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Study of new conductive materials for organic coatings

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Annotation

Presented dissertation work compares a wide range of conductive salts used as anticorrosion pigments while under different methods of surface treatment on silicate or ferrite particles. Each powder pigment was applied into organic resins, model organic paints were prepared/formulated and applied. The paint films were then tested and characterised by direct and indirect corrosion tests such as density determination, linen oil absorption, content of compounds extractable by cold or hot water, pH values and electric conductivity of aqueous extracts of pigments and of free paint films. The values of mass decrease of exposed steel panels covered by organic films were determined. The main part of presented work lies in corrosion tests in following environments: humid air at the condensation point, atmosphere of sulphide dioxide, atmosphere of neutral salt mist or atmosphere of mixed salt electrolyte of ammonium sulphate and sodium chloride. Corrosion effects such as blister formation in paint film or in testing cut were evaluated.

The results are written in the form of well-arranged tables and the commentary and the photographic evidence is provided in the discussion section. The most promising formulations with highest anticorrosion effectivity are the clay and talc particles functionalized by conductive salt of polyaniline primary doped with phosphate. By introducing the secondary doping salt in amounts around 20wt% to the polymer the effectivity of paint coats was increased significantly. The most effective secondary doping salt was the benzoic acid which contributed to the excellent result by its inhibition effect. Comparable results were achieved by testing composite ferrite polyaniline pigments primary doped with phosphate. By reprotonating this pigment system by benzoic acid one of the most resistant paint coats with the highest anticorrosion protection were achieved.

Keywords

corrosion protection
organic paint
conductive polymer
polyaniline
poly(*p*-fenylendiamine)
diethyl phosphite
heteropolyacid
benzoic acid
zinc ferrite

Anotace

Disertační práce porovnává různé druhy vodivých solí jako samostatných antikorozních pigmentů, různé druhy povrchových úprav těmito solemi na částicích křemičitanů či feritů. Veškeré práškové pigmenty byly aplikovány do organických pryskyřic, byly připraveny modelové nátěrové hmoty a z nich nátěrové filmy, které byly testovány přímými a nepřímými korozními testy jako jsou základní charakterizace materiálů pomocí hodnot hustoty, spotřeby lněného oleje, obsahu látek extrahovatelných za horka nebo za studena, hodnot pH a měrné elektrické vodivosti vodných výluhů jak pigmentů, tak volných nátěrových filmů a hodnot hmotnostních popř. korozních úbytků pozorovaných na ocelových panelech exponovaných ve vodných výluzích prášků a filmů. Hlavní část práce tvořily korozní testy v prostředí kondenzované vzdušné vlhkosti, atmosféře s obsahem oxidu siřičitého, prostředí s obsahem neutrální solné mlhy nebo prostředí směsného solného elektrolytu s obsahem síranu amonného a chloridu sodného. Následně byly dle příslušných postupů a norem vyhodnocovány korozní projevy.

Jednotlivé hodnoty měření byly zaznamenány do tabulek, v diskuzní části práce okomentovány a podepřeny fotografickými záznamy. Na konec byly vybrány nejlepší nátěrové filmy, které vykazovaly nejvyšší antikorozní účinnost, kde ze získaných výsledků byly jako nejperspektivnější materiály zvoleny křemičitany kaolín a mastek při nízkém povrchovém pokrytí vrstvou primární vodivé soli polyanilin fosfátem, kdy tyto kombinace vykazovaly nejvyšší antikorozní účinnost. Zavedením sekundárního dopantu do polymerního řetězce dosahovaly nátěrové filmy vysokých účinností při středním plnění 20hm%, solí vodivého polymeru. Nejúčinnější solí se stal dopant kyseliny benzoové, který při antikorozní ochraně kovového podkladu přispěl svým inhibičním efektem. Podobných výsledků bylo dosaženo i při testování kompozitních feritických pigmentů s obsahem primárního dopantu polyanilin fosfátu. Reprotonací pigmentového systému kyselinou benzoovou byly získány jedny z nejodolnějších nátěrových filmů s nejvyšší antikorozní ochranou.

Klíčová slova:
korozní ochrana
organický povlak
vodivý polymer
polyanilin
poly(*p*-fenylendiamin)
diethylfosfit
heteropolykyselina
kyselina benzoová
zinkferit

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Introduction

The protection of materials from degradation as well as corrosion issues have been some of the most discussed topics for several decades [1]. The main attribute of corrosion protection has been crude steel, whose production reached 1,600 million tons in 2014. World Production Association collects production reports from more than 60 countries around the world. Until May 25, 2018, 575.2 million tons of crude steel, the 34 % of expected 2018 production worldwide, was already produced. The Czech Republic, with an average annual production of 5 million tons, ranks among the top ten producers in the European Union as well as in the world rankings has been on the 25. position [2]. Degradation of material by corrosion processes in developed countries is reported as a loss of 3-5% of gross domestic income (GDP). For the year 2017, the Czech Republic lost about 140 million Czech crowns [3]. In order to make efficient use of steel and steel products, their surface protection against corrosion is important [4]. Atmospheric corrosion accounts for more than 80 % of the degradation of these materials. One possible way of protecting materials are organic coatings as protective coatings containing anti-corrosion pigments [5] which are under constant legislative supervision. In order to prevent the use of toxic and potentially hazardous corrosion pigments, the scientific community has focused on the topic of conductive polymers, which can be applied to coatings used for anti-corrosion purposes [6]. With the right and effective anti-corrosion treatment, it is possible to prevent corrosive effects and thus reduce the cost of repairing and replacing corroded materials [7].

