ENA STUDY OF POSSIBLE IMPROVEMENT IN FORMULATION DESIGN PRACTICES FOR OPTIMIZED PERFORMANCE OF Zn AND Al PIGMENTED EPOXY COATINGS

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Abstract

The effect of the ratio of the pigment volume concentration (PVC) to the critical pigment concentration (CPVC) belongs to well-known formulation design practices for optimized performance of pigmented organic coatings. The influence of this ratio in Zn an Al pigmented epoxy coatings on delamination kinetics of underlying steel has been investigated by electrochemical noise analysis (ENA) during 168 hrs immersion tests in 0.05 M NaCl. Two different Zn and Al pigmented epoxy coatings were prepared with different PVC/CPVC values but with the same vol. % Zn:Al ratio as well as with the same binder and hardener types applied. ENA was used to provide information about possible effect of PVC/CPVC values on delaminated corroding area time development in tested coating/steel systems. It has been concluded that in these systems it is recommended the use of certain low PVC/CVPC value in order to obtain high resistance to possible coating delamination from the metallic surface.

Keywords: Electrochemical noise, pigmented epoxy coatings, delamination

1. INTRODUCTION

As recent findings show [1] the composition as well as the structure of Zn and Al pigmented epoxy coatings should be considered as possible factors affecting delamination kinetics at the metal surface beneath the coating. At the same time correlation found between electrochemical noise (EN) measurements of delamination and results of physico-mechanical tests suggests that pigment inhomogeneity and localized voids formation can be one of possible reasons for increased tendency to delamination observed for some coating systems. In this case the question arises if by proper manipulations of the parameter whose variation have a significant effect on voids formation possible improvement in formulation of newly designed coating systems can be obtained. As the ratio of the pigment volume concentration (PVC) to the critical pigment concentration (CPVC), denoted by Λ is in relation to voids formation [2,3], an attempt was made to answer this question. For this purpose two different Zn and Al pigmented epoxy coating systems with different Λ were applied on steel substrate specimens. Electrochemical noise analyses (ENA) was then used to provide information about possible delaminated corroding area time development for both tested systems during 168 hrs immersion tests in 0.05 M NaCl. Apart of EN measurements more advanced microscopic methods were used for metallographic analysis of tested coatings after immersion tests. EDX mapping and structure (SEM-SE image) of cross-sections were chosen for this purpose. The main aim of this study was to improve formulation design practices for optimized performance of Zn and Al pigmented epoxy coatings.

2. EXPERIMENTAL

2.1. Materials

Two types of pigmented epoxy coatings were prepared using Zn dust 4P16 and Al paste Aluminium Stapa 2NL with the same binder and hardener combination but with different volumes of all pigments and polymer matrix components (**Tables 1 - 4**).

In order to avoid the particles settlement and for better dispersion ion-exchangeable inorganic pigment Syloid 244 based on synthetic amorphous silica was used in both types of tested coatings. Concerning preparation both types of coatings were prepared by mixing of Zn dust 4P16, Al paste Aluminium Stapa 2NL and Syloid 244. For dissolution of this mixture in given type of binder dissolver Netzsch and cooling water conditions were used.

Table 1 Characteristics of tested ZRP with Al additions

sample	OPVC (vol%)	Zn:Al ratio (vol%)	Filler	Binder	Hardener
AKAl 113	45	88:12	Alum.Stapa 2NL	Epikote 1001	Epicure 3115
AKAl 115	55	88:12	Alum.Stapa 2NL	Epikote 1001	Epicure 3115

Table 2 Characteristics of AKAl 113 in relation to volumes of components having effect on Λ value

component	V different pigment components (cm^3)	V different polymer matrix components (cm^3)
Zn4P16	38.25	-
Alum. Stapa 2NL	5.22	-
Syloid 244	1.53	-
Epikote 1001-X75	-	39.30
Epicure 3115-X75	-	15.70

Table 3 Characteristics of AKAl 115 in relation to volumes of components having effect on Λ value

component	V different pigment components (cm^3)	V different polymer matrix components (cm^3)
Zn4P16	46.75	-
Alum. Stapa 2NL	6.38	-
Syloid 244	1.87	-
Epikote 1001-X75	-	32.16
Epicure 3115-X75	-	12.84

Table 4 Characteristics of tested coating systems in relation to Λ values (calculated for Zn particles in tested coating systems)

sample	PVC	Λ
AKAl 113	0.4102	0.6133
AKAl 115	0.5095	0.7618

Both tested coatings were applied by spreader bar to steel C4Q panels previously polished and degreased.

