemical and corrosion resistance studied. In the same effort, inorganic oxides with Mg²⁺ cation content based on periclase and mixed magnesium-iron oxide and an industrial standard were also tested, the effectiveness of which had already been confirmed in previous studies. The properties of the prepared paint materials and organic coatings were investigated using standardized physical-mechanical tests together with accelerated cyclic corrosion tests in simulated corrosive atmospheres and electrochemical linear polarization technique. The results obtained with the coatings based on tested pigments containing epoxy-ester resin have confirmed the corrosion-inhibiting effect of the newly synthesized pigments.

Introduction

Corrosion of metallic materials causes great economic losses and leads to safety risks every year, which has for long time been considered a growing problem worldwide [1]. The universal and most common method of protecting metal substrates against corrosion is the application of suitable organic coatings.

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Application of an organic coating as a physical barrier between the corrosive environment and the metal substrate represents the oldest method of anti-corrosion protection of metals. However, more than mere barrier protection it is required to achieve high anti-corrosion efficiency. Long-term action of the factors, such as pH, dissolved oxygen, temperature, and penetration of electrolytes results in the degradation of such a barrier [2,3]. In addition to the binders used, paint formulations therefore include other components that favourably influence the resulting properties of coatings, i.e., pigments, fillers, additives, and solvents, when the appropriate combination of which allows one to obtain coatings with high anti-corrosion efficiency [4,5]. The protective effect of coatings also depends on the method of pre-treatment of the metal surface, the type and concentration of the anti-corrosion pigment used, the method of formation of the protective coating, and, eventually, mechanical properties of the entire coating system [6–8].

In terms of their function, anti-corrosion pigments can be defined as substances that, when applied to the binders of basic paint materials, can effectively reduce the rate of corrosion, thus increasing the life of the protective coating system [9]. Corrosion occurs when these three steps come into realisation – cathodic reduction, anodic oxidation, and the electrolyte ion transfer. If at least one of these steps is suppressed, corrosion will be slowed down. The group of anti-corrosion pigments includes such pigments that actively participate in corrosion-inhibiting protection. These pigments retard or completely prevent partial cathodic or anodic reactions by preventing the transition of the metal into the solution (electrochemical process at the anode) or the reduction of oxygen or hydrogen cations (electrochemical process at the cathode) [9–11].

In the past, heavy metals such as lead, cadmium, or chromium were the main components of a whole range of highly effective anti-corrosion pigments. However, with time, it became clear that these elements and their compounds would have a significant negative effect on human health and the environment, and it was, therefore, necessary to replace them with other compounds being less harmless to health and, at the same time, having a comparable anti-corrosion effect [12]. The oldest representative of non-toxic anti-corrosion pigments is zinc phosphate, which is approximately 50 times less toxic than chromate pigments. However, according to the European Directive 2004/73/CE, this pigment can no longer be classified as an environmentally friendly substance, as it represents a potential danger to the aquatic environment [13,14]. Due to the limitation of the use of zinc phosphate, it was therefore necessary to focus on the development of new anti-corrosion pigments that would ensure high anti-corrosion efficiency. In addition to compounds containing zinc cations, anti-corrosion pigments containing calcium or magnesium appear to be very effective. Such non-toxic pigments are, for example, pigments based on borates, molybdates, silicates, phospho- and borosilicates or some ion exchangers [15,16]. However, the selected non-toxic inhibitors alone do not surpass chromates and lead-based compounds by their potency.

However, if we combine two non-toxic inhibitors, a synergistic effect will occur between them, and then we can obtain an anti-corrosion pigment with comparable efficiency as that of toxic chromates and lead-based compounds [17].

Organic compounds with pigment properties are synthesized with the aim of finding other effective but non-toxic anti-corrosion pigments. Organic pigments are artificially synthesized substances with distinctive colors, almost insoluble in water and organic solvents. Their properties include resistance to UV-radiation, heat resistance, and resistance to acids, alkalis, as well as organic solvents [18]. Unlike inorganic pigments, organic alternatives usually have a larger surface, less density, and more intensive colors. Insoluble organic pigments are largely prepared from water-soluble organic dyes either by removing solubilizing groups (−COOH, –SO$_3$H) from the organic dye molecule or by forming an insoluble salt by replacing soluble metal ions with less soluble ones [19]. Organic pigments differ from organic dyes in the fact they have no affinity for the dyed substance (organic dyes show an affinity for the substrate) [20]. Thus, they are bound to the surface either with glue or via a film-forming substance. Common organic pigments include phthalocyanine pigments, quinacridone pigments, azo dyes, and other organic pigments with the ability to inhibit corrosion processes in paint materials, including the zinc salt of nitroisophthalic acid, the basic salt of *N*-benzosulfonylanthranilic acid or zinc mercaptobenzthiazole. The group of perylene pigments also belongs to the newly introduced organic pigments for coatings materials. They are produced mainly in the pigment and dye industry, when the production process, intermediate products, and equipment utilize generally the same principle for preparing organic dyes [20,21].

Experimental part

Synthesis and specification of pigments

In this work, new pigments of organic origin were synthesized from starting dyes based on metal complexes. The initial dyes were prepared by diazotization and coupling reactions, followed by metal complexation, washing with water, and drying in an oven at 80 °C [21]. The final product yield was in the range of 68–99 %. The inorganic mixed oxide-based pigment was prepared by the high-temperature synthesis in the solid phase and adjusted to the form necessary for application in the coating systems. The pigment synthesis process had therefore included four basic steps: homogenization, calcination, washing, and subsequent particle size adjustment by grinding [8].

The quality of powder pigments is determined by their physical-optical characteristics (parameters of the elementary lattice, density, color), chemical (the content of impurities, pH, etc.) and technological properties (dispersibility, oil sorption, texture, etc.). In the case of special pigments, there are also special

properties (anti-corrosion, magnetic, luminescent) that are being of interest. The structure of newly synthesized pigments with expected anti-corrosion properties was verified using X-ray powder diffraction. The morphology of the pigment particles was also identified using scanning electron microscopy (SEM). In order to compare the properties of organic pigments, inorganic pigments with magnesium cation were prepared and tested; namely those based on periclase, mixed magnesium-iron oxide, and an industrially used anti-corrosion pigment based on phosphate.

The properties of pigments in the powdered form, i.e., oil sorption – the so-called oil number, was performed using the "pestle-mortar" method based on Czech Standard CSN 670531, and the density of pigments was determined using a helium pycnometer (Micromeritics 1340). This quantification is necessary for the calculation of the critical volume concentration of the pigment (CPVC) [14], which is necessary for the formulation of paint materials.

Specification of binder and filler for the preparation of model paints

A solvent-type epoxy ester resin binder, often used to protect metal substrates, was chosen to prepare the model paint materials. Specifications: xylene as solvent, solids content: 60 %, viscosity: 2.5–5.0 Pa s^{-1}, acidity number: 4, composition: 60 % epoxy component, 40 % conjugated fatty acid of dehydrated ricin oil and soy oil, trade name: Worlée Dur D46. A Nuodex combi APB siccative containing zircon, cobalt, and calcium was used to accelerate the paint film drying. The dosage of the binder – siccative was in accordance with the recommendation by manufacturer. This substance exhibits excellent mechanical and chemical resistance of the resulting film, very good adhesion, and quick drying. Using the infrared spectroscopy technique, the spectrum of the epoxy ester resin was measured (see Figure 1). In the spectrum given, a wide band of the valence vibration of OH groups (hydroperoxides, alcohols, carboxyl groups) was found at 3590–3280 cm^{-1}. In the region of 3000–2809 cm^{-1}, the bands of CH vibrations of aliphatic fatty acid chains were found. Moderately intense bands at 1740 and 1235 cm^{-1} were then typical for the presence of ester groups (valence vibrations C=O and C−O). The intensive band at 1181 cm^{-1} was due to the presence of ether functional group.

