INTERPRETATION OF ENA DATA FROM ACCELERATED EXPOSURE OF ZN AND MIO PIGMENTED EPOXY COATINGS AS METHOD BASED ON MODELLING OF COATINGS ELECTRICAL PROPERTIES RELATED TO CORROSION OF THE SUBSTRATE

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Abstract

The possible differences in the protective performance of Zn and MIO pigmented epoxy coatings for different times of exposure performed during 533 hrs in 0.05 M NaCl were confirmed by new interpretation of ENA data in combination with single frequency (1 kHz) impedance test results. By this approach changes of resistivity and dielectric constant (identified on tested coating system at different times of exposure) can be related to delamination tendency as well as changing possibilities for new defects formation in tested type of coating for different time of exposure.

Keywords: Modified ZRP, ENA, SIFT, water uptake, interfacial delamination

1. INTRODUCTION

As recent findings show modified Zn pigmented epoxy coatings (with partial substitution of Zn by other type of fillers) when prepared with OPVC = 40 can ensure very low delaminated corroding area A_d values after 168 hrs exposure to 0.05 M NaCl [1]. In this case an estimation of delaminated corroding area A_d at the steel/coating interface can be made based on increase of double layer capacitance C_{dl} data obtained by analysis of noise impedance spectra during exposure. For different types of ZRP modified by combination of Zn dust with aluminium or carbon type fillers different ability of polymer matrix with Zn/Al or Zn/C particles combination for oxygen transport to the coating/steel interface was considered as possible explanation of found differences in A_d. In this case however question arises if for an explanation of found differences in A_d cannot be considered rather differences in water uptake usually tested by single frequency (1 kHz) test (SIFT) providing information concerning the coating capacitance C_c and the coating resistance (pore resistance) R_{po}. It should be remembered for mentioned type of ZRP no swelling (volume and area increase) was observed so that the capacitance should be considered to be proportional to product $\varepsilon.\varepsilon_0$ (ε is the coating dielectric constant, ε_0 is the permittivity constant for vacuum) and can so be used for monitoring of coating dielectric constant ε. On the other hand, for R_{po} values obtained by SIFT Haruyama et. al. [2] suggestions (that the decrease of R_{po} and the increase of C_{dl} with exposure time are due to increase of the delaminated area A_d) can be possible accepted and used for monitoring of coating resistivity ρ if value A_d (« A) is known (A = total specimen area).

In fact, the degree of delaminated area at the metal/coating interface (delamination ratio D = A_d/A) can also be estimated by the break point frequency f_b and minimum frequency f_{min} (the frequency of the phase-angle minimum) used for modelling of EIS spectra by Mansfeld and Tsai [3]. In this case information concerning the decrease of ρ and the increase of D can be obtained by analysis of EIS spectra from high to medium frequency data. In spite of some references indicating good correlation between visually determined A_d and A_d determined by f_b [4,5] procedure for determination of ρ by combination of ENA data (providing information concerning C_{dl} and A_d) with SIFT data (providing information concerning C_c and R_{po}) has not yet been checked from the point of view possible estimation of f_b and f_{min} values without use of EIS. In fact, estimation of these parameters can be interesting because considering Tsai and Mansfeld analysis [6] of f_b and f_{min} (dependent

on A_d and ρ) and f_b/f_{min} (dependent only on A_d) one can perform analysis of the ratio $(f_b-f_{min})/(f_b/f_{min})$ to obtain value of critical D at which this ratio becomes dependent on additional absorption of water in defects formed at the filler/binder interface. By this way critical value of D can be considered as value of D at which deterioration of the filler/binder interface increases the quantity of defects and promotes transport of water into coating with expected good barrier properties.

The main aim of this study was to verify how much this approach can help in study of water uptake and interfacial delamination of Zn and MIO pigmented epoxy coating with OPVC = 40 at longer times of exposure. Apart of electrochemical measurements more advanced microscopic method was used for metallographic analysis of tested coating system after the longest time of exposure (533 hrs) to 0.05 M NaCl. EDX mapping of structure (SEM SE image) of cross-sections were chosen for this purpose. The same analysis was used for non-exposed coating system in order to distinguish possible differences in the structure for exposed and non-exposed tested coating.

2. EXPERIMENTAL

2.1. Material

Tested type of Zn and MIO pigmented epoxy coating was prepared using zinc dust and MIO filler of given commercial quality (see **Table 1**).