2.2. Methods

Immersion tests using ENA for tested coatings on steel substrate specimens were performed with use of the same experimental set-up as described earlier [4]. The potential and current noise (ENP and ENC) values (for given data set measured for given immersion time) were collected for measurement periods of 600 s with sampling rate of 20 Hz (12 000 points for period) using GAMRY ESA 410 software. Similarity of MEM Noise Impedance Spectrum characteristics with simulated electrochemical impedance spectrum for which impedance analog for coated steel is accepted [5] was used to provide information about disbonded region of the coating/steel interface in relation to double-layer capacitance C_d values as well as delaminated corroding area A_d values changing with immersion time t. For this purpose A_d (t) can be estimated from C_d values measured at given time t (μF) by means of empirical equation $A_d = C_d (t)/20$ if 20 is the typical value of the bare steel double-layer capacitance adopted to estimate the underlying metallic active surface (μF.cm^{-2}) [6].

3. RESULTS AND DISCUSSIONS

Nine measurements were performed on type specimen AKAI113 as well as on type specimen AKAI115 during uninterrupted immersion tests performed on steel panels coated by tested coating systems. **Table 5** lists the parameters obtained by mentioned approach to analysis of 9 sets of ENA data for AKAI113 and AKAI115. These parameters included instantaneous C_d and A_d values estimated for given immersion time. Due to very dynamic changes of cathodic nature of steel surface with immersion time, the average delaminating area ($A_{d,av}$) time development in 168 hrs exposure of tested coating systems to 0.05 M NaCl was chosen for evaluation of delamination kinetics of underlying steel. $A_{d,av}$ development with immersion time in immersion tests using ENA and performed on tested steel/paint systems can be seen in **Figure 1**.

Table 5 Instantaneous C_d and A_d values for AKAI113 and AKAI115 after different immersion time

Immersion time t (hrs)	AKAI113		AKAI115	
	C_d (F)	A_d (cm^2)	C_d (F)	A_d (cm^2)
24	$5.91 \cdot 10^{-10}$	$2.96 \cdot 10^{-5}$	$6.52 \cdot 10^{-9}$	$3.26 \cdot 10^{-4}$
29	$8.95 \cdot 10^{-10}$	$4.48 \cdot 10^{-5}$	$5.54 \cdot 10^{-9}$	$2.77 \cdot 10^{-4}$
48	$6.49 \cdot 10^{-10}$	$3.25 \cdot 10^{-5}$	$1.41 \cdot 10^{-8}$	$1.41 \cdot 10^{-4}$
53	$1.63 \cdot 10^{-8}$	$8.16 \cdot 10^{-4}$	$7.54 \cdot 10^{-9}$	$3.77 \cdot 10^{-4}$
72	$5.40 \cdot 10^{-10}$	$2.70 \cdot 10^{-5}$	$3.25 \cdot 10^{-8}$	$1.62 \cdot 10^{-3}$
77	$1.06 \cdot 10^{-8}$	$5.31 \cdot 10^{-4}$	$2.67 \cdot 10^{-6}$	$1.34 \cdot 10^{-1}$
96	$5.48 \cdot 10^{-9}$	$2.74 \cdot 10^{-4}$	$3.27 \cdot 10^{-6}$	$1.64 \cdot 10^{-1}$
101	$9.05 \cdot 10^{-9}$	$4.52 \cdot 10^{-4}$	$1.11 \cdot 10^{-7}$	$5.53 \cdot 10^{-3}$
168	$2.27 \cdot 10^{-9}$	$1.14 \cdot 10^{-4}$	$8.93 \cdot 10^{-8}$	$4.46 \cdot 10^{-3}$

From **Table 5** as well as from **Figure 1** can be seen the C_d value can be used as a measure of the area over which coating had been disbonded. It should be noticed this parameter can be well measured only when some minimum degree of deterioration of coating is reached. For AKAI113 it was found this value can be very low ($A_{d,av}$ = 3.10^{-5} cm^2 after 24 hrs of exposure to 0.05 M NaCl) when comparing with AKAI115 (see **Table 5**). This finding is not surprising because value of Λ for AKAI113 is so low it can be considered to be even lower than the random densest packing value for mono-sized spheres which is 0.64 [2,7]. In spite of some modification of this value for a distribution [3] of pigment sizes, with a possible absorbed layer of polymer [8] (considered as may be larger or smaller than 0.64) for reasons of simplicity value 0.64 can be used as boundary condition for possible voids formation in pigmented organic coatings. If this suggestion is accepted, the structure of AKAI113 is in the state on no voids formation so that only O_2 permeability of this coating can be considered as affecting kinetics of delamination by possible formation of NaOH in disbonded region. In fact water and O_2 permeability can be supposed to be also decreased but only just to degree allowing the rate of dissolution of Zn and Al particles was able to modify friendly the interfacial environment beneath the coating.