Titanium dioxide of rutile structure (Figure 2) was used as a filler (TiO$_2$, manufactured by Precheza a.s., Přerov, Czech Republic), density: 3.79 g cm^{-3}, molecular weight: 79.88 g mol^{-1}).
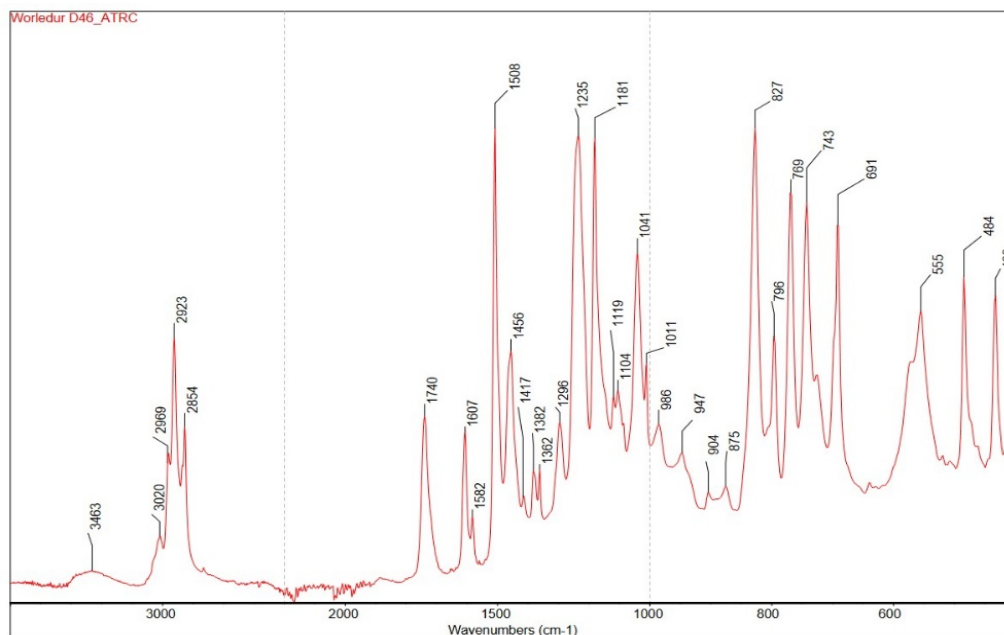
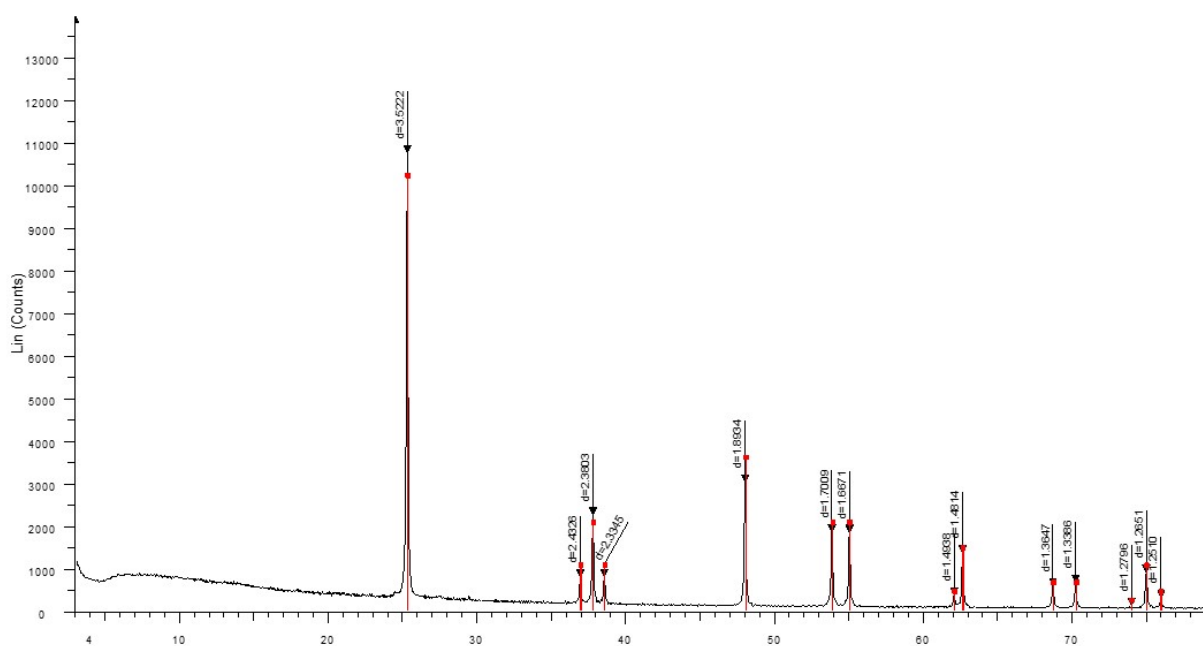**Fig. 1** FTIR spectrum of epoxy ester resin

Fig. 2 Difractogram of filler TiO$_2$

Structure and morphology of pigments and filler

The organic and inorganic pigments tested were studied using a scanning electron microscope (model LYRA 3, Tescan Brno; Czech Republic). Each pigment was sampled and this take coated with a carbon conductive layer (Leica ACE 200, Leica Microsystems, Wetzlar, Germany) with a thickness of 20 nm and measured

in five different sites at an accelerating voltage of 20 kV. The pigments tested were also coated with a gold conductive layer, for which SEM images were shot at an accelerating voltage of 10 kV.

Formulation and preparation of model organic coatings

Model organic coatings containing both inorganic and organic pigments; the latter being based on magnesium cation and titanium dioxide and with pigment volume concentration (PVC_{Pig}) = 3 %, and the PVC/CPVC ratio adjusted to a constant value of 1 : 2 for all model paints when using a neutral titanium dioxide filler. The coatings were prepared by pre-dispersing and dispersing all components in an attritor (Dissolver Dispermat, VMA-Getzmann, Reichshof, Germany). The paint materials no longer contained any other fillers and additives that could affect the effectiveness of the individual formulations. The mixture of liquid components (binder), additives, and powder pigments was dispersed for 40 min at 3500 rpm under the given conditions and geometry of the mixed system, volume, and the content of the dispersed mixture filling. The prepared paint materials were kept in closed containers under standard conditions (23 °C, 50 % RH).