1. Theoretical part

Corrosion protection of materials is an issue which has been addressed by human society for many years. Metal surfaces are protected from corrosion by applying various coating materials. The binders, inorganic and organic pigments contained in the coating materials and the paints themselves are subjects under constant research, development and innovations with a view to making them environmentally friendlier and improving their properties and anticorrosion efficiency [8]. The most widespread method of anticorrosion metal protection consists in application of organic coatings in anticorrosion paints [9]. The efficiency of the organic coatings can be increased by adding inorganic pigments, which prevent the corrosion medium from penetrating to the substrate surface [10]. A silicate component exhibits a partial inhibiting effect, supported by the barrier effect of the individual pigment particles [11, 12]. Diatomite, talc, calcinated clay or wollastonite representat the group of basic pigments. For an effective barrier the system must contain at least 30 vol% of a silicate pigment [13, 14]. That is why these pigments were combined with conductive polymers.

The conductivity of polymeric materials is a result of a chain of partial processes. In conductive polymers the carbons in sp^2 hybridization form a conjugated system of double bonds by overlapping and subsequent hybridization of valence orbitals. Electrons positioned in these p_z orbitals became delocalized and exhibit a high mobility along the conjugated double bond system. If the material is doped by using an oxidative reaction, some of the electrons start moving. The conjugated p-orbitals give rise to a one-dimensional electronic band in which the electrons are mobile provided that the orbital is partly empty. An inorganic or organic acid can serve as mentioned dopant. Conductive polymers are not conductors in the full meaning as inorganic conductors. Actually, the term semiconductors would be more appropriate. The conductivity of the undoped conjugated polymers is very low ranging from 10^{-10} to 10^{-8} S/cm [15]. They include, e.g. cis-polyacetylene, polythiophenes, polyethylene and the polyaniline base. Each doping level increases the electrical conductivity by 0.1 S/cm. Trihydrogen phosphoric acid and benzoic acid were selected as the primary dopants of the conducting polymer. The conductive salt is deprotonated in a 1M solution of ammonium hydroxide followed by a reprotonation by secondary dopant. In presented dissertation work the diethyl phosphite, heteropoly acids and benzoic acid as secondary dopant for conductive polymers were used.

Diethyl phosphite is a novel and unexplored material in the domain of paints, its use with PANI as a secondary dopant has not been described so far. Interactions between this diester and PANI have been studied by Šeděnková et al., who pointed to the fact that no proton capable of providing direct interaction with the PANI chain exists in diethyl phosphite. In fact, the phosphite molecule is bonded to the PANI segments through P···HN and POH···N hydrogen bonds [16].

Heteropolyacids are compounds that were used only once in paints [17]. The behaviour of molybdophosphoric type HPAs in paints was described by Xu, who applied this HPA to a steel substrate, exposed it to a corrosive environment and analysed the protective film's composition. The components included mainly complex compounds such as $Fe_n[PMo_xO_y]$ and $M_n[PFeMo_xO_y]$ where M = K, Na [18].

The last doping was benzoic acid known for its inhibitory properties.

2. The aim of the thesis

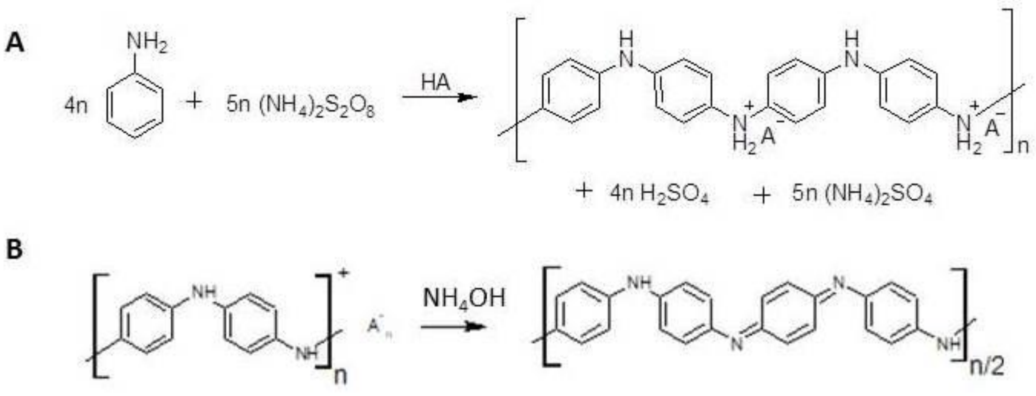
The aim of the thesis was to prepare combinations of powdered pigments containing a conductive polymer salt which have not yet been used in the field of organic coatings and paints or not given sufficient attention. On this basis, the research part of the work, which provides already-known information, is also processed, but it also maps the current state of the issue of the use of conductive polymers in the field of organic coatings and anticorrosion protection. For this reason, a basic description of conductive polymers was presented, focusing on selected representatives of these substances, where the focus was mainly on their mechanism of protection as anticorrosive pigments in paints. The objectives of the dissertation could be summarized as follows:

