Protective primers with reduced zinc powder content caused by the addition of core-shell micro talc/polyaniline pigment

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Abstract. This study aims to verify the possibility of replacing a portion of zinc (up to 30wt.%) with a newly designed micro talc/polyaniline (PANI) core-shell pigment that can be used in the protective primer compositions for metals. Measurements of the electrode potential of painted steel and the electrical capacity of the steel/coating/electrolyte system showed that synthesized pigment bears two functions. Firstly, its presence in the epoxy-amine coatings provides a cathodic protection mechanism for steel with the lower zinc content. Secondly, it allows long-term preservation of the sacrificial metal activity and passive state of the substrate due to the autocatalytic redox cycle based on the reversible conversion of PANI from its emeraldine to leucoemeraldine form. The corresponding mechanism that allows the retaining of sacrificial metal activity and the passive state of the substrate is proposed.

1. Introduction
In order to prevent a corrosion damage of metals painting is considered to be an efficient and economical method. It involves the application of anticorrosion primers on a substrate to protect [1]. There are several approaches to describe the protective action of primers, although the nature of the anticorrosion pigments as a constituent of the paint composition is the decisive factor. As an example, zinc powder is a highly effective anticorrosion pigment, and it has been studied extensively in recent years [2-4].

High level of zinc filling is specially attributed to the process called "cold galvanization" that provides an electrical contact between zinc particles (percolation). This, in turn, is pre-requisite for a cathodic protection of a substrate [5-6]. However, exceeding a certain volume of dispersed additives in the paint film (critical filling level) causes severe deterioration of the physical and mechanical, adhesion and other operational properties of the coating [7, 8]. In order to utilize less zinc several approaches were suggested, for example use of flake-like or nanometer sized zinc particles [9, 10].

Another approach for dealing with this problem is a usage of intrinsically conducting polymers (ICPs), as polyaniline (PANI), polythiophene or polypyrrole as a partial replacement of the zinc powder in coatings. These electrically conductive polymers are capable of participating in the redox reactions which render its anticorrosion properties. The general notion of using ICP is a possibility to exchange some amount of zinc with the conducting polymer maintaining the needed percolation.

Studies have revealed that the addition of different conductive polymers at a rate of pigment volume concentration (PVC) equal to 3% along with zinc at PVC equal to 50% has led to the best improved mechanical and anticorrosion properties of the coatings against 3.5 wt% NaCl solution as was shown by electrochemical tests [11].

Armelin et al. demonstrated that addition of just 0.3 wt. % of PANI emeraldine salt to the 60wt.% of zinc dust leads to the good protection ability of the epoxy coating exposed to the 3.5 wt.% NaCl...
environment through the specially designed controlled cycles [12]. Authors proposed that the reversible transformations between the doped and neutral forms of the PANI are responsible for such performance.

Akbarinezhad et al. studied the systems composed of both undoped and doped forms (2 wt.%) of PANI-nanoclay composites in the zinc-rich (78 and 80 wt.% of Zn) ethyl silicate matrix and their protection properties were evaluated [13]. Results from open circuit potential, electrochemical impedance spectroscopy (EIS) and salt spray chamber investigations showed that the barrier properties of the coatings improved for modified samples. Same authors also investigated the zinc-rich epoxy coating with the addition of nanocomposites made of PANI-clay synthesized via in-situ polymerization at the interface of water and supercritical CO₂ [14]. In that study 1 wt.% of zinc content was replaced by nanocomposites. Again, results from electrochemical tests revealed that the implementation of new additives leads to improved protective properties.

Moreover, Zn is a relatively expensive and toxic substance [15], thus, research, focused on the substitution of this component in a paint formulation to the effective analogue or reduction of zinc, is an important subject [4].

For this purpose, in the current study, the newly designed composite was utilized. It has a core-shell structure. Micro talc is a core and PANI doped with oxyethylidenediphosphonic acid (OEDPA) is a shell. This composite was used as pigment in the composition of protective zinc-containing primer. Two following considerations guided the selection of this pigment. Firstly, OEDPA has complexing properties and ability to suppress corrosion of steel [16]. Secondly, the anisotropic shape of the micro talc particles enhances the barrier properties of the coatings and the formation of conjugated structures with zinc particles. Thus, utilizing these electrochemical active clusters of particles, it is possible to achieve a percolation with the reduced content of the sacrificial metal.