Preparation of test samples of organic coatings for testing

The test coatings for corrosion and mechanical assays were applied to cold-rolled steel panels. It is a carbon structural steel with the elements added (sulfur and phosphorus). Steel panels with dimensions of 102 × 152 × 0.81 mm were used for corrosion tests, whereas lesser steel panels (45 × 215 × 0.81 mm) served for mechanical tests. A box applicator was used to create test coating films of the desired thickness. The first layers of the primer were applied with an applicator with a gap of 250 μm, and the second layers of the paint then applied after 24 hours with an applicator with such a gap that the resulting coating thicknesses (DFT) were around 100 μm. The reverse side of the panel was also devised with coating using an applicator with a gap of 200 μm. The edges of the steel panel were moistered with commercially produced anti-corrosion synthetic paint (EPAX S2318, which is an epoxy based two-component formula), thus preventing unwanted under-corrosion of the test coatings during exposure in an aggressive environment. For samples intended for corrosion tests, artificial vertical cuts were made (100 mm long and 0,5 mm deep) on the front side up to the metal base using a special cutter.

The dry film thickness (DFT) on the metal substrate was measured with an Elcometer magnetic thickness gauge according to ISO 2808, when calibration was performed before the actual measurement. The dry film thickness was measured at five different locations on the test sample.

The arithmetic mean of all five measurements was taken as the final value of the dry film thickness. Before exposure to the accelerated corrosion tests, the samples tested were conditioned for 30 days at a temperature of 21 °C with 50 % RH.

Paint films were also applied on dimensions 15 × 20 cm polyethylene sheets using an applicator with a gap of 350 μm. After drying (for 30 days), the paint film was removed from the polyethylene sheets and cut into pieces (1 × 1 mm). This procedure obtains loose paint films for electrical conductivity, pH measurement, and corrosion loss determination from aqueous suspensions [22].

Determination of pH and electrical conductivity from aqueous extracts of loose paint films

The pH values of the aqueous extracts from the loose paint films were determined using a procedure derived according to the ISO 787-9 standard. For the measurement, paint films were used with a $PVC_{pig} = 3$ % [22]. For the determination, suspensions of paint film (10 g) and redistilled water (90 g) were prepared, in which the pH value was measured every seven days for 28 days. A pH meter (model WTW 320, Labexchange − Laborgerätebörse GmbH, Burladingen; Germany) with a glass electrode was used for measurement.

Electrical conductivity from aqueous extracts of loose paint films was measured according to the procedure derived from CSN EN ISO 787-14 [8]. The respective value was measured using a Handylab LF1 conductometer (Schott-Geräte GmbH, Landshut; Germany). Samples were measured every seven days for 28 days until conductivity remained nearly constant.

Mechanical resistance of coatings

Tests on mechanical resistance of organic coatings give us an important information about the paint film's flexibility, strength, elasticity, and adhesion. Thus, these experiments are necessary to supplement the corrosion tests. With the help of mechanical and corrosion tests, we can obtain comprehensive information about the mechanism of the protective action of the organic coating given as only a high-quality coating may ensure high corrosion resistance [21].

Bend test

The resistance of the paint film during bending is its ability to resist deformation, without forming cracks nor damage due to peeling off. The test was performed according to the CSN EN ISO 1519 standard.

A steel panel with an organic coating was fixed close to a 4 mm diameter mandrel and then bent 180° with a lever. Damage of the paint film sample was then assessed by the pass/fail method.

Impact test

This test determines the mechanical properties of coatings while simultaneously evaluates adhesion during impact deformation, which causes a rapid deformation. The paint film is assessed for its resistance to cracking or peeling. The test was performed according to the CSN EN ISO 6272-1 standard. The coating is first cut into the substrate with two lines of about 5 cm long perpendicular to each other. Then the height of the free fall of the weight (1000 g) is determined, at which there is no visible mechanical damage to the surface of the organic coating.

Cupping test

The resistance of organic coatings to cracking or peeling from the metal substrate is determined by a cupping test according to the CSN EN ISO 1520 standard. The organic coating applied to the steel panel is subjected to a gradual deformation using a cupping tester. The principle of this test is to press a steel ball with a diameter of 20 mm into a steel panel with a coating and measure the indentation of the steel panel (in mm) at which the coating is damaged for the first time.

Cross-cut test

The degree of adhesion of the coating was determined according to the CSN ISO 2409 standard. The essence of the method is the formation of a lattice in the coating with the help of a cutter and a visual assessment of the coating condition according to a scale of 0–5, when a special cutting tool (Cross-cut tester, Byk Gardner GmbH, Geretsried; Germany) with a blade spacing of 1 mm was used. The lattice obtained was subsequently evaluated on a scale of 0–5, according to the degree of damage.

Pull-off test

This test enables to define the adhesion of single-layer or multi-layer coatings by measuring the minimum tensile stress required to tear the coating perpendicularly from the steel substrate. The pull-off test used to determine the cohesive and adhesive strength of two and multilayer systems was performed according to the CSN EN ISO 4624 standard. Before the measurement, it was first necessary to glue

20 mm diameter steel targets to the steel panels with the coating using a two-component adhesive (Loctite EA 9466) to obtain a continuous and uniform bond between the roller and the coating film. The pull-off test was performed on an instrument (COMTEST®OP3P, Coming plus a.s., Praque, Czech Republic). The test targets had to be placed so that the tensile force was evenly transmitted over the entire test area without a bending moment. The measured pull-off force was converted to the pull-off strength according to Equation 1:

$$\sigma = \frac{4F}{\pi d^2} \tag{1}$$

where: F – pull-off force [N], d – diameter of the test target [mm], σ – pull-off strength [MPa].

Cyclic corrosion laboratory tests

The respective procedures used to evaluate the protective properties of coatings are based on the intensification of the main factors that determine their service life under common conditions. In the industrial environment, it is mainly solar radiation, humidity, and temperature, but also pollution of the air by chemical substances – sulfur dioxide (SO_2) and constituents of marine environment (NaCl). The resistance of the organic coating primarily determines resistance to the effects of the environment. The protective effect of organic coatings is based mainly on barrier properties, and the main criterion for protective ability is the permeability of the coatings to environmental components [23].

The cyclic corrosion test in a NaCl solution spray environment

The cyclic corrosion test in a 5% salt fog environment was performed according to the CSN EN ISO 9227 standard with some modifications. The test was conducted in 12-hour cycles consisting of 3 parts. In the first part, epoxy ester coatings applied to steel panels were exposed to 5% NaCl solution for 10 hours. In the second part, the coatings were allowed to condense moisture at a temperature of 40 °C; in the third part, the coatings were dried at 23 °C. Before the exposures, a vertical cut was made in the paint film using a cutter.

Determination of resistance to SO_2 and high humidity

Epoxy-ester coatings applied to steel panels were also tested for resistance to humid atmospheres containing SO_2. The cyclic corrosion test was performed in 24-hour

cycles according to the CSN EN ISO 3231 standard. In the first cycle, the samples were exposed to humidity and SO_2 at 38 °C for 8 hours. In the second cycle (lasting 16 hours), the samples were dried at 23 °C with humidity lower than 75 %.

Determination of corrosion-induced steel weight loss

The purpose of this test is the evaluation and classification of the inhibitory effect of loose paint films containing corrosion-inhibiting components. The test was carried out while simultaneously monitoring the pH values and resistivity of the aqueous extracts of the loose paint films. The proper procedure was carried out according to CSN 67 3004 [23]. The loose paint films prepared were cut into pieces of approximately 1 × 1 mm in size. From these, fragments of loose paint films were prepared as 10% suspensions in redistilled water and left to stand for six days at 23 °C. Suspensions were filtered after 30 days, and then steel panels inserted into them. Before the test, the steel panels were properly cleaned with chloroform, measured with a digital caliper, and weighed on an analytical balance to the nearest ±0.0001 g.