- based on the research work select a suitable and representative conductive polymer
- based on the properties choose the preferred primary and secondary dopants of conductive polymer
- prepare the paints and organic coatings for further testing
- study and use the silicate pigment as a carrier for the salt of conductive polymer
- choose the composition and suitable preparation method for ferrite-based pigments in combination with conductive polymer as composite pigments

3. Experimental part

3.1. Surface treatment silica pigment by polyaniline

Polyaniline salt was prepared by standard oxidation of 0.2M aniline salt with 0.25M ammonium peroxodisulphate in an aqueous medium at laboratory temperature (equation 1A). Than silicate powder was added in volume to be obtained surface layer on 10 wt.%, 20 wt.% and 30 wt.%. The ferrite powder was added in volume 30 wt.% only. The reaction was accompanied by colour changes from dark blue to the final dark emerald. The final substance was filtered out, rinsed with acetone, dried in air and then in dryer (60 °C). The surface layer was checked by DTA analysis (heating 5 °C/min). This was designation as primary doping. The solids were subsequently converted to polyaniline base in 1M ammonium hydroxide, and dried at laboratory temperature (equation 1B) in air and then over silica gel. The PANI base was suspended in solution of secondary dopant. After 24 hours, the solids were collected on a filter, washed with ethanol, and dried in air and then over silica gel.



Equation 1: Oxopolymeration reaction of aniline salt

The ferrite powders were prepared by calcination of a ZnO or $MgCO_3$ and iron oxide in 1:1 ratio at 980 °C for 2 hours; this temperature was reached at the rate of 5 °C per minute. The ferritic pigments possessed different particle sizes: specularite (lam.α-Fe_2O_3) had lamellar particles, whereas hematite (α-Fe_2O_3) had spherical particles, goethite (FeOOH) with needle shape particles and the last magnetite ($FeO.Fe_2O_3$) in isomeric form. The calcinated powders were wet milled at 390 rpm for 4.5 hours with a 30-min holdup and reverse run and then dried at 90 °C. Powder preparation describes equations 2 A-E:

$$2\ \mathrm{FeOOH\ (goethite)} \xrightarrow{\Delta T;\, -H_2O} Fe_2O_3 + ZnO \rightarrow ZnFe_2O_4 \qquad \text{(A)}$$

$$2\ \mathrm{FeOOH\ (goethite)} \xrightarrow{\Delta T;\, -H_2O} Fe_2O_3 + MgCO_3 \xrightarrow{-CO_2} MgFe_2O_4 \qquad \text{(B)}$$

$$2\ Fe_3O_4\mathrm{(magnetite)} + 3\ ZnO + \frac{1}{2}O_2 \rightarrow 3\ ZnFe_2O_4 \qquad \text{(C)}$$

$$2\ Fe_2O_3\mathrm{(magnetite)} + 3\ MgCO_3 + \frac{1}{2}O_2 \rightarrow 3\ MgFe_2O_4 + 3\ CO_2 \qquad \text{(D)}$$

$$\alpha\text{-} - Fe_2O_3\mathrm{(specularite\ or\ hematite)} + MeO \rightarrow MeFe_2O_4 \qquad \text{(E)}$$

where Me is Zn^{2+}or Mg^{2+}

Equation 2: Preparation of ferrite pigments

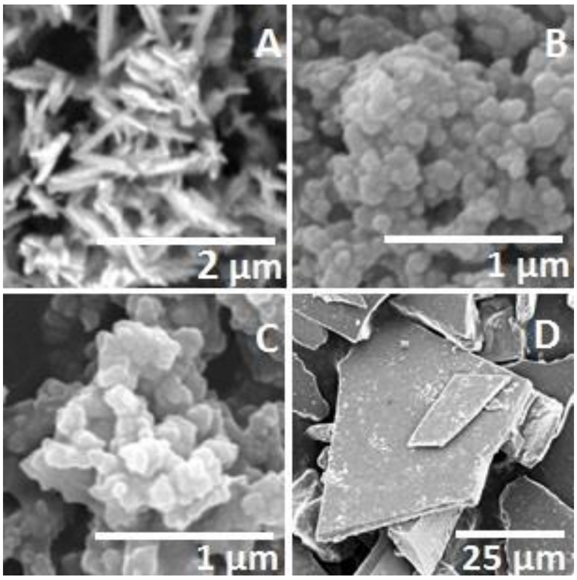


Figure 1: Different shape of particles ferrite oxide: A - goethite, B - magnetite, C - hematite, D - specularite

3.2. Characterization of pigment powders

The basic pigment properties were determined pycnometrically (CSN ISO 787-10). The critical pigment volume concentration (CPVC) was determined via linseed oil consumption per 100 g of the pigment (CSN ISO 787-5) by the pestle-and-mortar method as per CSN 67 0531. The CPVC value served to set up a concentration series. Silicates/PANI pigment particle morphology and shapes were examined on a LYRA3 TESCAN electron microscope. Matter soluble in hot water ($M_{w,h}$) and in cold water ($M_{w,c}$) was also determined according to CSN EN ISO 787-3 and 787-8, respectively. The pH and specific electric conductivities (X) of a 10% aqueous extract of the pigment powder were measured during 28 days as per CSN EN ISO 789-9 and CSN EN ISO 787-14. The suspension was filtered and a clean and pre-weighed steel panel was submerged in the filtrate for 15 days, after which the panel was removed from the extract and the corrosion loss ($X_{cor.loss}$) was measured.

