Barrier Properties of Some New Organic Coatings

ECATERINA VASILESCU[1]*, PAULA DROB[1], CORA VASILESCU*[1], MIHAELA HRISCU[2], SILVIU IULIAN DROB[1]
[1]Institute of Physical Chemistry "Ilie Murgulescu", 202 Spl. Independentei, 060021, Bucharest, Romania
[2]Mechanical Engineering and Research Institute, 103 Sos. Oltenitei, 041303, Bucharest, Romania

The new organic coatings were realised from polyurethane resin and alkyd+melamine-formaldehyde resins. The electrochemical techniques of the electrochemical impedance spectroscopy (EIS), cyclic potentiodynamic polarisation and linear polarisation were applied and the tests were carried out in a normal aerated 3% NaCl solution at ambient temperature. Also, open circuit potentials in 3% NaCl solution were monitored for 300 immersion hours. Salt spray tests were carried out according to ASTM B117 Standard. An electric equivalent circuit with two time constants representing the barrier characteristics of the intact organic coating, and the corrosion process occurring at the substrate/paint interface was fitted. The both coatings revealed very good protective properties, assuring a very good resistance for about 8 years in the ambient environment.

Keywords: protective films, immersion tests, salt spray tests, EIS, cyclic polarisation.

Organic coatings are commonly used for protection of metals due to their low cost and easy use [1-6]. Organic coatings act as a barrier between environment and metallic substrate being a physical barrier, chemical inhibitor and electric resistor [7-11]. However, all polymers are permeable to corrosive species as oxygen, water and ions [12-14]. Water molecules can penetrate through the coating pores and can reach the metal/coating interface; in this case, the water molecules can reduce the coating adhesion, favouring the corrosion of metal under the film [15-17]. The rate of corrosion depends upon the transport of the corrosive species through the film: water diffusion through the coating pores and its accumulation on the coating/metal boundary (water uptake), diffusion of the metal ions and ion conduction through the coating and finally, the nature of the corrosive reactions [18-20].

Many types of coating systems were investigated: epoxy resins [19], epoxy-polyamide resins [8,14,21], alkyd resins [22], acryl resins [18], polyester resins [10], polyurethane resins [13,20], chlorinated rubber [9], etc. Their anticorrosive performances were established using electrochemical methods, especially electrochemical impedance spectroscopy (EIS), cyclic and linear polarisation and also technique of the salt spray.

The electrochemical impedance spectroscopy provides some information on the degradation mechanisms of the coating (intact part of the paint, electrolyte diffusion through the paint layer, etc.), for the analysis of the time dependence of the impedance parameters; under the low frequencies, the process become more and more slow and the results are not easy to interpret [7,8,12,14-16,19-21].

Scanning electrochemical spectroscopy (SEM) [10,13] was used for to determine the surface topology, degradation processes and blistering.

Cyclic polarisation depicts the electrochemical reactions associated with oxygen reduction and metallic ion dissolution and released from the corroding metal [9,13,15,17].

Salt spray test is a corrosive accelerated attack by salt spray that increases the corrosion power, reduces the experiment duration and facilitates the comparison between results and their control samples. The samples can be qualitatively classified by visual inspection or semi-quantitatively by the measure of the extortion degree [12].

The barrier properties of some new organic coatings based on polyurethane resin and alkyd+melamine-formaldehyde resins were studied in this paper.

Experimental part

The protective films were realised from polyurethane resin and alkyd+melamine-formaldehyde resins (table 1). The composition of the paints is proprietary. The carbon steel support was previously polished and degreased. For the application of paints, it used the spray method. All films were stabilised for 14 days before testing. Three different samples, prepared by the same way were employed in the experiments and satisfactory reproducibility of the results was obtained.

The electrochemical techniques of the electrochemical impedance spectroscopy (EIS), cyclic potentiodynamic polarisation and Tafel polarisation were applied and the tests were carried out in a normal aerated 3% NaCl solution at ambient temperature.

The electrochemical impedance spectroscopy measurements were performed at open circuit potential using Voltalab equipment; the frequency range was 0.1 Hz – 100 kHz; sinusoidal voltage signal of 10 mV was used. The EIS results were modelled with EQUIVCRT programme [23]. The number of the time constants

Table 1
PROTECTIVE FILMS

Coating symbol	Resin	Curing temperature (^{0}C)	Dry thickness (μm)
PU	polyurethane	ambient	50-55
AK+MF	alkyd+melamine-formaldehyde	ambient	50-55

---

* *email: cvasilescu@chimfiz.icf.ro; Tel.: 0724559289*

Table 2
EQUIVALENCE BETWEEN THE EXPOSURE TIMES IN SALT SPRAY WITH THE EXPOSURE TIME IN ENVIRONMENT

Salt spay (hours)	196	210	228	240	250	286	292	312	340
Environment (years)	8	8.6	9	9.8	10	11	11.5	12.8	14

Table 3
DEGREE OF PAINT RUSTING (ASTM D160) FOR THE SALT CHAMBER

Degree	10	9	8	7	6	5	4	3	2	1
Percentage area rusted (%)	0	0.03	0.1	0.3	1	3	10	16	32	50

needed to fully describe the spectra was based on the condition of a fit with a minimal systematic deviation between the measured and the calculated results.