Afterward, the panels were removed from the extracts and freed of corrosion products in a pickling bath with a composition of 1000 mL 20% HCl and 5 g of urotropine; the pickling time being 10 minutes. The panels were then immersed in chloroform, cleaned, dried, and weighed on an analytical balance. From the measured values, surface corrosion values were determined by calculation (see below, equation 2). The steel weight loss values (equation 3) for the individual loose pigmented films can also be expressed as a percentage relative to the weight loss of the metal panels relative to the steel weight loss in pure distilled water (blank), which are considered to be 100 % [22].

$$K_m = 10^4 \cdot \frac{m_1 - m_2}{2S} \tag{2}$$

where: K_m – corrosion losses per unit surface area [g cm^{-2}], m_2 – the weight of corroded steel panel, m_1 – the weight of steel panel before exposure, S – the surface area of the steel panel [cm^2].

$$X_H = \frac{K_m}{K_{m(H_2O)}} \tag{3}$$

where: X_H – relative corrosion weight loss of metal panels related to redistilled water [%], $K_{m(H_2O)}$ – corrosion weight loss of metal panel in redistilled water [g m^{-2}], K_m – corrosion weight loss of the metal panel in the aqueous extracts of the loose paint films [g m^{-2}].

Evaluation of the results of accelerated corrosion tests

After the samples of tested pigments in the coatings were exposed to the aforementioned accelerated corrosion tests, the surface of the paint film was evaluated, before the paint was removed and the condition of the metal substrate after the paint removed as well. Corrosion in the vicinity of the test cut was evaluated according to ASTM D 1654-92, the degree of corrosion in the panel surface according to ASTM D 610-85, and, finally, blistering assessment after ASTM D 714-87 (see Figure 3).
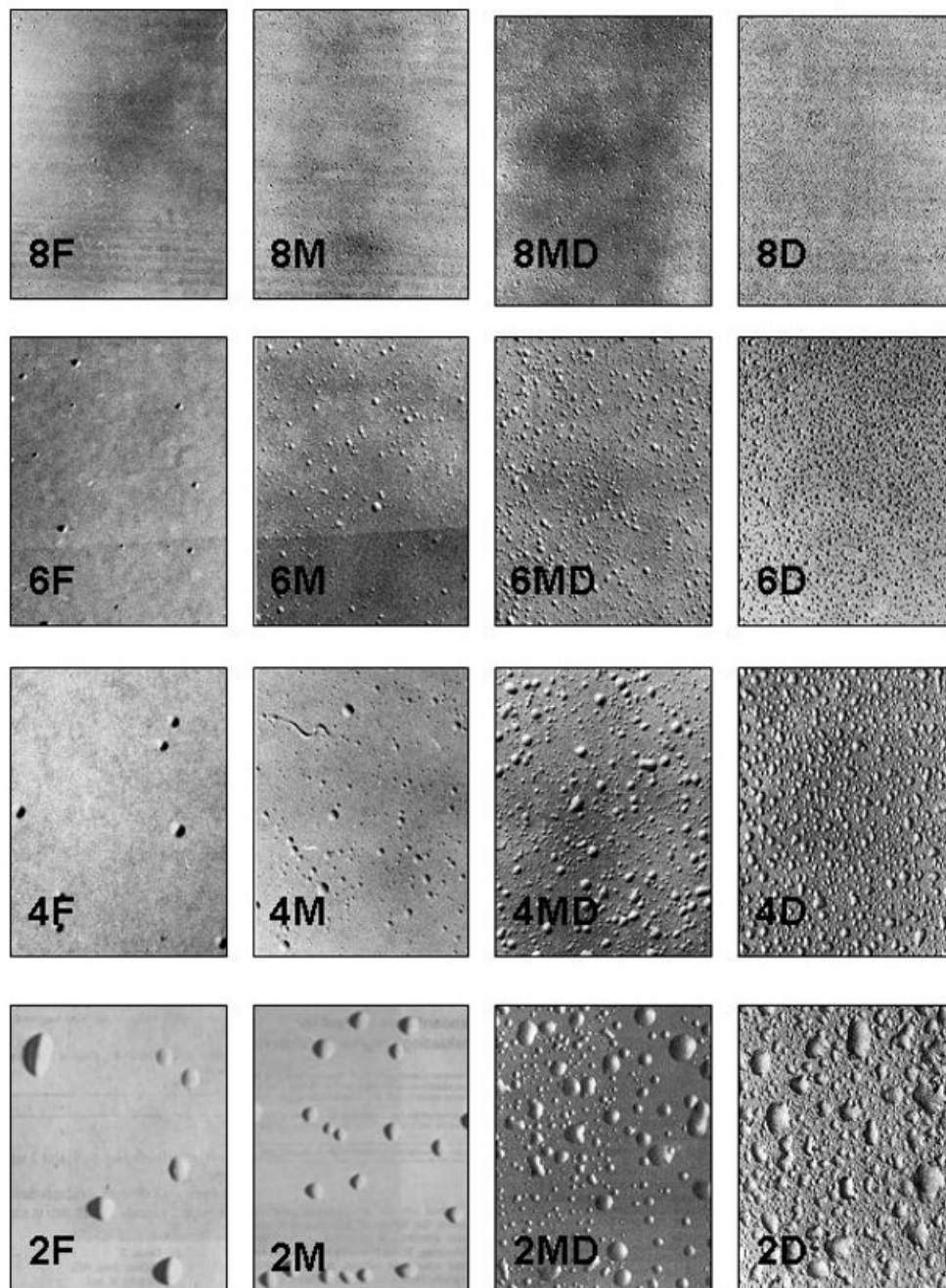

Fig. 3 Evaluation of the degree of blistering on the surface of paint films according ASTM D 714-87

Note: Blistering can be defined as a violation of the protective function of the coating, in which the organic coating has lost its adhesion towards the substrate. The individual blisters were compared with standards, when blister size was graded from 2 (largest size) to 8 (smallest size), and their frequency graded as F (few), M (medium), MD (medium dense), and D (dense).

Results and discussion

Pigment particle morphology

Figure 4 (given overleaf) shows the SEM images of the individual organic and inorganic pigments. The $C_{12}H_6MgO_4$ pigment formed loose clusters of square particles, pigment $C_{14}H_8Mg_2O_8$ and pigment $C_{16}H_{10}MgN_{12}O_{12}$ showed both polyhedral particles with a relatively wide distribution of the particle size. The pigment $C_{34}H_{26}MgN_8O_6$ was the only material composed of needle-like particles with a width of 100–400 nm and a length of 0.6–2 μm. Compared to this, pigments $C_{26}H_{19}MgN_3O_5$, $C_{17}H_{10}MgN_2O_3$, and $C_{25}H_{18}MgN_4O_6$ showed amorphous particle shapes with a particle diameter of 0.1–0.9 μm and also had a higher tendency to agglomerate. The MgO pigment produced polyhedral particles with a narrow size distribution. On the contrary, the remaining inorganic pigments $Mg_2Fe_2O_4$ and $Ca-Mg-HPO_4$ exhibited polyhedral particles with a relatively wide distribution ranging from 100 nm to 1 μm.

