Applying of non-toxic oxide alloys and hybrid polianiline compounds as anticorrosive pigments in organic epoxy coatings

W Szymański, A Halama[1] and J Madaliński
Electrotechnical Institute Division of Electrotechnology and Materials Science M. Sklodowskiej-Curie 55/61 50-369 Wroclaw, POLAND

E-mail: halama@iel.wroc.pl

Abstract. The objective of this work was to study inorganic oxide pigments as well as polyaniline heptamolybdes anticorrosive efficiency in epoxy coating. Antycorrosion resistance of modified coatings was examined by accelerated corrosion test in comparison to coatings of the suitable commercial epoxy paint. The carried out investigations shoved much bigrs anticorrosion performance of coatings modified with elaborated, new pigments.

1. Introduction

Growing demands of health and environment protection, drastically restricted application in organic coatings, highly effective but toxic chromate and lead active pigments. Applying of harmful for water organism zinc phosphate was also strongly limited. Thus, in the world industry of an anticorrosive paints raised demand of new, non-toxic and efficient active pigments. For the last twenty years many research attempts were devoted to use of conducting polymers (CP) as anticorrosion pigment in the organic coatings. Among them, thanks to good stability, low cost, low toxicity and good electrochemical properties, polyaniline(PANI) gained the highest importance. However, foregoing research works entirely applied basic form of PANI (emeraldine EB) or its salts with mineral acids (emeraldine ES). Presumably, because of applied toilsome method of their producing, the possibility of appliance of hybrid organic-inorganic PANI compounds hasn't been studied yet. The objective of this work was to study in organic oxide pigment and hybrid PANI compounds anticorrosion action in epoxy coating.

2. Inorganic anticorrosive pigments

Ten, active inorganic pigments with different stoichiometric composition have been obtained by high temperature synthesis. As a result of thermal decomposition of selected initial reagents, such as: zinc phosphate, ammonium heptamolybdate, boric acid, calcium and sodium carbonates, raised oxides entering the composition of well know anticorrosion pigments and possessing the ability to form glassy phase by their alloys.
Molar portions of particular oxides in received alloys are presented in table 1.

[1] Agnieszka Halama PhD

Table 1. Molar portions of oxides in received alloys.

Pigment	1	2	3	4	5	6	7	8	9	10
					[% mol]					
ZnO	22.68	22.22	21.84	21.48	20.97	22.84	22.97	23.11	23.26	23.44
P_2O_5	7.56	7.41	7.28	7.16	6.99	7.61	7.66	7.70	7.75	7.81
MoO_3	12.49	10.92	9.67	8.45	6.69	12.57	12.64	12.72	12.80	12.90
CaO	16.91	19.92	22.34	24.68	28.04	18.44	20.02	21.58	23.21	24.84
B_2O_3	25.47	24.95	24.53	24.13	23.55	25.65	25.79	25.95	26.12	26.32
Na_2O	14.89	14.58	14.34	14.10	13.76	12.90	10.92	8.93	6.86	4.70

After theirs grinding to grain diameter <10 µm, an appropriate solubility of obtained pigments was proved in agreement to suitable standard. The coefficients of inhibitive efficiency of particular pigments were determined by potentiodynamic and impedance spectroscopy methods in 3.5 mas % NaCl solution, and are presented in figure 1.