Table 1 Characteristic of ZRP modified by different type of fillers

Sample	OPVC (vol %)	Vol% ratio Zn:filler	Filler	Binder	Hardenner
AKMM 104	40	7:3	MioxMicro 30	CHS Epoxy 222	Telalit 160

Zinc dust used for preparation of coating was 4P16 (supplied by UMICORE Zinc Alloys and Chemicals Co.). In combination with Zn dust was used filler MioxMicro 30 (supplied by Kärtner Montan Industrie, Austria). Tested coating was applied by a spreader bar to steel C4Q panel previously polished and degreased. The average thickness of dry film was 55 μm.

2.2. Method

Immersion test using above mentioned special monitoring approach was performed using the same experimental assembly as in 2013 referred to as "Possibilities of ENM to evaluate anti-corrosion performance of new types of zinc roch epoxy paints in relation to ZRP formulations" in the EUROCORR 2013 proceedings, pp. 217. The potential and current noise (ENP and ENC) values for given data set measured at given immersion time in 0.05 M NaCl were collected for measurement periods of 600 s with sampling frequency of 20 Hz (12 000 points per period) using GAMRY ESA 410 software. These data were used to obtain MEM noise impedance spectrum characteristics (MEM curves) providing information about C_{dl} values as well as A_d values changing with immersion time t. For this purpose, $A_d(t)$ can be estimated from C_{dl} values measured at given time t (μF) by means of empirical equation $A_d = C_{dl}(t)/20$ if 20 is the typical value of the bare steel double layer capacitance adapted to estimate the underlying metallic active interface (μF/cm^2) [8]. In addition to it immediately after every EN measurement at given time of exposure single frequency (1 kHz) impedance test with the use of HIOKI LCR HITESTER was performed to estimate values of R_{po} and C_c for the same time of exposure.

3. RESULTS AND DISCUSSION

Four EN measurements together with four single frequency tests were performed on type AKMM 104 specimens in different times of exposure (5, 197, 365 and 533 hrs). As can be seen from (**Figure 1**) MEM

Impedance spectrum is for every of different times of exposure different confirming by this way quite different barrier properties changing with time of exposure.
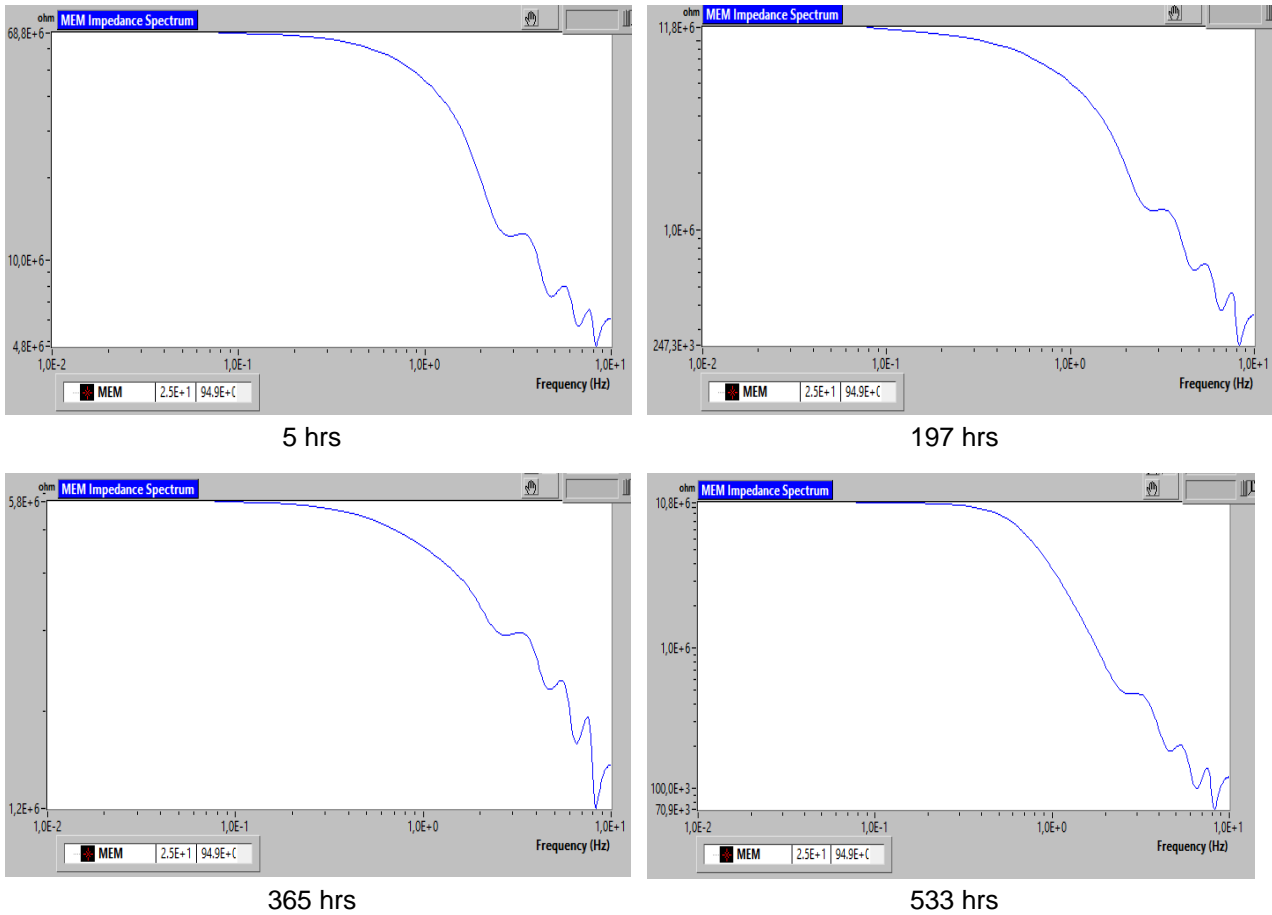