Determination of pH, specific electrical conductivity, and corrosion losses from aqueous extracts from free paint films

Knowledge of the physical properties of pigments is important for the assumption of protective properties of the paint film. When considering specific electrical conductivity, pH values, and corrosion losses in aqueous extracts from free paint films, assumptions can be made about the behavior of a given anti-corrosion pigment in the paint materials [15].

Regarding pH of aqueous extracts, this is a parameter used for technological control of pigment washout in the production process, when an insufficient washout could affect the quality of the coating [22]. The pH values were measured in aqueous 10% suspensions of finely cut pieces of paint films containing the tested pigments at PVC = 3 % and redistilled water, whereas pH of aqueous extracts from the free paint films was measured on the 8th or 28th day. From the results obtained (from pH_8 to pH_{28}), it can be stated that most of the extracts had slightly alkaline to more alkaline pH. In extracts from free paint films containing organic pigments, neutral pH values (in the range of 6.98–7.42) were found only for pigments of the $C_{12}H_6MgO_4$ and $C_{14}H_4Mg_2O_8$ type.
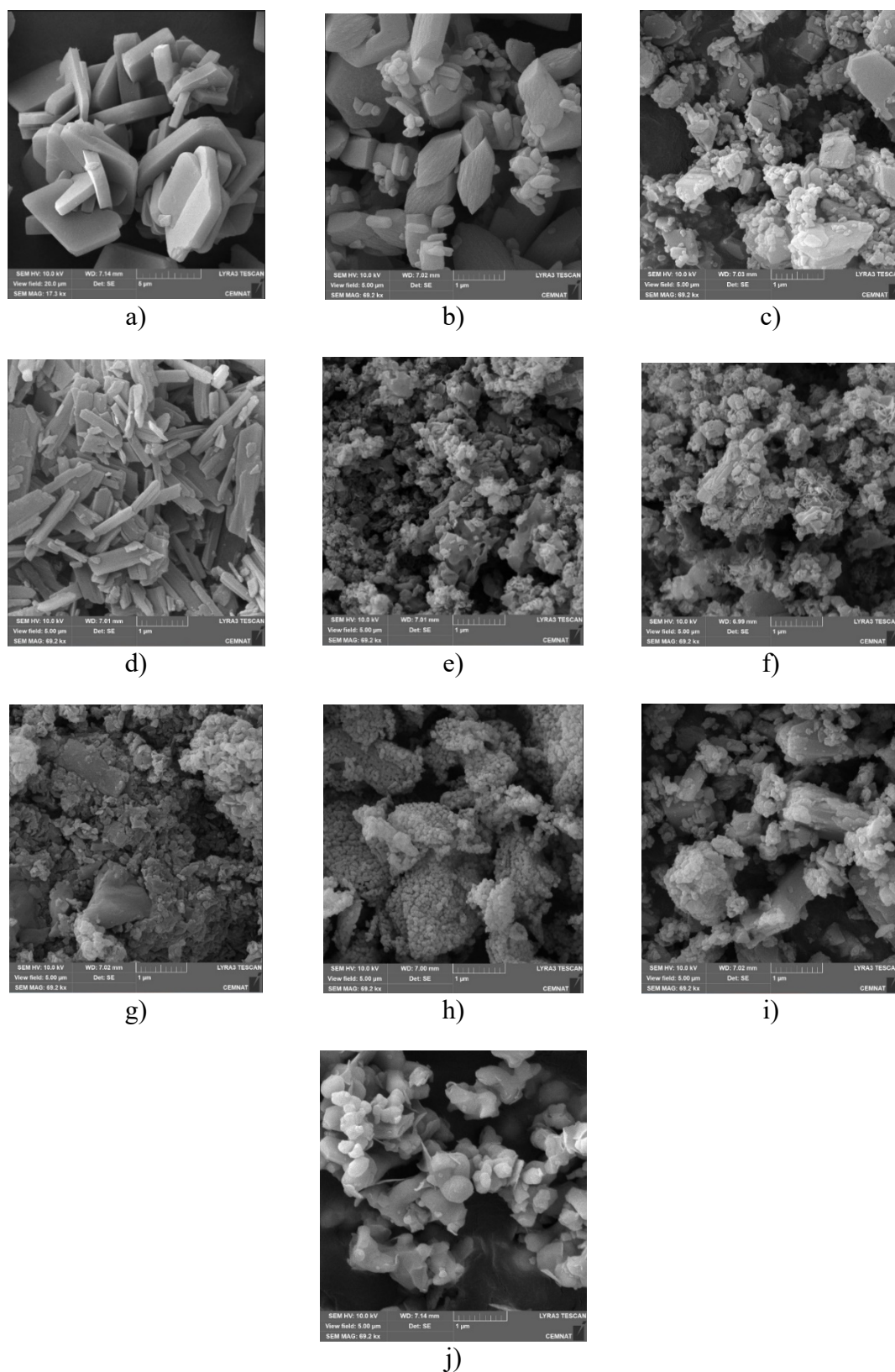
Fig. 4 SEM micrographs of pigments tested

a) $C_{12}H_6MgO_4$, b) $C_{14}H_6Mg_2O_8$, c) $C_{16}H_{10}MgN_{12}O_{12}$, d) $C_{34}H_{26}MgN_8O_6$, e) $C_{26}H_{19}MgN_3O_5$, f) $C_{17}H_{10}MgN_2O_3$, g) $C_{25}H_{18}MgN_4O_6$, h) MgO, i) $MgFe_2O_4$, j) Ca-Mg-HPO_4

Such a neutral behavior was caused by the composition of the given pigments, as they are monomagnesium and dimagnesium salts. The remaining organic pigments showed higher pH values in the range of 8.43–9.81, caused by the release of Mg^{2+} ions present in the pigments given. The shift of pH values to the alkaline range enabled the creation of metal soaps with acidic components of the binder when these pigments were applied to a suitable coating.

For extracts from free paint films containing inorganic pigments, pH values in the range of 6.41–10.44 were found. From neutral to slightly acidic pH (6.41) were values only for the Ca-Mg-HPO_4 pigment, in which the presence of an acidic phosphate anion suppressed the presence of alkaline ions (Ca^{2+} and Mg^{2+}). The remaining inorganic pigments could be included in the alkaline group with pH values of 9.75 and 10.44.

The value of specific electrical conductivity depends on the amount of water-soluble substances in the pigment and upon the chemical composition. The more water-soluble substances the given pigment contains the higher its specific electrical conductivity. The specific electrical conductivity was measured from aqueous 10% suspensions of finely cut pieces of free paint films containing the tested pigments at PVC = 3 % and redistilled water. The measurements were performed on the 8th and 28th day. Extracts from free paint films containing organic pigments showed specific electrical conductivity values in the range of 124.4–430 $\mu S\ cm^{-1}$. The highest values of specific electrical conductivity were achieved with aqueous suspensions of films with pigments $C_{12}H_6MgO_4$ and $C_{14}H_4Mg_2O_8$ (350.0 $\mu S\ cm^{-1}$ and 430.0 $\mu S\ cm^{-1}$) related to the presence of water-soluble substances – salt solutions. Changes in the specific electrical conductivity for extracts prepared from free epoxy ester paint films could be related to the degradation of the film itself and the subsequent formation of degradation products. Higher values of specific conductivity always carry the risk of osmotic blisters on the surface of the coatings.