The cyclic potentiodynamic polarisation was applied beginning from -0.9 V to +0.5 V (vs. saturated calomel electrode –SCE) using a scan rate of 2 mV/s. The polarisation curves have been recorded after various periods (190 h, 220 h, 250 h, 300 h); the electrochemical set-up consisted from the same Voltalab equipment.

The linear polarisation method in Tafel plot form was applied for ±150 mV around the open circuit potential with a scan rate of 2 mV/s. The main electrochemical parameters: i_{corr} – corrosion current density, V_{corr} – corrosion rate and R_p – polarisation resistance were determined at the same time periods as cyclic curves. The same Voltalab equipment with its software was used.

Also, open circuit potentials in 3% NaCl solution were monitored for 300 immersion hours using a performing Hewllett-Packard multimeter.

Salt spray tests were carried out according to ASTM B117 Standard (50 g/L NaCl solution at 35^0C, pressure of 0.1MPa). Samples of 50 x 40 x 1 mm dimensions were deposed in vertical position. The visually inspection was realised at regular intervals up to 300 exposure hours conforming to ASTM D-610-01 Standard.

Table 2 show the equivalence between the hours of exposure in the salt spray and the real period of exposure in environment, in accordance with ISO 2409/1994 Standard.

Also, the degree of the paint rusting in the salt chamber, according with ASTM D160 Standard is presented in table 3, the rust distribution type is defined by the letter S for spot rusting or G for general rusting.

Results and discussions

Anticorrosive properties obtained from EIS data

Nyquist (imaginary component of impedance – Z" as a function of real component –Z') plots (fig. 1) for both coating films revealed the existence of one depressed semicircle, one capacitive loop (one time constant) for 190 exposure hours in 3% NaCl solution; this fact indicates the protective effect of the coatings: a film like a barrier against the water or ion transport; the diameter of the semicircle is equal with the resistance of the coating R_c and show high values, i.e. very resistant film. After 200 immersion hours, two semicircles appeared on the Nyquist spectra, two capacitive loops, one high frequency loop (on the left) and one low frequency loop (on the right) attributed to the resistance and capacitance of the coating (R_c and C_c) characterizing its pores network structure (the coating-electrolyte interface, inside the coating) and the resistance and capacitance of the charge transfer reactions (R_{ct} and C_{dl}) on the steel surface (the steel/electrolyte interface), respectively. The presence of two semicircles, the development of the second time constant show the degradation process of the coating, the barrier effect of the film is partially lost in certain areas, thus allowing the underlying metal to come in direct contact with the aqueous environment [24-26]. The first semicircle accounts for the barrier characteristics of the intact organic coating, and the second describe the corrosion process occurring at the substrate/paint interface, in the defective areas of the coating, specifically the charge transfer process between metal and solution. So, an electric equivalent circuit with two time constants may be used after 200 immersion hours [18,19,27,28]. This equivalent circuit (fig. 2) consists of the electrolyte resistance R_{Ω}, the capacitance of the intact coating layer C_c, the pore resistance R_c due to the penetration of the electrolyte, the charge transfer resistance of the substrate R_{ct} and the double layer capacitance C_{dl} of the substrate/electrolyte interface.

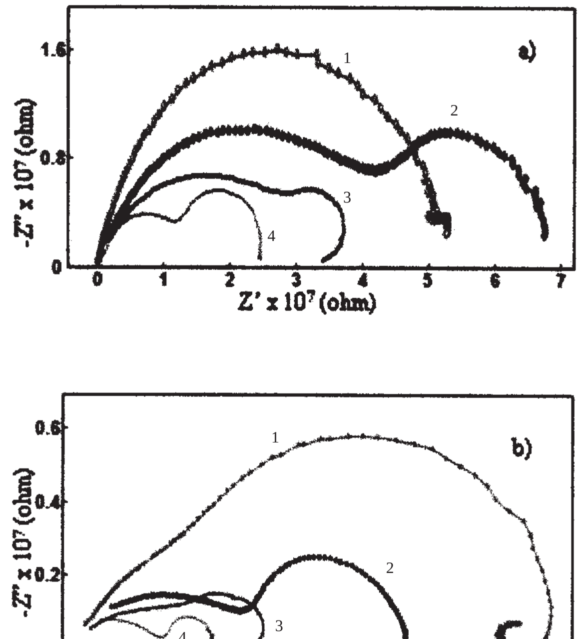

Fig. 1. Nyquist plots for AK+MF (a) and PU (b) coatings for 300 exposure hours in 3% NaCl solution: 1 -190 h; 2 -200 h; 3 - 210 h; 4 -220 h