During the synthesis of PANI, aniline molecules interact with the according acid (in the current case with OEDPA) as follows (Figure 1). Upon dissociation, these ions are divided on positively charged phenylammonium ions and negatively charged phosphonate ions. It is known that clay particles possess two types of surface formed upon grinding, the first one, called “basal”, is produced as a result of interlayer gliding, whereas the second – “lateral” – is formed after the scission of ionic bonds [17]. Thus, when phenylammonium ions are introduced in the system with clay, they physically interact due to two following reasons. First, on the inert hydrophobic basal side, the adsorption is caused by a physical nature. There are van der Waals forces of attraction between clay’s coating and aryl radical of phenylammonium ions. The second is the presence of silanol groups and cations on the lateral side. They have tendency to accept electrons in the course of red-ox reactions. Silanol groups and cations possess an acidic nature and phenylammonium ions bind to it due to ionic interactions (Figure 2).

![Figure 1](image1.png) ![Figure 2](image2.png)

**Figure 1.** Scheme of salt-forming reaction between aniline and OEDPA molecules. **Figure 2.** Structure of the clay particle with aniline molecules bind to its different surfaces.
2. Experimental part

2.1 Materials

Aniline was purified by a steam distillation. Micro talc was a MT-EGS-1 grade filler with a particle size of 5-20 μm manufactured by CJSC "Geokom", Russia. Zinc powder was produced by SMP, South Korea. Epoxy resin E-40 represented bisphenol A and epichlorohydrin with a weight content of epoxy group equal to 13-15%. Polyethylene polyamine was used as a hardener for E-40. OEDPA was utilized as a dopant for PANI. Ammonium peroxydisulfate (APS) was used as an oxidant for PANI. Xylene, 2-ethoxyethanol, mineral spirit and acetone were utilized as solvents. All reagents were commercially available products.

All chemicals were of reagent grade except for aniline, which was of technical grade, and were used without further purification.

2.2 Synthesis of core-shell pigment

A suspension of micro talc in a mixture of aniline and 0.4 M aqueous solution of OEDPA was firstly prepared. Then aqueous solution of APS was dosed into the suspension. The molar ratio between aniline and dopant was 1:1, and molar ratio between aniline and oxidant equals 1:1.25. The micro talc/aniline ratio was calculated so that the resulting product contained 5 wt.% of PANI. After a few minutes from the start of the addition of the oxidant, a change in the color of the solution from grey to dark blue was observed, which then changed to dark green, indicating that the polymerization process had passed. The procedure was carried out at room temperature and monitored by recording the redox potential of the reaction mass using a pH meter Hanna HI-8314 (Hanna Instruments, USA) with silver-chloride and platinum electrodes. The stability of the redox potential value after the reduction in the synthesis process was considered a criterion for completing the polymerization.

The resulting product was separated from the mother solution by centrifugation, rinsed with water and dried to a constant weight at 100 ± 5°C.

Synthesis of pure PANI was performed with the same approach as above excluding the addition of micro talc.

2.3 Pigment parameter determination

Two methods were implemented in order to prove the formation of PANI on the surface of the micro talc as a result of the hetero phase polymerization reaction. First, a surface topography examination on high resolution photomicrographs of both pristine and modified micro talc particles made with the help of laser confocal microscope Olympus LEXT OLS 4000 (Olympus Corporation, Japan) was conducted. Second, values of the hiding power (received in accordance with ISO 6504-3) of the core-shell pigment and simple mechanical mix between micro talc and PANI were compared.

2.4 Formulation and preparation of the organic coatings

The obtained micro talc/PANI pigment was used to partially replace zinc powder in protective primers, and the formulation calculations considered the need to maintain a constant volume content of pigment portion in coatings prepared from compositions both containing core-shell pigment and without it.

Epoxy oligomer E-40 was used as the film-forming base of coatings and its hardener was polyethylene polyamine. For the production of protective primers, the specified amount of 65% solution of E-40 in the mixture of xylene and 2-ethoxyethanol in mass ratio 1:1 was used. This mixture was stirred in a laboratory dissolver with a calculated weight of zinc powder. Later it was dispersed with the aid of a laboratory beaded dispersant (VELP Scientifica, Italy) at 1000 rpm to a fineness of grind less than 30 μm determined according to ISO 1524. The process of the production of zinc-containing primers with a composite pigment part differed from the initial composition only by the presence of one additional stage of dosing micro talc/PANI pigment to the formulation.