Definition of corrosion losses in the extracts from loose paint films (K_m, X_H) is used to determine the mass, when dimensional changes on steel panels and is, therefore, a direct indicator of surface corrosion. Accurately measured and weighed steel panels were exposed for seven days. The different values in Tables 1 and 2 characterize the probable rate of corrosion. The values of corrosion loss for organic pigments ranged from 0.842 to 1.438 $g\ m^{-2}$; the lowest value of 0.842 $g\ m^{-2}$ being ascertained for pigment of the $C_{14}H_4Mg_2O_8$ type. The reason for the lower value of the corrosion loss is probably the presence of a larger amount of Mg^{2+} cation, increasing the pH value of the aqueous extract and providing greater protection to the steel substrate. Corrosion losses for inorganic pigments ranged from 0.890–1.1293 $g\ m^{-2}$. The lowest value of corrosion loss (0.890 $g\ m^{-2}$) was found for pigment $MgFe_2O_4$. The alkaline nature of this spinel pigment forms an alkaline environment, thus ensuring greater protection to the steel substrate. It can therefore be said that the effectiveness of the pigment behaviour is dependent on its ability to release inhibitory components into the environment, when the presence of an inhibitory anti-corrosion pigment supports the anti-corrosion effect.

Table 1 Physical-chemical properties of organic pigments at $PVC_{pig} = 3\%$

Pigment	[a]pH_8	[a]pH_{28}	[b]λ_8 [$\mu S\ cm^{-1}$]	[b]λ_{28} [$\mu S\ cm^{-1}$]	K_m [$g\ m^{-2}$]	X_H [%]
$C_{12}H_6MgO_4$	7.14	6.98	250.3	350.0	1.438	84.80
$C_{14}H_4Mg_2O_8$	7.50	7.42	268.6	430.0	0.842	49.68
$C_{16}H_{10}MgN_{12}O_{12}$	10.12	9.81	141.9	241.1	1.034	61.02
$C_{34}H_{26}MgN_8O_6$	9.94	9.67	158.8	255.5	0.892	52.61
$C_{26}H_{19}MgN_3O_5$	9.59	9.45	173.6	182.6	1.190	70.22
$C_{17}H_{10}MgN_2O_3$	9.32	8.43	97.6	126.7	1.376	81.17
$C_{25}H_{18}MgN_4O_6$	9.00	8.48	106.3	124.4	1.391	82.07
Dest. H_2O	7.18	7.09	36.3	89.6	1.695	100.00

[a] pH was measured with an accuracy ± 0.01. [b] Specific electric conductivity was measured with an accuracy ± 0.5. Parameters are given as arithmetic averages within three measured values

Table 2 Physical-chemical properties of inorganic pigments at $PVC_{pig} = 3\%$

Pigment	[a]pH_8	[a]pH_{28}	[b]λ_8 [$\mu S\ cm^{-1}$]	[b]λ_{28} [$\mu S\ cm^{-1}$]	K_m [$g\ m^{-2}$]	X_H [%]
MgO	10.53	10.44	219.0	291.1	1.179	69.55
$MgFe_2O_4$	9.97	9.75	78.0	111.0	0.890	52.51
Ca-Mg-HPO_4	7.52	6.41	163.3	215.5	1.293	76.26
Dest. H_2O	7.18	7.09	36.3	89.6	1.695	100.00

[a] pH was measured with an accuracy ± 0.01. [b] Specific electric conductivity was measured with an accuracy ± 0.5. Parameters are given as arithmetic averages within ten measured values

Results of mechanical resistance of coatings

Organic coatings containing titanium dioxide and the pigments tested at PVC = 3 % applied to steel panels were examined for mechanical resistance. The individual values of the bend test are summarized in Table 3. The results show that all the epoxy-ester coatings could withstand bending over the 4 mm mandrel without damage. In the impact test, a cross-cut was first made into the coating prior to the impact test was carried out both from the front and back sides of the paint film and, in neither case, there was any damage to the coating. In the cupping assay using the Erichsen cupping tester, there was also no damage nor cracking of the paint film after the steel ball was pushed to a depth of 10 mm. On organic coatings, their adhesion was also evaluated using the cross-cut test. Most coatings have shown a high resistance to cracking and peeling, rated as degree 0. All organic coatings held tightly to the metal surface; the only exception being the coating

with $C_{25}H_{18}MgN_4O_6$ pigment, where the damage of the lattice did not exceed 5 % of the area, and the process was thus rated as the adhesion degree 1. Table 3 also gathers the results of the pull-off tests that were performed on steel panels with coatings before exposure in corrosion chambers. Coatings containing organic pigments at PVC = 3 % showed pull-off strengths in the range of 1.29–2.72 MPa. Organic coatings with pigments $C_{12}H_6MgO_4$, $C_{34}H_{26}MgN_8O_6$, $C_{26}H_{19}MgN_3O_5$, and $C_{17}H_{10}MgN_2O_3$ achieved pull-off strength higher than the coating with titanium dioxide alone (2.29 MPa). At the same time, these coatings also exhibited a cohesive fracture in the layer in the range of 80–90 %. The epoxy ester coating with $C_{34}H_{26}MgN_8O_6$ pigment revealed the highest pull-off strength at 2.72 MPa (Figure 5). Epoxy ester coatings containing inorganic pigments (Table 4) had pull-off strengths in the range of 1.39–2.41 MPa, achieving an adhesive fracture between the tested coating and the steel substrate as being more than 90 %. In conclusion, it can be stated that the newly synthesized pigments do not deteriorate excellent properties of the epoxy ester binder.

Table 3 Mechanical resistance values of epoxy ester coatings pigmented with organic pigments with Mg^{2+} cation content at PVC_{Pig}= 3 % and $PVC_{Pig}/CPVC = 0.50$ (TiO_2)

Pigment	Bend test [mm]	Impact test [m]	Cupping test [mm]	Pull-off streigth* [MPa]	Adhesion [dg.]
$C_{12}H_6MgO_4$	< 4	> 1	> 10	2.64	0
$C_{14}H_4Mg_2O_8$	< 4	> 1	> 10	1.85	0
$C_{16}H_{10}MgN_{12}O_{12}$	< 4	> 1	> 10	1.29	0
$C_{34}H_{26}MgN_8O_6$	< 4	> 1	> 10	2.72	0
$C_{26}H_{19}MgN_3O_5$	< 4	> 1	> 10	2.54	0
$C_{17}H_{10}MgN_2O_3$	< 4	> 1	> 10	2.49	0
$C_{25}H_{18}MgN_4O_6$	< 4	> 1	> 10	2.11	1

* Fracture type: cohesion in the coating < 80 %; DFT = 50 ± 10 μm

Table 4 Mechanical resistance values of epoxy ester coatings pigmented with inorganic pigments with Mg^{2+} cation content at PVC_{Pig}= 3 % and $PVC_{Pig}/CPVC = 0.50$ (TiO_2)

Pigment	Bend test [mm]	Impact test [m]	Cupping test [mm]	Pull-off streigth* [MPa]	Adhesion [dg.]
MgO	< 4	> 1	> 10	1.39	0
$MgFe_2O_4$	< 4	> 1	> 10	2.41	0
Ca-Mg-HPO_4	< 4	> 1	> 10	1.46	0
TiO_2	< 4	> 1	> 10	2.29	0