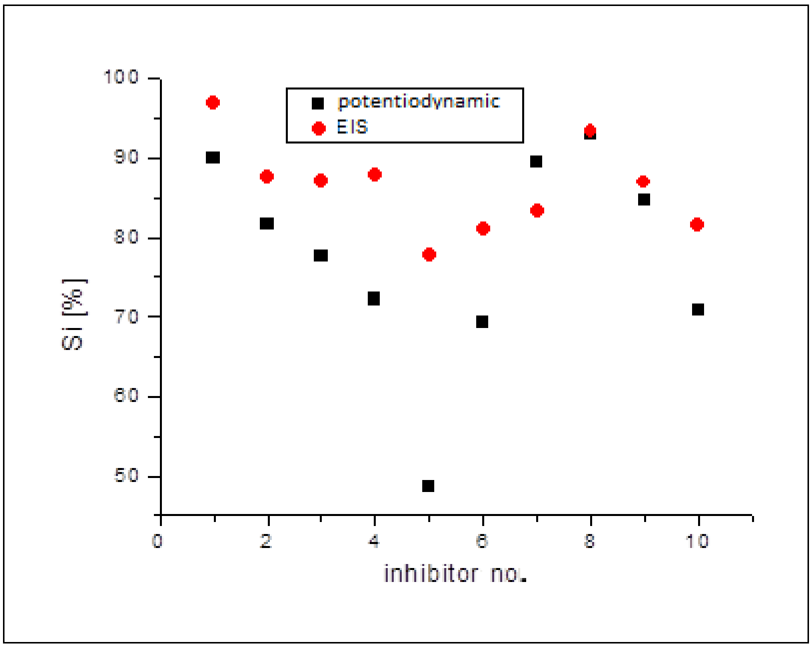

Figure 1. The coefficients of anticorrosive efficiency of inorganic pigments.

The highest efficiency was showed by pigments no. 1 and no. 8 according to table 1. In amount of 1 mas % grinded pigments were emulgated in a resin of epoxy paint not containing any other additions. The test plates covered with modified coatings were tested in wet SO_2 atmosphere in comparison to coating of suitable commercial epoxy paint pigmented with zinc phosphate (0 plate). The plates after 20 daily cycles of testing were presented in figure 2.

The best anticorrosion resistance showed coating modified with pigments no. 1, 4, 6 and 10, which remain almost unchanged after testing, whereas reference coating showed scratch corrosion in the range of 2 mm and about 3% of a roasted surface.

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3. Polyaniline pigments

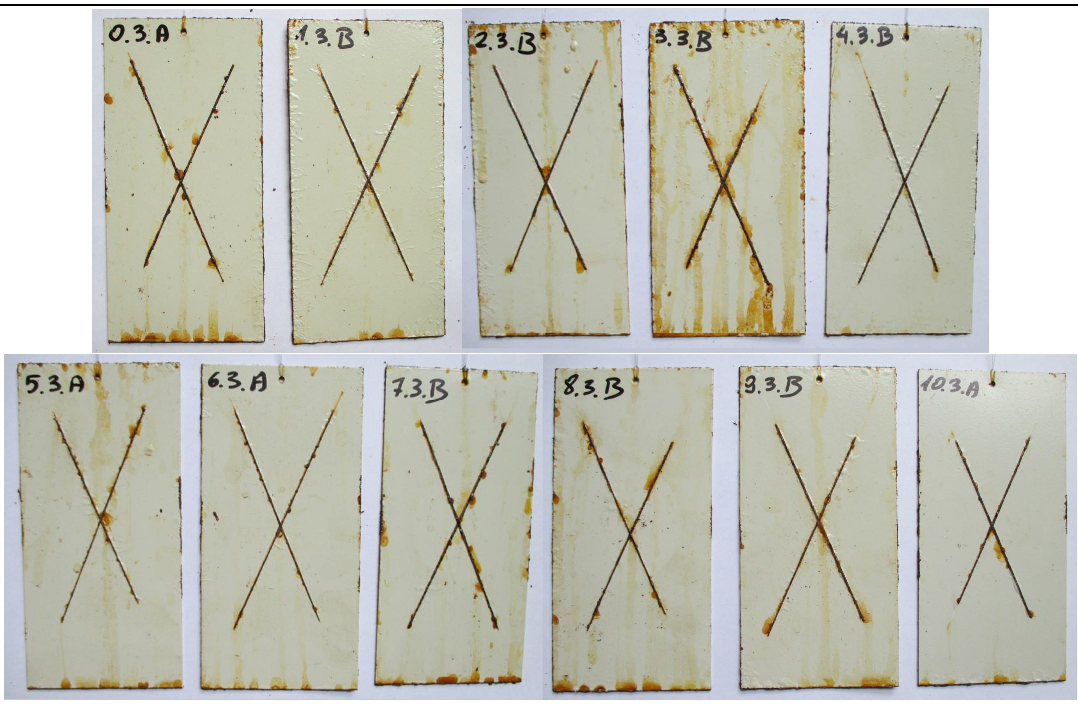

Figure 2. Test plates after stressing in wet SO_2 corrosion chamber.