3.3. Determination of mass coverage of particles by conductive polymer

The principle of the method is based on the fact that the material under investigation is subjected to thermal stress, while the temperature is monitored for the whole time with another characterizing property of the material. In case of thermogravimetry, this is a weight dependence on temperature change. To determine the polymer part of the mixture, an oxidizing atmosphere or air was chosen. Measurements were made at an interval from room temperature to 950 ° C. Measured results were recorded using thermogravimetric curves.

3.4. Paint formulation and preparation

The paint systems were formulated on computer program FORMUL. As a binder was used epoxy-ester resin on solvent-type (WorléeDur D46). The model paints were prepared by adding the pigment to the binder and homogenizing the system. The pigment volume concentration (PVC) in the paint was 1 vol.% to 10 vol.%. The paints were prepared in a laboratory bead mill at operating speed 10-15 m/s for 45-60 minutes. Before applying to panels, Nuodex Combi HS(mix of salts Co/Ca/Zr) was added at 0.1 wt.% as a siccative. Than the paints were applied to glass and low-carbon steel panels where physico-mechanical tests were done.

3.5. Characterization of paint films by physico-mechanical tests

The physico-mechanical properties of the paint films were determined by subjecting the films to mechanical and destructive stress according to ISO standards 2409, 6272, 1519, and 1520.

3.6. Corrosion tests

The coated steel panels 152 mm x 102 mm x 0.8 mm size (Q-LAB Corporation) were subjected to an accelerated corrosion test. A vertical cut 8 cm long was made through the paint film to the substrate metal of all the samples tested. The corrosion effects in the cut area were then evaluated.

The samples were exposed to a salt fog atmosphere with 100% relative humidity (ISO 927) and humid atmospheres containing sulphur dioxide (ISO 3231). The test chamber was run in 12-hour cycles, a cycle comprising 6 hours of exposure to the salt fog solution (pH 6.5 – 7.2) at 35 °C ± 2 °C; 2 hours of exposure at 23 °C ± 2 °C; and 4 hours in condensed moisture at 42 °C ± 2 °C.

The following corrosion effects were evaluated according to ISO 4628-2 to 4628-5 after removing the panels from the chamber: blister formation on the entire paint film surface (ASTM D 714-78), degree of corrosion in the test cut (ASTM D 1654-92) and degree of steel substrate surface corrosion after removing the paint film (ASTM D 610-85). The paint's anticorrosion efficiency in the test environment was expressed through the arithmetic mean of the scores.

4. Results and discussion

The amount of conductive polymer in the system was determined by thermogravimetric analysis of the pigment powder. Its amount was determined based on weight loss. This method verified the empirical determination of the amount of conductive polymer in the pigment mixture. Determination of the amount expressed by weight percent of the conductive polymer content in the pigment blend was one of the objectives of the thesis. Figure 2 shows the surface-treated talc with a conductive PANI-P layer of 20wt% and 30wt%.

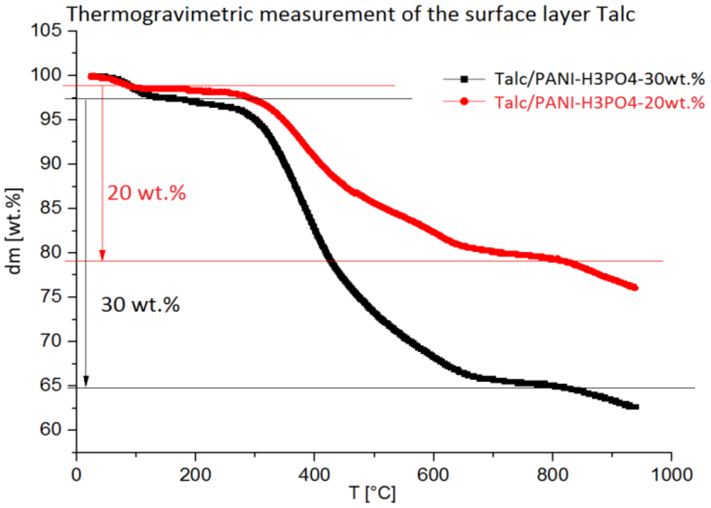


Figure 2: Thermogravimetric measurement of the surface layer talc

The results presented in the dissertation thesis are selected on the basis of this key. These are samples of pigments and coatings that have the best results from their chapters. The newly synthesized pigments were basic characterization of their properties. Table 1 shows silicate-treated pigments by a layer of primarily conductive salt. The selected silicates were calcined kaolin and talc. Surface treatment was carried out with polyaniline phosphate = PANI-P and polyaniline benzoate = B1.