* Fracture type: adhesion in the coating < 90 %; DFT = 50 ± 10 μm

$C_{34}H_{26}MgN_8O_6$ (2.72 MPa) $MgFe_2O_4$ (2, 41 MPa).
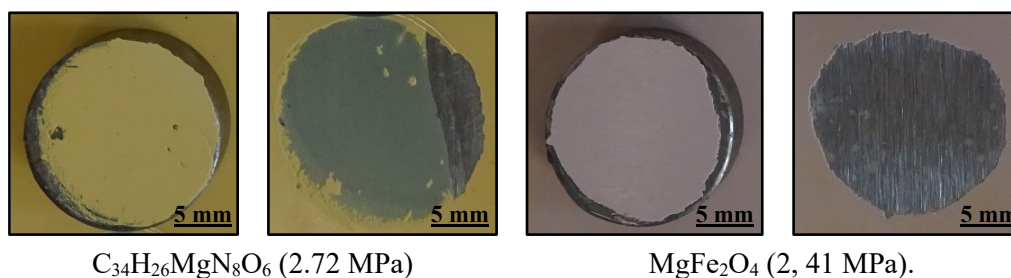
Fig. 5 Photographs of targets after separation of the coatings

Results of cyclic corrosion tests

Cyclic corrosion test in a neutral salt fog environment

Epoxy ester coatings with titanium dioxide and tested pigments at PVC = 3 % were subjected to a cyclic corrosion test in an atmosphere containing 5% salt fog. The organic coatings were evaluated after 1440 hours of exposure, and the results are given in Table 5. During and after the 1440-hour exposure, each paint film was evaluated in terms of corrosion manifestations. The amount of blisters on the paint film surface and in the test cut together with the amount of corrosion products on the paint film surface and in the test cut were evaluated. Except for the organic coatings with $C_{14}H_4Mg_2O_8$ and Ca-Mg-HPO$_4$ pigments, all the coatings achieved a higher anti-corrosion efficiency than that of the coating with titanium dioxide alone, which indicates the formation of an anti-corrosion effect because of the presence of TiO$_2$ pigment in the coating of the inert pigment type. Of the organic coatings containing organic pigments, the coating with the pigment $C_{26}H_{19}MgN_3O_5$ were found to offer the highest anti-corrosion efficiency, in which no blisters had appeared on the paint film surface after 1440 hours of exposure. The blisters in the test cut were rated 2M; the corrosion in the test cut being 1–1.5 mm, whereas the corrosion on the paint film surface yielded 0.1 %. The organic coating with $C_{25}H_{18}MgN_4O_6$ pigment also achieved a similar rating, where the corrosion in the test cut was 1.5–2 mm (Figure 6). The excellent protection against corrosion in the test cut testifies to a fine chemical activity of these new organic pigments. Organic coatings containing inorganic pigments achieved a lower anti-corrosion efficiency (see Table 6) than organic coatings containing organic pigments, as all coating films had blisters in the test cut evaluate 2D, when corrosion in the test cut ranged from 2–4 mm.

Table 5 Corrosion resistance values of epoxy ester coatings pigmented with organic pigments with Mg^{2+} cation content at $PVC_{Pig}= 3\ \%$ and $PVC_{Pig}/CPVC = 0.50\ (TiO_2)$ after 1440hour exposure in an atmosphere containing 5 % NaCl

Pigment	Blistering		Corrosion	
	On the paint surface [dg.]	Near the cut [dg.]	Metal base [%]	In a cut [mm]
$C_{12}H_6MgO_4$	6M	2MD	0.1	3–3.5
$C_{14}H_4Mg_2O_8$	6M	2MD	16	2.5–3
$C_{16}H_{10}MgN_{12}O_{12}$	8F	2MD	1	2.5–3
$C_{34}H_{26}MgN_8O_6$	8F	2D	–	2.5–3
$C_{26}H_{19}MgN_3O_5$	–	2M	0.1	1–1.5
$C_{17}H_{10}MgN_2O_3$	6M	2D	0.3	1–1.5
$C_{25}H_{18}MgN_4O_6$	–	4M	0.1	1.5–2

DFT = 90 ± 10 μm

Table 6 Corrosion resistance values of epoxy ester coatings pigmented with inorganic pigments with Mg^{2+} cation content at $PVC_{Pig}= 3\ \%$ and $PVC_{Pig}/CPVC = 0.50\ (TiO_2)$ after 1440hour exposure in an atmosphere containing 5 % NaCl

Pigment	Blistering		Corrosion	
	On the paint surface [dg.]	Near the cut [dg.]	Metal base [%]	In a cut [mm]
MgO	8F	2D	0.1	2–2.5
$MgFe_2O_4$	8F	2D	0.1	2.5–3
Ca-Mg-HPO_4	8M	2D	10	3.5–4
TiO_2	6F	2D	10	2–2.5

DFT = 90 ± 10 μm

$C_{26}H_{19}MgN_3O_5$ $C_{25}H_{18}MgN_4O_6$ TiO_2

Fig. 6 Epoxy ester coatings containing TiO_2 and tested pigments at PVC = 3 % after 1440hour exposure in an atmosphere containing salt fog

Cyclic corrosion test in an atmosphere containing SO$_2$

Here, epoxy-ester coatings with titanium dioxide and tested pigments at PVC = 3 % were subjected to a cyclic corrosion test in an atmosphere containing SO$_2$. The organic coatings were evaluated again after 1440 hours of exposure, and the results are gathered in Tables 7 and 8. During and after the 1440-hour exposure, each paint film was evaluated with respect to its corrosion characteristics. Compared to the cyclic corrosion test in sprayed neutral salt, the coating films given showed smaller blisters in the test cut (in the range of 6M-2MD), when blisters on the paint film surface occurring in the interval from 8F-8MD. The coating with C$_{14}$H$_4$Mg$_2$O$_8$ pigment achieved the highest anti-corrosion efficiency, where no blisters appeared on the surface of the coating after 1440 hours of exposure. Blisters in the test cut were graded 6M, corrosion at the test cut was in an interval of 0–0.5 mm, and there was no corrosion in the panel area. The coating film with C$_{16}$H$_{10}$MgN$_{12}$O$_{12}$ pigment also exhibited a higher anti-corrosion efficiency, in which blisters on the paint film surface were graded 8F, blisters in a test cut grade 4M, corrosion in the test cut lied in the range of 0–0.5 mm (Figure 7). All organic coatings achieved the same or higher anti-corrosion efficiency than that of the comparative coating with TiO$_2$ alone.

Table 7 Corrosion resistance values of epoxy ester coatings pigmented with organic pigments with Mg^{2+} cation content at PVC$_{Pig}$= 3 % and PVC$_{Pig}$/CPVC = 0.50 (TiO$_2$) after 1440hour exposure in an atmosphere containing SO$_2$

Pigment	Blistering		Corrosion	
	On the paint surface [dg.]	Near the cut [dg.]	Metal base [%]	In a cut [mm]
C$_{12}$H$_6$MgO$_4$	8F	4MD	–	0.5–1
C$_{14}$H$_4$Mg$_2$O$_8$	–	6M	–	0–0.5
C$_{16}$H$_{10}$MgN$_{12}$O$_{12}$	8MD	4M	0.1	0–0.5
C$_{34}$H$_{26}$MgN$_8$O$_6$	8F	4MD	0.03	0–0.5
C$_{26}$H$_{19}$MgN$_3$O$_5$	–	2M	–	1–1.5
C$_{17}$H$_{10}$MgN$_2$O$_3$	8F	2D	0.03	1–1.5
C$_{25}$H$_{18}$MgN$_4$O$_6$	8MD	2M	0.1	0.5–1

DFT = 100 ± 10 μm.