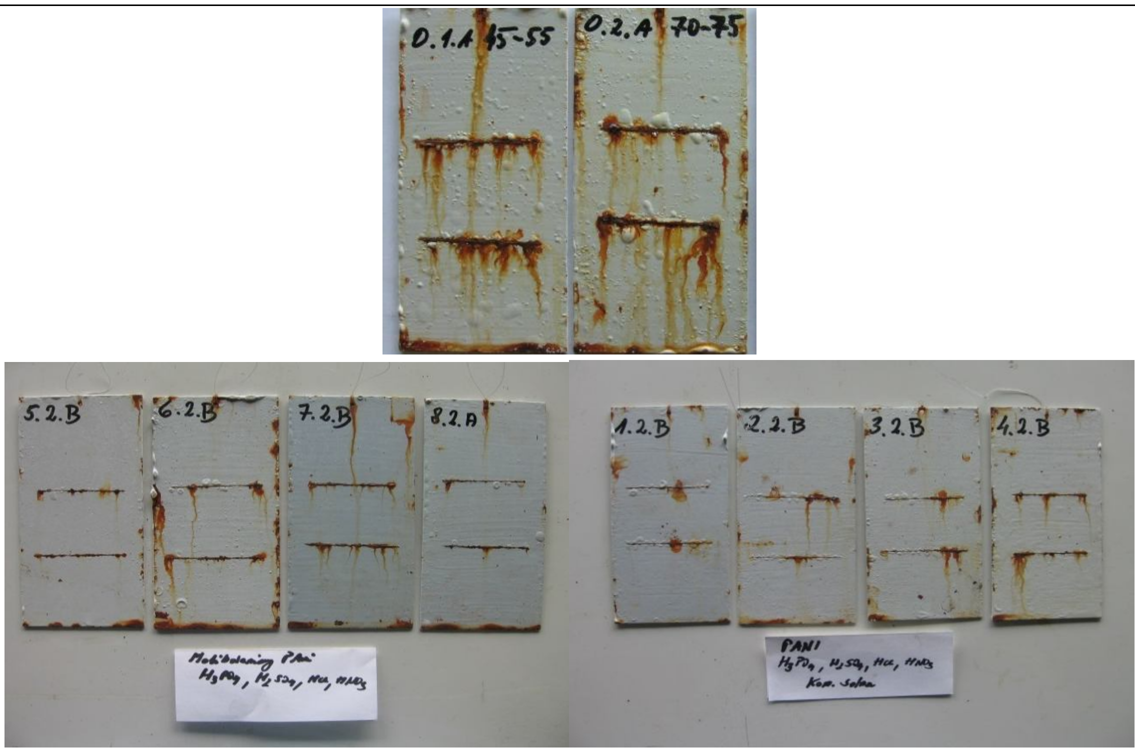

Figure 3. Test plates after 1800 h of stressing in salt spray chamber.

The polyaniline heptamolybdates as anticorrosive pigments. Applying a new simple method of synthesis, four forms of PANI heptamolybdates were received in solutions of phosphoric, sulphuric, hydrochloric and nitric acids. Depending on used acid, an obtained compounds showed different FTIR spectra and characteristics of thermal analysis curves. These compounds as well as PANI salts obtained in solutions of the same acids, were applied in an epoxy resin with concentration of 0.5 mas %.

The modified paints were deposited on the test plates and subjected to accelerated corrosion testing in neutral salt spray together with reference coating of appropriate commercial epoxy paint.

The plates after 1800 h of testing are presented in figure 3.

The reference coatings of commercial epoxy paint showed distinct blistering and very extensive scratch corrosion in the range 10-15 mm. The coating which was modified with PANI salts showed scratch corrosion in the range of 3-4 mm and much lower level of blistering, whereas the coatings containing PANI heptamolybdates received in solution of H3PO4 and HNO3 acids (plates 5.2.B and 8.2.A) except of scratch roasting, were not distinctly damaged after testing.

4. Conclusions

The preliminary estimated cost of producing and relatively low level of application in the coating with satisfactory anticorrosion performance makes the most effective from tested pigments, competitive to commonly and currently used zinc phosphate. The little zinc concentration in inorganic pigments, together with relative, low level of their concentration in organic coating, cause their practical applying quite allowable. The use of presented pigments in practice, may contribute to bridge the technological gap ensuing in the world industry of anticorrosive paints, after limitation in using pigments harmful for health and an environment.

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