Table 1: Physico-mechanical properties of pigment powders

Pigment	Density	Oil absor.	CPVC	Corr. lost	Extraction		pH	Conductiv.
	ρ±0.002	OA		$c_{cor.loss}$	Mw,c	Mw,h	pH_7	X_7
	[g/cm^3]	[g/100g]	[-]	[g/m^2]	[%]		±0.01%	[µS/cm]±0.5%
C/PANI-P10	2.482	68.8	35	22	3.24	3.45	2.07	11440
T/PANI-P10	2.428	56.6	40	13	3.69	3.88	2.95	8930
C/PANI-B1-20	2.325	102.6	28	10	0.96	1.13	2.29	5050
C/PANI-B1-30	2.257	116.5	26	14	1.41	1.81	2.10	8300
M/PANI-B1-20	2.336	75.2	35	8	1.06	1.69	2.57	6790
Pb_3O_4	8.790	5.00	70	1	0.07	0.05	7.33	17
$ZnCrO_4$	3.862	14.00	63	18	1.20	0.75	6.82	383

The powders were synthesized in order to replace toxic and non-organic pigments such as red lead and zinc chromate. The density of conductive polymers was always about 2.2 ± 0.2 g/cm^3. Another parameter was the consumption of linseed oil. It was high because they were porous particles of conductive polymers which have the ability to adsorb linseed oil on its surface. Red lead and zinc chromate do not have the ability of these pigments. The critical volume concentration of the pigment (CPVC) was determined from the density and oil absorption values. The surface treatment of the conductive polymer salts reduced this CPVC from 26 to 40 as opposed the CPVC 70 to the comparative pigments. As a result, paint films containing the conductive polymer pigment have the same properties as those of the comparative pigment at lower volumes of the pigment. This would help lower the final product. Parameters that directly affect the corrosive efficacy of films were corrosion-loss values determined on steel panels that have been immersed in 10% aqueous pigment suspensions. Also, the pH and conductivity values were measured at the same time. There were acidic substances, a condition for successful doping, pH around 2.5 ± 0.5. The conductivity value was different, since the variable was the amount of conductive polymer contained in the test system. The highest conductivity is PANI-P. Doping with benzoic acid gave lower conductivity values because it is a weaker acid eg C / PANI-B1-20 X7 = 5050 µS/cm. The amount of corrosion loss determined how much material would be lost if the pigments were to be washed out of water-extractable substances. The limit of $c_{cor.loss}$ was 15 g/m^2. At the boundary of the extracted substances should not exceed $M_{w,c}$ and $M_{w,h}$ 2%, the ideal state was 1%.

Table 2: Characteristics and corrosive effects on the coating film and steel substrate in a neutral salt mist atmosphere

Paint	PVC	Blisteing		Corrosion		Adh.	pH	Cond.	Cor. loss
		in area	in cut	in area	in cut		pH_7	X_7	$X_{cor.loss}$
	[%]	ASTM [dg]		[%]	[mm]	[dg]	±0.01%	[µS/cm] ±0.5%	[%]
C/PANI-P10	1	8F	4MD	-	0.3	0	7.63	801	4.82
	3	8F	4M	-	0.2	0	7.67	693	1.91
	5	8F	2F	-	0.1	0	7.39	593	1.42
T/PANI-P10	3	-	8MD	-	0.3	0	7.20	528	8.91
	5	-	8MD	-	0.2	0	7.10	617	0.09
C/PANI-B1-20	5	-	4MD	0.1	0.3	0	7.55	640	1.27
C/PANI-B1-30	1	-	4MD	-	0.2	0	7.67	889	0.19
T/PANI-B1-20	5	-	4F	-	0.2	1	7.24	92	0.09
Pb_3O_4	10	-	4F	-	0.3	0	5.97	92	4.9
$ZnCrO_4$	10	8F	2F	0.01	5.5	0	6.70	45	4.1

The dopant benzoic acid had this limit eg T/PANI-B1-20wt% had $M_{w,c}$ = 1.06% and $M_{w,\ h}$ = 1.69% with the lowest corrosion loss value $c_{cor.loss}$ = 8 g/m^2. From industrially produced comparative pigments, water-soluble substances were eliminated at a minimum.

Table 2 shows selected corrosion results from the atmosphere containing salt electrolyte (ammonium sulfate and sodium chloride). The samples were immediately transferred to a neutral salt mist environment. The results were as follows. The pigment added to the epoxy-ester resin was stabilized, the pH was higher than 7. The conductivity is decreased by one order. There has also been in films for the lowering of corrosion losses compared to powder form and especially over the comparative pigments. The lowest values were T/PANI-P10wt% film at PVC 5% ($X_{cor.loss}$ = 0.09%) and film T/PANI-B1-20wt% with PVC 5% with the same value. The corrosive effects of these two films were the smallest. The blisters in the area were not formed, the steel panel did not corrode, the cross-sectional corrosion was very low, 0.2 mm. The T/PANI-P10wt film coating at PVC 5% did not lose adhesion to the metal substrate degree 0. Film T / PANI-B1-20wt% with PVC 5% had adhesion degree 1. The pH around 7 was very important. This value meant that the coating system was maintained in the neutral region with the highest corrosion protection. Newly prepared talc with phosphate coating films as well as benzoic acid did not form blisters in the film area as opposed to zinc chromate.