5 hrs

197 hrs

365 hrs

533 hrs

Figure 1 Noise Impedance spectrum (MEM curves) for AKMM 104 at different exposure times

Table 2 lists the parameters including instantaneous C_{dl} and A_d values obtained from MEM curves together with parameters R_{po} and C_c obtained from single frequency tests together with calculated values of ρ and ε.

Table 2 Variations of C_{dl}, A_d, R_{po} and C_c together with calculated values of ρ and ε for tested coating system during 533 hrs exposure in 0.05 M NaCl

Exposure time (hrs)	C_{dl} (F)	A_d (cm²)	R_{po} (Ω)	C_c (F)	ρ (Ω.cm)	ε
5	2.12E-09	1.06E-04	57.65E+06	40.42E-12	1.11E+06	6.58
197	1.59E-08	7.93E-04	3.12E+06	111.48E-12	4.58E+05	18.14
365	3.10E-08	1.55E-03	1.36E+06	163.46E-12	3.85E+05	26.59
533	3.59E-08	1.79E-03	9.64E+05	197.70E-12	3.15E+05	32.16

Considering possible interpretation of coating deterioration according to f_b and f_{min} values [3] it should be remembered break point frequency f_b is given by the expression

$$f_b = \frac{1}{2\pi\varepsilon\varepsilon_0\,\rho}\,D \tag{1}$$

while minimum frequency f_{min} is given by the expression

$$f_b = \frac{1}{\left(4\pi^2 \varepsilon\varepsilon_0\, C_{dl}^0 \rho^2 d\right)^{\frac{1}{2}}}\, D^{\frac{1}{2}} \qquad (2)$$

In both expressions is involved ε_0 = 8.85E-14 F/cm (the permittivity constant for a vacuum) and in expression for f_{min} also thickness of coating d (cm) and specific double layer capacitance C_{dl}^0 = 2E-05 (F/cm^2) [8]. If for calculation f_b and f_{min} values of parameters involved in **Table 2** were used time dependance of ratio (f_b-f_{min})/(f_b/f_{min}) as well as value of ε (reflecting absorption of water in the coating) was obtained for tested coating system (**Figure 2**).
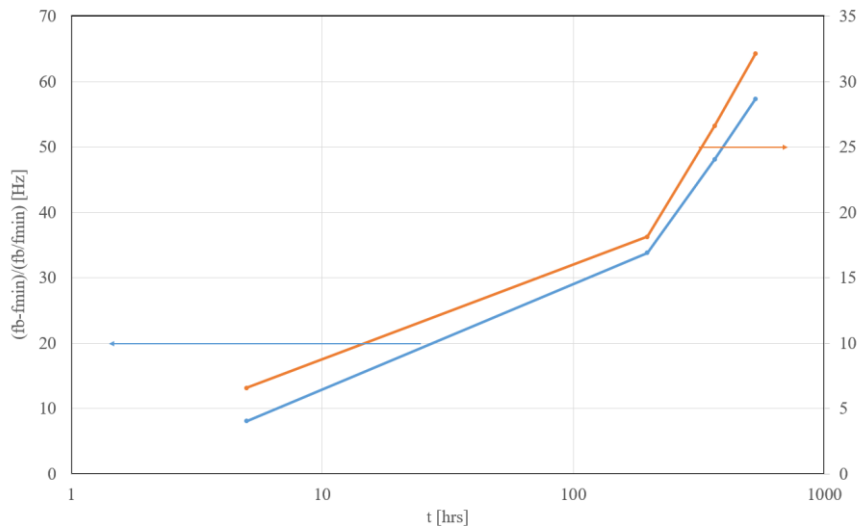