Before applying the paint composition on a substrate, it got through mixing and filtration through a
sieve with mesh numbers 01-02, with the subsequent dilution to working conditional viscosity with the mixture of solvents.

As metal substrates for studying the properties of paint coating, the plates of cold-rolled low-carbon body steel substrates type 08kp that is analogues to type DC 04 B with a chemical composition (maximum nominal composition in wt.%) of 0.40% Mn, 0.08% C, 0.03% P, 0.03% S and balance Fe were used. The dimensions of the substrate panels were 70.0 × 70.0 × 0.8 mm cut from one metal piece.

Prior to the application of coatings, the preparations were carried out on steel samples by mechanical and chemical ways including cleaning of a surface with an emery cloth No.100 to the identical degree of roughness followed by degreasing with mineral spirit and acetone and drying at room temperature.

The painting was carried out by a three-layer air spraying technique with an intermediate drying for 1 hour and final coating formation for at least 72 hours under natural conditions before exposure to the electrolyte solution. The dry film thickness of coatings was measured using a universal coating thickness gauge TT210 (Beijing TIME High Technology Ltd., China). The thicknesses of the three-layer coatings were equal to 75±5μm.

2.5 Corrosion test procedure
In order to determine the mechanism of protective action and the level of barrier properties of the formed coatings, the painted steel samples were brought into contact with the corrosion-active medium, 3% NaCl solution, and its electrode potential and electrical capacity of the steel/coating/electrolyte system were measured. For this purpose, a two-electrode electrochemical cell (Figure 3) was used.

![Figure 3. Two-electrode electrochemical cell: (a) scheme, where 1, stainless steel disc (first electrode); 2, electrolyte solution; 3, glass cylinder; 4, coating; 5, steel plate (second electrode); 6, electrode contact; (b) photo of the real set-up.](image)

For the detailed description of the procedure and the theory behind it refer to the relevant literature [18,19].

3. Results and discussion
3.1 Pigment specification
As it can be seen from the photomicrographs, shown in Figure 4 as a result of the PANI polymerization, the micro talc particles are colored green on the PANI surface without changing its original shape. Note, that the samples were rinsed with a solvent several times before taking photographs, thus all the separate individual particles were washed off.

A comparison of the hiding power of the core-shell pigment and the mechanical mix between the same composition of micro talc and PANI (Figure 5) suggests an almost twice higher value of this characteristic in the first case. This method was applied as an indirect proof of the development of the PANI “shell” on the surface of the “core” talc particles, rather than a mix of two individual species.
Figure 4. Photomicrographs of the surface of the original micro talc (a) and micro talc modified with PANI (b).

Figure 5. Hiding power of the core-shell pigment (right bar) and simple mechanical mix (left bar) of micro talc and PANI.

As an explanation there is a schematic depiction of two types of coatings given in Figure 6, simple mechanical mix (a) and core-shell micro talc/PANI pigment (b). The value of hiding power is dependent on the light absorbance of a coating and the pigment that used is mainly defines it. The darker the color of the pigment the more light can be absorbed by a coating [20]. In case of presence of two types of particles in the system, the light absorbance of the coating would be lower than in the second case, as free talc particles present in the system, so more light can pass through the coating [21], thus the value of hiding power is higher.

Figure 6. Schematic depiction of mechanical mix (a) and core-shell micro talc/PANI pigment (b) dispersed in coating on the metal surface.

3.2 Electrochemical experiments
Electrode potential and electrical capacity values were determined for the intact zinc-rich epoxy-amine primers. By analyzing the obtained results for investigated systems, a shift of the electrode potential to the value of -540 mV (100 mV below the electrode potential of iron) [22] was chosen as a sufficient criterion for the reliable establishment of the cathodic protection mechanism of the investigated samples.

The chronopotentiometry results shown in Figure 7 suggest that specimen of zinc-rich epoxy-amine coatings with the filling level of 80 wt.% possesses sacrificial protection of steel.

The shape of the capacitance chronogram curves (Figure 8) changes as the zinc powder content in the primer increases. For the sake of simplicity and in order not to overload the plot two concentrations that clearly show two types of dependencies are picked, i.e., 60 and 80 wt.%. When the filling level is low (60 wt.%), this dependence has the view typical to coatings, the protective effect of which is provided by the insulating properties of the applied paint material. The water absorption process inside the coating is responsible for the capacitance values. In the beginning when it just starts, capacitance goes up, and when it is finished, capacitance is almost constant. The re-growth of
Capacitance is generally associated with the destruction of the coating as a result of an aggressive environment and the direct contact of the electrolyte with the surface of a substrate to be protected. As a result, the emerged electrochemical capacitance makes a significant contribution to the measured electrical capacitance value of the steel/coating/electrolyte system.