Another aim of this thesis was to change the primary dopant for secondary dopant. The primary salt (PANI-N) was first neutralized and then reprotonated again. Diethyl phosphite (PANI-D), benzoic acid and heteropoly acids (PANI-HPA) were chosen as properties as the secondary dopants of the polyaniline chain for their excellent properties. The effectiveness of these compounds has been verified in previous research where they were used as anti-corrosion pigments. Secondary doping improved primarily the value of corrosion loss. Some dopants such as phosphoric acid (PTA) and silicotungstic acid (STA) have a $c_{cor.loss}$ value of up to 2 g/m^2. Water soluble substances were up to 2% in most of the secondary salts tested (Table 3).

The content of water-soluble substances decreased with benzoic acid. Conversely, for diethyl phosphite the values were relatively high $M_{w,c}$ = 5.27% for sample C/PANI-D10 and $M_{w,h}$ = 9.06%. This increase was due to the high acidity of substances that eluted pH$_7$ = 1.84. In neutral states, the pH was confirmed to neutralize pigment powders, pH = 6.32 for T/PANI-N30 pigment. Table 4 shows the results of coating films containing secondary dopants. The neutral salt mist was chosen as one of the test environments. In order for secondary doping to be effective, the results of corrosion have to be milder than in the neutralized form of PANI-N. $X_{cor.loss}$ values were highest at C/PANI-N30 = 70.7%. Secondary doping decreased as with C/PANI-D10 by PVC 3% $X_{cor.loss}$ = 10.0%, C/PANI-D30 $X_{cor.loss}$ = 0.8%. Metal protection was higher with increased weight percentages of diethyl phosphite dopant. This contention was supported by the results of the corrosion test the higher percent by weight blisters do not form a section with a frequency from 6MD to 6M.

Table 3: Physico-mechanical properties of pigment powders with secondary doping

Pigment	Density	Oil absor.	CPVC	Corr. lost	Extraction		pH	Conductiv.
	ρ±0.002	OA		$c_{cor.loss}$	Mw,c	Mw,h	pH$_7$	X$_7$
	[g/cm^3]	[g/100g]	[-]	[g/m^2]	[%]		±0.01%	[µS/cm]±0.5%
C/PANI-N30	2.109	61.8	42	12.3	1.69	1.69	5.54	4700
T/PANI-N30	2.044	83.9	35	8.1	1.85	2.47	6.32	4010
C/PANI-D10	2.302	71.2	36	23.2	5.27	9.06	1.84	20200
C/PANI-D30	2.009	51.4	47	9.1	1.68	2.06	2.31	3600
T/PANI-D20	2.416	83.8	36	7.5	3.05	3.09	3.79	7090
C/PANI-B2-30	2.028	89.2	34	11.2	0.31	0.34	3.82	679
T/PANI-B2-20	2.234	79.0	35	9.8	0.49	0.63	5.28	1240
C/PANI-STA-10/1:1	2.553	63.1	37	1.5	1.41	1.32	2.71	1736
C/PANI-PTA-20/1:1	2.776	64.7	34	2.0	1.51	1.60	2.68	1820
C/PANI-PTA-10/2:1	2.713	55.6	38	2.3	1.61	1.75	3.68	2280

Also, the value of corrosion in cut decreased from 0.2 mm to 0.1 mm. It follows that the ideal amount of diethyl phosphite is 30wt% when X$_7$ is 453µS/cm. Diethyl phosphite molecule of phosphorus in their structure increased the adhesion to the metal film formed as the complex compounds containing phosphates. Secondary diethyl phosphite dopant was not bound to the PANI-chain by a solid covalent bond (as the primary PANI-P dopant) but by hydrogen bonds (Figure 3). This weak bond but can easily be broken, therefore, the values of extracted substances in pigments containing diethyl phosphite are higher than, for example, in heteropoly acids. If there is a combination of diethyl phosphite with talc, the size of blisters was large sectional 4MD as well as corrosion of cut 0.4 mm.

The blisters were smaller for pigment mixtures containing heteropoly acids than for diethyl phosphite, C/PANI-STA10/1:1 PVC 3% 6M, C/PANI-STA20/1:1 PVC 3% 8M. The steel panels did not corrode in the area, the corrosion in the cut was minimal up to 0.2 mm. Corrosion losses were also low in $X_{cor.loss}$ to 1.3%. Organic coatings containing STA and PTA were one of the most resistant coatings that resisted chloride and ammonium sulphate and sodium chloride. The last doping was benzoic acid which formed blisters similar to heteropoly acids, namely 8M for T/PANI-B2-20 at PVC of 3% with a corrosion value of 0.4 mm. This value was reduced when the talcum was altered by 0.3 mm. The pH system value which was the best for corrosion protection it is possible to read from Table 4 at the same time. Although they were powders of an acidic nature, they were stabilized upon application to the epoxy-ester resin. Substances of acidic nature ceased to be excreted from the pigment. They could start corrosion. The ideal pH of the system on the 7th day of the measurement was the value above 7.3, which is the passivation area of the steel.