In comparison with AKAI113 coating system AKAI115 seems not to be able to exhibit the same effect. In opposite to AKAI113 some localized voids formation with accumulation of Cl^- ions in it was observed for AKAI115 when metallographic analysis has been performed after the test (see **Figures 2 and 3**).

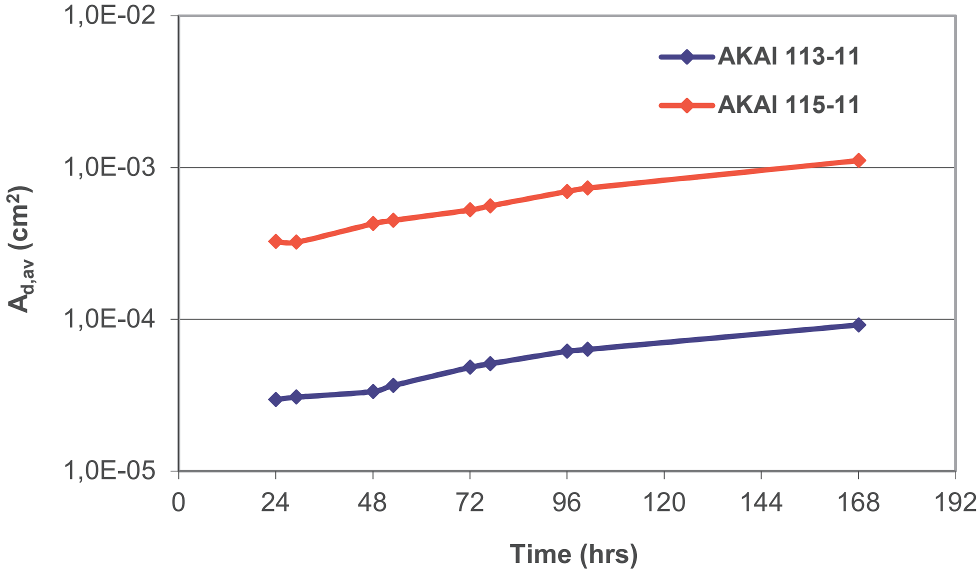

Figure 1 Time development of $A_{d,av}$ values in 168 hrs exposure

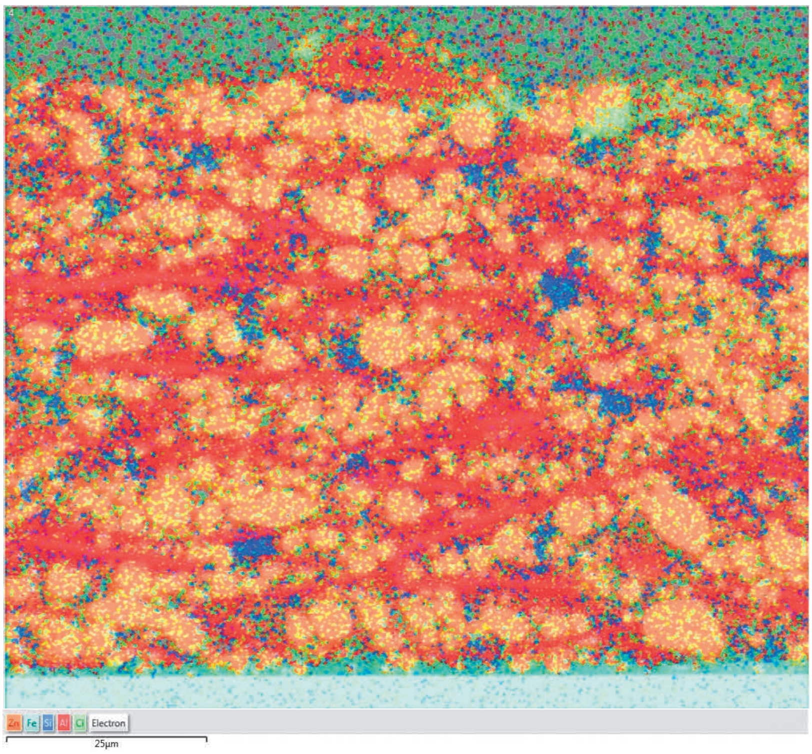

Figure 2 EDX mapping and structure (SEM-SE image) of cross-section for AKAI113 after 168 hrs exposure in 0.05 M NaCl

For this type of coating formulated with somewhat higher Λ value (allowing some voids formation) the formation of new paths in the coating for Cl^- ions penetration into the coating is probably easier. By this way not only water and O_2 permeability but also Cl^- permeability of this coating should be considered as affecting delamination kinetics of underlying steel. In spite of that still rather low Λ value for AKAI115 seems to be able to ensure some degree of competition between disbonding conditions and conditions for formation of corrosion products with passivating effect at the metallic surface beneath the coating.