When the zinc filling level in the coating increases, the shape of the capacitance dependencies is changed (80 wt.%). There is a sharp initial increase in capacitance followed by a decrease to the values corresponding to the coating with a low filling level.

![Figure 7. Electrochemical potential versus time of steel painted with epoxy-amine primers in contact with electrolyte at different zinc powder contents in coating (in wt.%). The lines are guides for the eyes.](image)

![Figure 8. Chronograms of electric capacity of steel painted with epoxy-amine primers in contact with electrolyte at different zinc powder content in the coating (in wt.%). The lines are guides for the eyes.](image)

There are two possible simplified options of how exactly zinc particles in the volume of a paint film can be placed and oriented. First, it is when these particles touch each other and also the surface of the substrate, thus an electrical current exists, and the anticorrosion action is on. Second, when zinc particles, present in the system, are not in contact with each other, they are inactive.

Zinc particles are electrochemically active species, and when the amount of added Zn reaches a limit, i.e., there is a critical zinc content in the coating, in addition to the electrochemical active species some zinc chains are included in the paint system. These correspond to the zinc chains that come out on the surface of capillary defects filled with electrolyte penetrating into the film. This is the second option. When the surface of the zinc particles is in contact with the electrolyte, an electrochemical capacitance is generated, and as a result the measured value of the capacitance increases as well. But there is also a situation when the capacitance would be lowered. It can happen when the surface of zinc is coated with insulating oxide or hydroxide layers.

Based on the results from Figures 7 and 8, it can be concluded that the zinc filling level of 80 wt.% in the epoxy-amine primer is sufficient for the cathodic protection. This system was utilized as a reference. Three concentrations of newly synthesized core-shell micro talc/PANI particles (10, 20 and 30 wt.%) were used to separately replace the corresponding amount of zinc powder in the epoxy-amine primer, and the same electrochemical investigations were performed on these paint materials.

The data presented in Figure 9 suggest that the replacement of zinc powder in the coating up to 30% with synthesized core-shell pigment does not affect the mechanism of the corrosion protection. All the tested coatings provide a cathodic mechanism of steel protection during testing, as suggested by the constant high values of the electrical capacity throughout the test. Also, the same samples were tested on the determination of the electrical capacity values and the corresponding data of the systems indicate some specifics of electrochemical processes that take place when the corrosion-active medium is exposed to the tested samples (Figure 10). Usually, in such systems, there is a drop of the capacitance value seen e.g., in Figure 8, but in the current case it located in the plateau region for
every investigated concentration. Discontinuation of both zinc oxides and hydroxides formations, caused by the presence of micro talc/PANI pigment in the system, is an explanation for this phenomenon. Therefore, electrochemical activity of the system is stable and constant.

![Image](Image URI)

**Figure 9.** Electrochemical potential versus time of steel painted with epoxy-amine primers containing zinc powder with the according replacement of different amount of micro talc/PANI (in wt.%) in contact with electrolyte. The lines are guides for the eyes.

**Figure 10.** Chronograms of electric capacity of steel painted with epoxy-amine primers containing zinc powder with the according replacement of different amount of micro talc/PANI (in wt.%) in contact with electrolyte. The lines are guides for the eyes.

We explain this phenomenon by the following mechanism (Figure 11) taking into account the results from the electrochemical tests:

- First, leucoemeraldine form of PANI appears after the initial protonated emeraldine takes two electrons from the zinc being in this case a reductant.
- Second, the released OEDPA reacts with the zinc ion forming a water-soluble salt, preventing the formation of zinc oxide and zinc hydroxide. The formed zinc phosphonate is able to participate in the formation of passivating layers on the steel surface [23, 24].
- Third, as a result of oxidation with oxygen dissolved in the electrolyte, the leucoemeraldine form of PANI is converted to the protonated emeraldine form with the chloride ion, thereby reducing its content in an aqueous medium.

![Image](Image URI)

**Figure 11.** Mechanism of variations of PANI doped with OEDPA in electrochemical processes during cathodic protection of steel by zinc-rich primers.