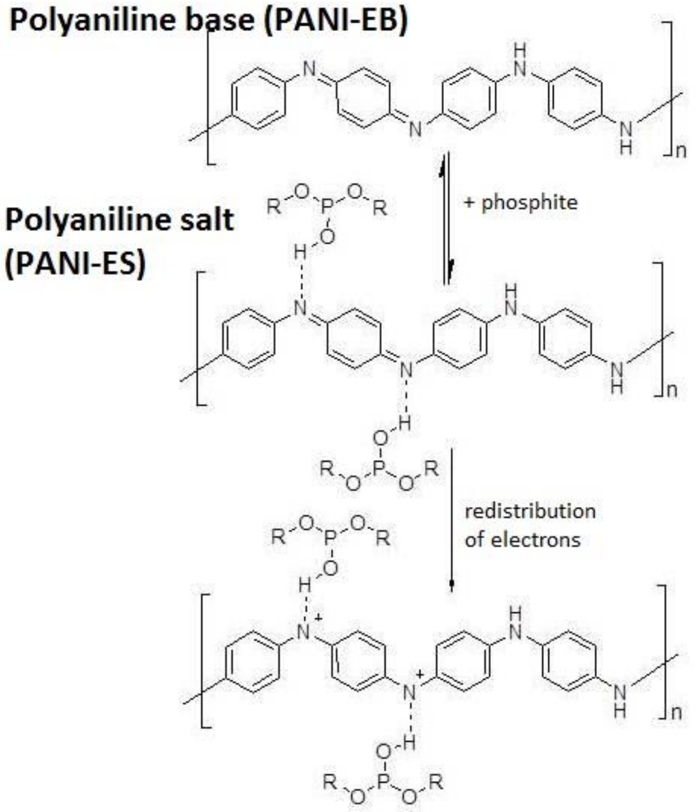


Figure 3: Bond of diethyl phosphite in polyaniline chain

Table 4: Characteristics and corrosive effects on the coating film and steel substrate in a neutral salt mist atmosphere

Paint	PVC	Blistering		Corrosion		Adh.	pH	Cond.	Cor. loss
		in area	in cut	in area	in cut		pH_7	X_7	$X_{cor.loss}$
	[%]	ASTM [dg]		[%]	[mm]	[dg]	±0.01%	[µS/cm] ±0.5%	[%]
C/PANI-N30	3	-	4D	50	0.4	2	7.56	677	70.7
T/PANI-N30	3	8F	6D	1	0.6	2	7.33	375	10.0
C/PANI-D10	1	-	6MD	-	0.2	0	7.63	774	6.5
C/PANI-D30	1	-	6M	-	0.1	0	7.86	453	0.8
T/PANI-D20	1	-	4MD	0.01	0.4	0	7.33	469	1.0
C/PANI-B2-30	1	-	6MD	-	0.3	0	7.71	776	3.3
T/PANI-B2-20	3	-	8M	-	0.4	0	7.33	325	3.5
C/PANI-STA-10/1:1	3	8M	6M	-	0.1	0	7.61	840	1.3
C/PANI-PTA-20/1:1	3	-	8M	-	0.2	0	7.49	612	1.2
C/PANI-PTA-10/2:1	3	-	6F	0.03	0.2	1	7.52	499	1.1

The protective mechanism of conductive polymer was activated with the insertion of a negative potential into the system (electron exchange process in the electrolyte environment). The principle of basic protection is the same and does not matter the doping component. First, emeraldine is transformed into the leucoemeraldine form of polyaniline (Figure 4). It is only at a later stage that the dopant component starts to act, such as benzoic acid, which makes the iron ions insoluble salts that inhibit the corrosion process.