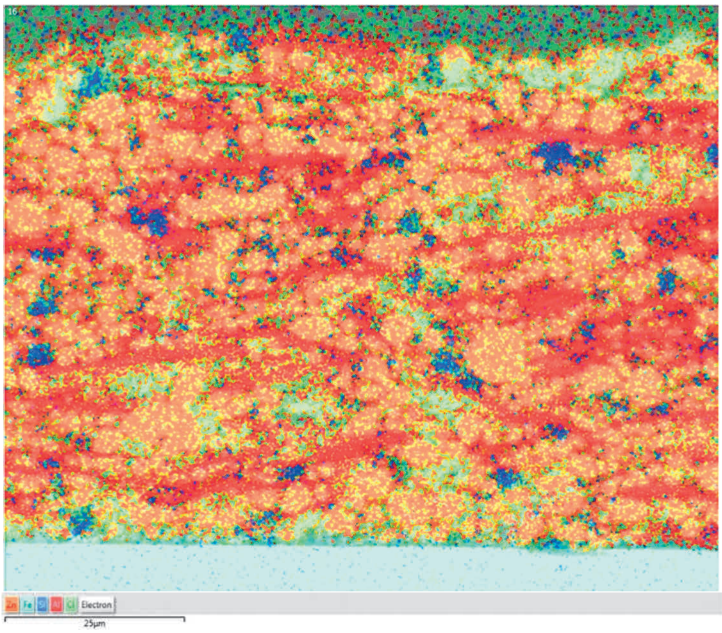

Figure 3 EDX mapping and structure (SEM-SE image) of cross-section for AKAl115 after 168 hrs exposure in 0.05 M NaCl

At the same time reasonable correlation between increasing of Λ and decreasing of barrier properties was found when MEM Noise Impedance Spectrum characteristics of tested coatings (MEM curves) estimated in the end of test were compared (**Figures 4** and **5**).