4. Conclusion
The results of the electrochemical tests demonstrated that the newly designed core-shell pigment of micro talc/PANI composition can be successfully used as the electroconductive pigment in the formulation of an epoxy-amine primer. The series of epoxy-amine paint systems with the varied zinc powder content from 60 to 90 wt.% with 10 wt.% step was initially investigated. Results from electrochemical studies revealed the optimum concentration that provides for a cathodic
protection of the paint. That system was used for the following experiments comprising the separate replacement of the 10, 20 and 30 wt.% of zinc powder to the corresponding amount of core-shell micro talc/PANI pigment and same electrochemical tests were performed in order to see how such replacement affects the anticorrosion performance of the newly designed paint systems. Zinc powder content up to 30 wt.% in the paint material can be replaced while maintaining its high anticorrosion properties. The latter was explained with the proposed mechanism based on a redox cycle caused by the reversible conversion of PANI from the emeraldine to the leucoemeraldine form.

This study shows a clear prospect of using a flake filler like micro talc with a ICP like PANI shell as a component of the pigment portion of zinc-containing protective primers. However, in order to implement this direction of optimization of the composition of the latter, it is necessary to organize the production of such core-shell pigment on an industrial scale.

References
[1] Stepin S N 2018 Properties of anti-corrosive ferrite pigment synthesized with the use of production waste 18th Int. Multidiscip. Sci. GeoConf.SGEM2018 Nano, Bio and Green Technologies for a Sustainable Future
[2] Marchebois H, Savall C, Bernard J and Touzain S 2004 Electrochimica Acta 49 2945–54
[3] Al-Husein I, Kasi R, Shafaamri A, Ma I A W and Subramaniam R 2020 Pigment & Resin Technology 49 33–40
[4] Langer E, Zubilewicz M, Kuczyńska H, Królíkowska A and Komorowski L 2019 Science and Technology 54 627–35
[5] Abreu C M, Izquierdo M, Merino P, Nóvoa X R and Pérez C 1999 Corrosion 55 1173–81
[6] Meroufel A and Touzain S 2007 Progress in Organic Coatings 59 197–205
[7] Baczoni A and Molnár F 2011 Acta Polytechnica Hungarica, 8(5) 43–51
[8] Schaefer K and Miszczyk A 2013 Corrosion Science 66 380–91
[9] Vilche J R, Bucharsky E C and Giúdice C A 2002 Corrosion Science 44 1287–309
[10] Liu B, Li Y & Wang F 2009 J. of Chinese Society for Corrosion and protection 23(6) 350-354
[11] Kohl M, Kalendová A and Schmidová E 2017 Chemical Papers 71 409–21
[12] Armelin E, Martí M, Liesa F, Iribarren J I and Alemán C 2010 Prog. in Organ. Coat. 69 26–30
[13] Akbarinezhad E, Ebrahimi M, Sharif F and Attar M 2011 Corr. Eng., Sci. and Tech. 46 777–81
[14] Savin R R 1996 U.S. Patent 5,580,907
[15] Akbarinezhad E, Ebrahimi M, Sharif F, Ghanbarzadeh A 2014 Prog. in Org. Coat. 77 1299–308
[16] Kayumov A A 2018 Core-shell pigments based on microcalcite with phosphate and phosphonate/amine shells 18th Int. Multidiscip. Sci. GeoConf. SGEM2018 Nano, Bio and Green Technologies for a Sustainable Future
[17] Tournassat C, Neaman A, Villiéras F, Bosbach D and Charlet L 2003 Amer. Mineral. 88 1989–95
[18] Rammelt U and Reinhard G 1992 Progress in Organic Coatings 21 205–26
[19] Vakhitov T R, Katnov V E, Grishin P V, Stepin S N and Grigoriev D O 2017 Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences 473 20160827
[20] Gueli A M, Bonfiglio G, Pasquale S and Troja S 2017 Color Research & Appli. 42 236–43
[21] Freitag W and Stoye D 2008 Paints, coatings and solvents (John Wiley & Sons)
[22] Semenova I V, Florianovich G M, and Khoroshilov A V 2010 Corrosion and corrosion protection (Moscow: FIZMATLIT) p 416
[23] Stepin S N, Kouznetsova O P, Vahin V A and Habibrahmanov B I 2012 Herald of Technological University 15(13) 88-98 (in Russian)
[24] Stepin S N, Xolmurodov T A, Mirzaev O O and Katnov V E 2020 Optical properties of sol-gel coatings containing silver nanoparticles IOP Conference Series: Materials Science and Engineering 911 012007