Table 8 Corrosion resistance values of epoxy ester coatings pigmented with inorganic pigments with Mg^{2+} cation content at PVC_{Pig}= 3 % and $PVC_{Pig}/CPVC$ = 0.50 (TiO_2) after 1440hour exposure in an atmosphere containing SO_2

Pigment	Blistering		Corrosion	
	On the paint surface [dg.]	Near the cut [dg.]	Metal base [%]	In a cut [mm]
MgO	8F	6MD	0.03	0–0.5
$MgFe_2O_4$	8MD	6M	0.03	0–0.5
Ca-Mg-HPO$_4$	6M	4MD	0.03	0–0.5
TiO_2	8MD	4MD	0.1	0–0.5

DFT = $100 \pm 10\mu m$.

$C_{14}H_4Mg_2O_8$ $C_{16}H_{10}MgN_{12}O_{12}$ TiO_2
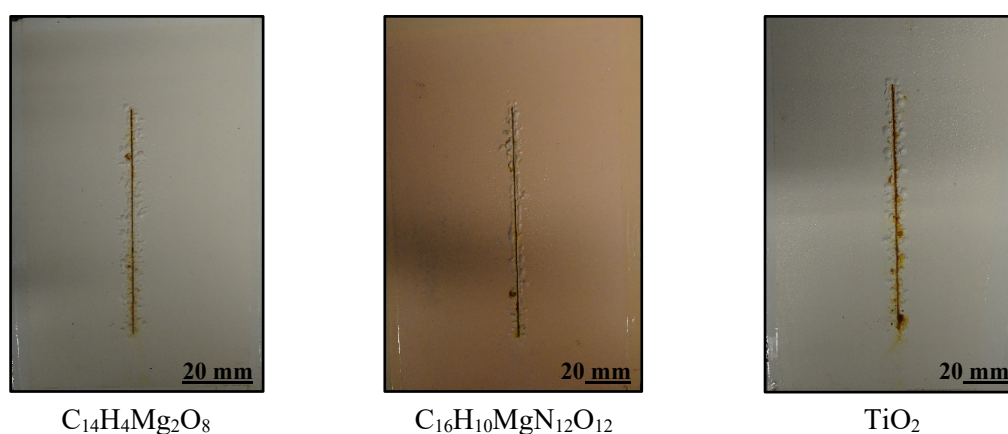
Fig. 7 Epoxy ester coatings containing TiO_2 and tested pigments at PVC = 3 % after 1440hour exposure in an atmosphere containing SO_2.

Conclusions

The aim of this work was to study the properties of coatings based on epoxy-ester resin containing titanium dioxide and of organic and inorganic pigments with Mg^{2+} cations chosen for environments with a lower corrosion load C3. The physical properties of the tested pigments have then been determined.

Namely, of interest were pH, specific electrical conductivity, and corrosion losses from the aqueous extracts from the loose paint films. The organic coatings were also subjected to a series of mechanical tests and cyclic corrosion assays in an atmosphere containing 5% salt spray or in the presence of SO_2.

The pH values of the aqueous extracts from the loose paint films were found to be in the alkaline range of 8.43–10.44 for a majority of paint films. They could therefore be included in the group of alkaline-acting suitable for paint materials enabling the creation of metal soaps with acidic components of the binder. Neutral

pH values (6.98–7.42) were ascertained only for $C_{12}H_6MgO_4$ and $C_{14}H_4Mg_2O_8$ pigments. This neutral behavior was caused by the composition of the pigments given, as they are mono-magnesium and di-magnesium salts. At the same, these two pigments showed the highest specific electrical conductivities (350.0 µS cm^{-1} and 430.0 µS cm^{-1}). The values of corrosion loss for organic pigments ranged from 0.842 to 1.438 g m^{-2}; the lowest value, 0.842 g m^{-2}, being then measured for the pigment $C_{14}H_4Mg_2O_8$. The reason for such a lower corrosion loss was probably the presence of a larger amount of Mg^{2+} cation, increasing the pH value of the aqueous extract and providing thus greater protection to the steel substrate. A lower value of corrosion loss (0.890 g m^{-2}) was also found for the MgFe$_2$O$_4$ spinel type pigment, whose alkaline nature forms the respective environment that is able of providing higher protection of the steel substrate.

All the organic coatings were also tested for mechanical resistance. The results of the individual tests have shown a high mechanical resistance and it can therefore be concluded that the newly synthesized pigments do not impair, in any way, the excellent properties of the epoxy-ester binder itself.

Epoxy ester coatings were also tested for corrosion resistance in an atmosphere with salt fog and a humid atmosphere containing SO$_2$. The total exposure time had been kept for 1440 hours and, during and after such exposure, each paint film was evaluated for its corrosion characteristics. After 1440 hours of exposure in a salt spray atmosphere, most of the paint films achieved a higher anti-corrosion efficiency than that of the coating with titanium dioxide alone, which has indicated the formation of an anti-corrosion effect due to the presence of TiO$_2$ pigment in the coating used as an inert pigment. The excellent protection against corrosion in the test cut testifies to a fine chemical activity of these new organic pigments. The highest anti-corrosion efficiency after exposure in an atmosphere with neutral salt fog was achieved by the coating film with pigment $C_{26}H_{19}MgN_3O_5$, in which no blisters had appeared on the paint film surface after 1440 hours of exposure; the blisters in the test cut being rated 2M, the corrosion in the test cut as 1–1.5 mm, and the corrosion on the paint film surface equal to 0.1 %. Organic coatings containing inorganic pigments achieved a lower anti-corrosion efficiency than organic coatings with organic pigments. Organic coatings based on titanium dioxide and organic and inorganic pigments tested at PVC = 3 % were taken to a cyclic corrosion test in an atmosphere containing SO$_2$. Compared to the cyclic corrosion test in neutral salt spray, such coating films showed smaller blisters in the test cut (in the range of 6M-2MD), when blisters on the paint film surface occurred in the interval from 8F-8MD. All the organic coatings achieved the same or higher anti-corrosion efficiency than the comparative coating with TiO$_2$ alone. The highest anti-corrosion efficiency after exposure in an atmosphere containing SO$_2$ was achieved by the coating film with pigment $C_{14}H_4Mg_2O_8$, where no blisters appeared on the surface of the coating after 1440 hours of exposure. Blisters in the test cut were graded 6M, corrosion at the test cut was 0–0.5 mm, and there was no corrosion in the panel area.

The first results have shown that the anti-corrosion organic pigments under testing have a beneficial effect on the properties of the epoxy ester resin and the mechanism of their action can develop in it, consisting the formation of a complex-forming compound in the area of the interphase interface between the steel substrate and the organic coating.

Finally, newly synthesized pigments showed synergistic effects in corrosion tests and were therefore able to effectively inhibit the corrosion processes in organic coatings.

Acknowledgement

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