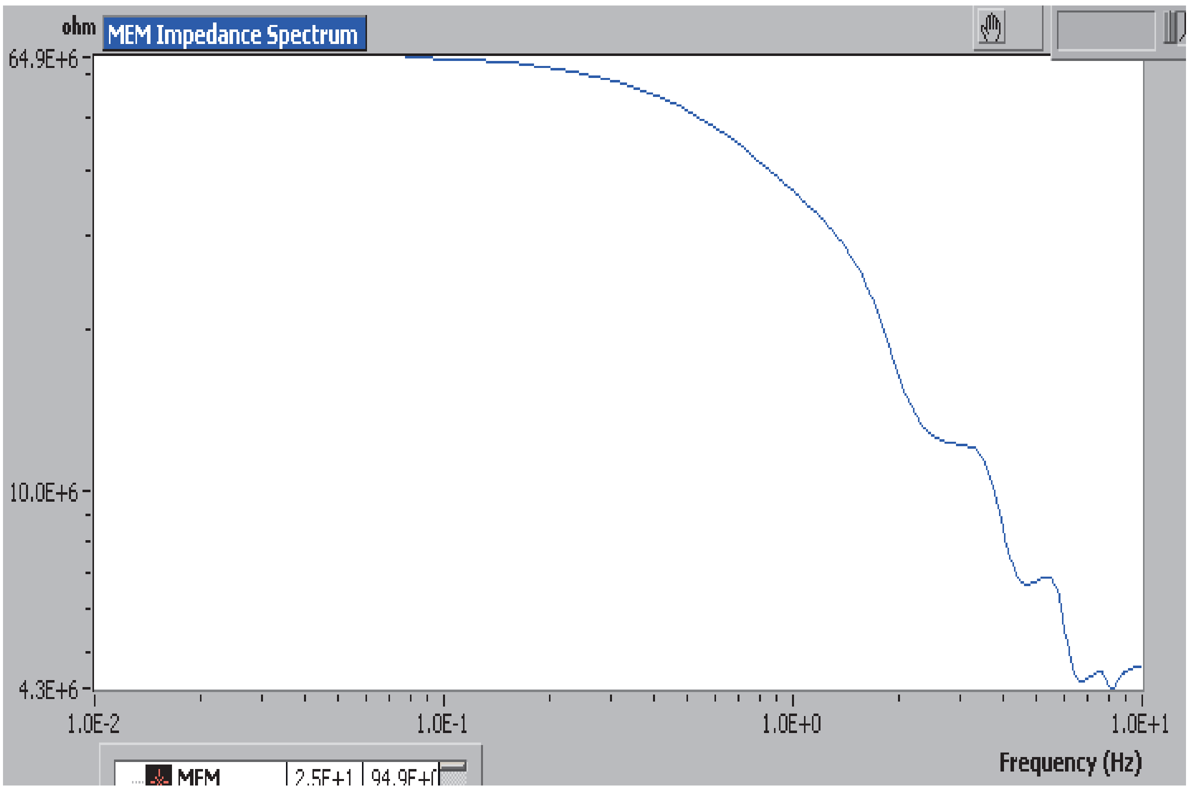

Figure 4 Noise impedance spectrum (MEM curve) for AKAl113 after 168 hrs exposure

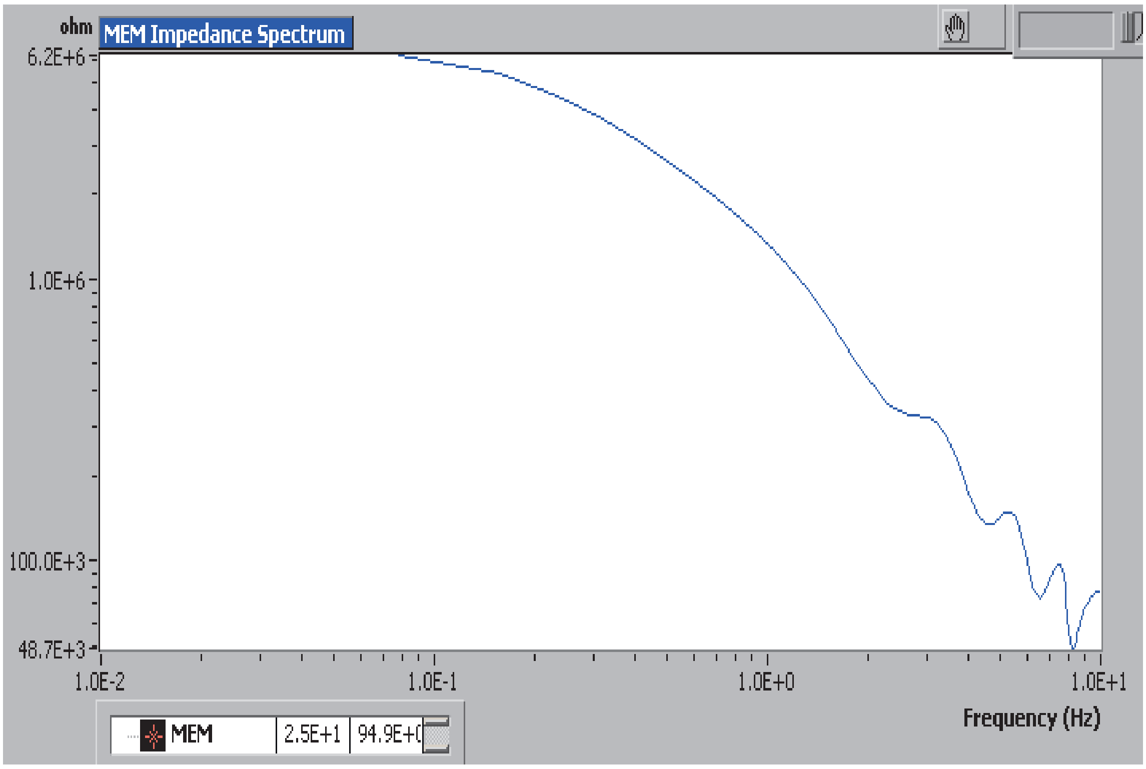

Figure 5 Noise impedance spectrum (MEM curve) for AKAl115 after 168 hrs exposure

4. CONCLUSIONS

The effect of possible balancing the PVC/CPVC ratio in Zn and Al pigmented epoxy coating for optimized performance of this type of coating systems has been investigated with use of ENA. In order to obtain high resistance to possible coating delamination from metallic surface value of PVC/CPVC = 0.61 is recommended for tested coating systems.

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