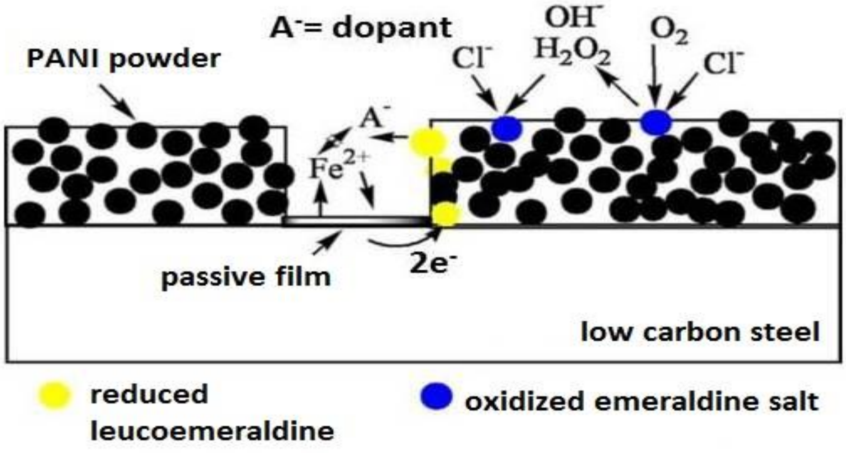


Figure 4: Passivation process of organic coating with polyaniline pigment

Composite materials containing ferrites and salts of conductive polymers functioned similarly. These composites have similar protective mechanism where also consisted of Insoluble salts of soaps-base that neutralized acidic substances from the corrosive environment. Based on the research presented in the thesis, pigments of specularite and hematite particles with lamellar and isometric particle shape were used as carriers for salts of conductive polymers. Trihydrogenphosphoric acid for PANI and PPDA was selected as the primary dopant. The lamellar type of specularite showed good results with PANI-P and isometric hematite with PPDA-P. The highest anticorrosion protection has been achieved with ST/Zn-Fe(S)/PANI-P coating (Figure 5). There were no blisters on the film, type of the blisters were 4MD in the test cut. The lamellar type of particles prevented penetration of the corrosion environment into the steel panel. So, the surface of the panel did not corrode and the corrosion in the cut was only 0.3 mm. The degree of adhesion was low, dg. 0. Only benzoic acid with an inhibitory effect was chosen as secondary dopant. All of the paint films shown here showed better results than the neutralized form of PANI-N. Another technological process is beneficial. The films were subjected to electrolyte mixtures and 480 hours of neutral salt fog for 720 hours. New pigments have been able to alleviate corrosion. Compared with toxic pigments red lead and zinc chromate, it was an effective substitute these substances.

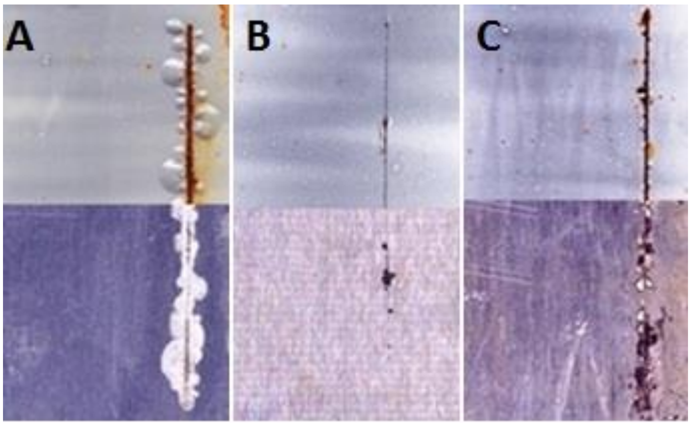


Figure 5: Example of corrosive effects on the surface of the paint film and in the steel panel after 1200 exposure in mixed electrolyte and neutral mist: A - C/PANI-PTA20/1:1 PVC 3%; B - C/PANI-B2-30 PVC 1%; C - ST/Zn-Fe(S)/PANI-10 PVC 10%

Conclusion

There were presented the most interested results of dissertation thesis which examining the anticorrosion properties of surface-treated silicates demonstrate that the anticorrosion efficiency of silicates can be enhanced by application by surface layers or treatments. Calcined clay and talc were found to be good silicate representatives for surface treatment in paints, where synergistic effects take place. Paints containing silica pigment whose surface had been oxopolymeritation modified with salt of conductive polymers or ferro-spinels layer were studied. The paint films exhibited higher relative surface hardness and better physico-mechanical properties. The anticorrosive efficiency improvement was associated with value of corrosion loss in aqueous media for pigment or the paint film. The samples were resistant to a neutral salt mist environment for 1200 hours of the test, so the paints are categorised as C5-I according to ISO 12 500 (medium or high degree-resistance to enhanced salinity environment). Anticorrosion efficiency increase compared to the non-pigmented epoxy-ester resin and toxic pigments was attained. The low volume concentration of the conductive polymer was sufficient for the highest corrosion protection. Thus, the variable component of the system was the percentage by weight in which the conductive salt was present. The test amount was 10wt%, 20wt% and 30wt%. For each type of dopant, it was preferred to use different weight percentages. Diethyl phosphite was most effective at 30 wt%, benzoic acid at 20 wt% and heteropoly acid at 10 and 20 wt%. These substances have been chosen as secondary dopants for their exceptional properties in the coating film. Primary doping of conductive polymers is known and provides good results. Values of secondary doping results show that they are often better.

Ferro-spinels differing in the primary particle shapes were synthesized and added as pigments to a paint formula, and the paints containing them were investigated with respect to their anticorrosive properties. Every property of a pigmented paint is at its optimum at a specific pigment concentration; this applies particularly to the physical and anticorrosive properties. So it is possible to identify a pigment concentration at which a specific property is at its best. It is convenient that such pigment concentrations are usually not very high. The spinels fall in the class of chemically acting pigments that help slow down corrosion processes on the metal surface beneath the paint film through their alkaline nature and by neutralization of the carboxy groups. The lamellar shape of the pigment particles enhances paint film adhesion to the substrate and its cohesion and reduces the formation of blisters on the paint film surface (and around the test cut). The pigmented paint films exhibited very good physico-mechanical properties, commensurable with those of the epoxy-ester resin alone. The best anti-corrosive efficiency in the accelerated corrosion test in the atmosphere with neutral salt was found for the paint containing lamellar or isometric shape particles.

Paints with the all secondary dopants or ferro-pigments tested are also advantageous in that they protect the metal against corrosion. And they are environmentally friendly and might be favorably used to replace the toxic red lead or chromium (VI)-based pigments.

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