Figure 2 Time dependance of ratio (f_b-f_{min})/(f_b/f_{min}) and ε calculated for Zn and MIO pigmented epoxy coating during exposure to 0.05 M NaCl

From (**Figure 2**) can be seen the additional absorption of water at defects formed at the filler/binder interface occurs for tested coating system after 197 hrs of exposure. It should be remembered that the start of additional absorption of water means also the start of some Cl$^-$ ions penetration into coating and redistribution of Zn and MIO particles in polymer matrix. Both of these effects can be confirmed by (**Figure 3**).
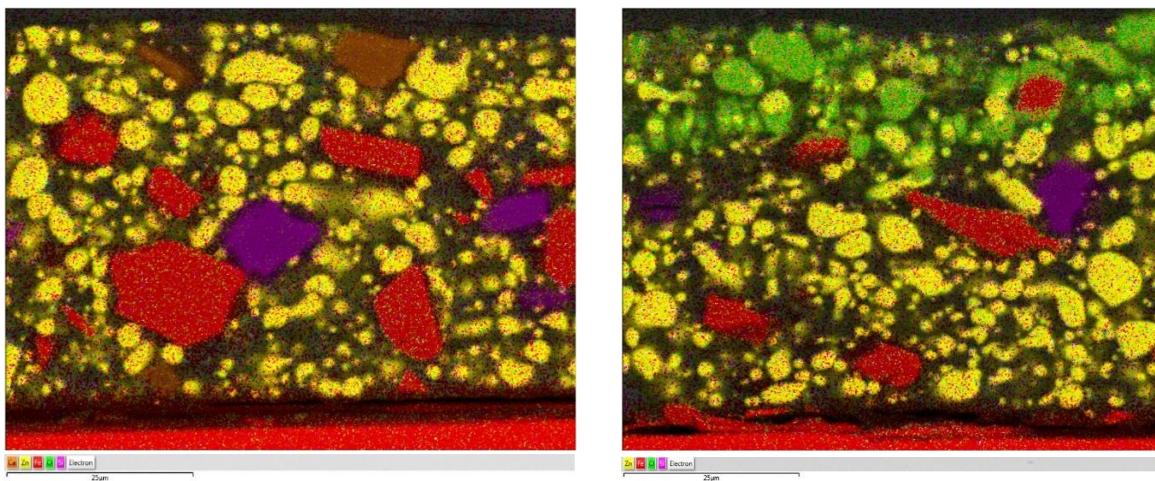

Figure 3 EDX mapping and structure (SEM-SE image) of cross-sections for AKMM 104 (left non-exposed, right exposed)

From (**Figure 3**) can be seen the interconnectivity of Zn as well as MIO particles close to the steel/coating interface is decreased for the exposed coating system after 533 hrs of exposure to 0.05 M NaCl. At the same

time in spite of some Cl⁻ ions penetration observed for outer part of coating it seems this penetration is concerning only the corrosion products and not passivating film which can still inhibit the corrosion process at the steel/coating interface.

4. CONCLUSIONS

New interpretation of ENA data in combination with single frequency (1 kHz) impedance test results was checked for estimation of parameters of f_b and f_{min} (used for determination of coating deterioration by EIS). It was found this method based on modelling of coating electrical properties related to corrosion of substrate can help in study of water uptake and interfacial delamination in modified Zn pigmented epoxy coatings with OPVC = 40.

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