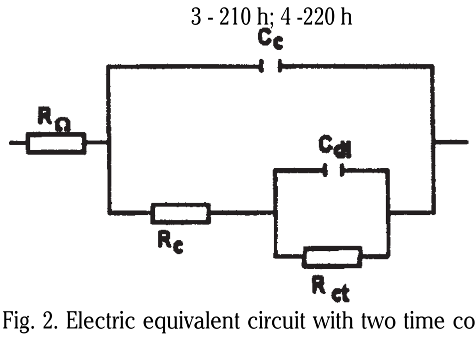

Fig. 2. Electric equivalent circuit with two time constants

Time (h)	Coating	R_c ($\Omega.cm^2$)	C_c ($F.cm^{-2}$)	R_{ct} ($\Omega.cm^2$)	C_{dl} ($F.cm^{-2}$)
190	AK+MF	$1.1x10^7$	$2.3x10^{-10}$	-	-
	PU	$0.4x10^7$	$3.7x10^{-10}$	-	-
250	AK+MF	$3x10^5$	$5.5x10^{-9}$	$4x10^4$	$2.5x10^{-7}$
	PU	$2x10^5$	$6.8x10^{-9}$	$1.1x10^4$	$1.6x10^{-6}$

Table 4
PARAMETERS OF THE ELECTRIC EQUIVALENT CIRCUITS

Parameters of the electric equivalent circuit with two time constants (table 4) show that the both studied films are able to offer protection up to 190 h which can be evidenced by the high R_c values, almost 0.4 x 10^7 $\Omega.cm^2$ for polyurethane film and 1.1 x 10^7 $\Omega.cm^2$ for alkyd+melamine-formaldehyde film. After 250 h of immersion, the resistance values of the coatings decreased and reached almost 10^5 $\Omega.cm^2$, showing the occurrence of the charge transfer reactions by the existence of the charge transfer resistance R_{ct} of $1.1x10^4$ $\Omega.cm^2$ and $4x10^4$ $\Omega.cm^2$, respectively.

Anticorrosive properties obtained from cyclic polarisation curves

Cyclic polarisation curves (fig. 3) on their anodic branch exhibited passive regions from -0.7 V to +0.5 V both for polyurethane and alkyd+melamine-formaldehyde coatings in the first 190 exposure hours, confirming the EIS data, showing the very good protective properties of the coatings for this immersion period [29-31]. In time, the passive region decreased very much and the current density increased due to the dissolution of iron ions in the electrolyte [13].

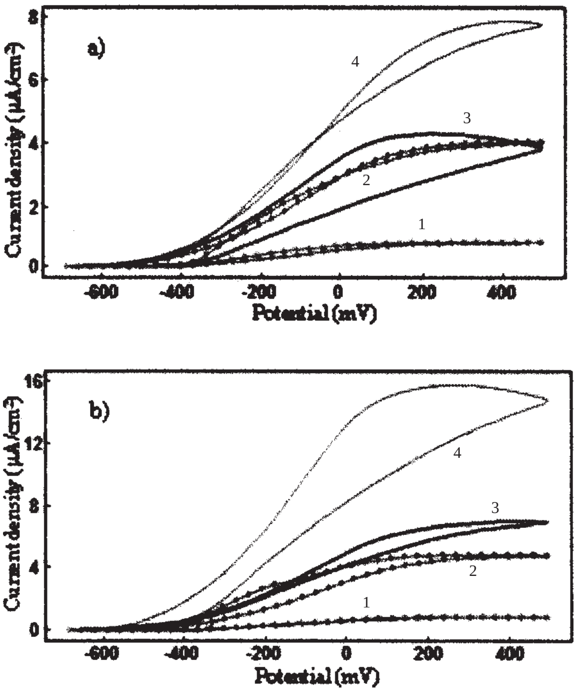

Fig. 3. Cyclic polarisation curves for AK+MF (a) and PU (b) coatings for 300 exposure hours in 3% NaCl solution: 1-190 h; 2 - 220 h; 3 - 250 h; 4 - 300 h.

Anticorrosive properties obtained from Tafel plots

Table 5 summarizes the values of the corrosion current densities (i_{corr}), corrosion rates (V_{corr}) and polarisation resistance R_p of the tested films for a period of 300 h. In comparison with the bare metal, the corrosion current densities of the films are lower (ten times). The corrosion current densities and corrosion rates for coatings increased in time due to the dissolution of the carbon steel substrate. Also, polarisation resistance values R_p decreased in time, showing the process of the coating degradation. For 190 immersion hours, the both coatings reveal very good protective properties, assuring a very good resistance for about 8 years in the ambient environment.

Anticorrosive properties obtained from monitoring of the open circuit potentials

The open circuit potentials (fig. 4) exhibited some low oscillations at the beginning and then became nobler at values around of -0.5 V ÷ -0.6 V for about 200 h; these electropositive values are due to the barrier effects of the coatings and confirm their good protective properties for 200 h. After that, the open circuit potentials tend to slight more electronegative values (-0.65 V), showing that the coatings became defective.

Anticorrosive properties obtained from salt spray tests

According to the results from table 6, the both studied coatings remained about intact with a rate of damage of 0.1% for 190 h, corresponding to 8 years of exposure in atmosphere. After 220 h, corrosion rust spots appeared, and after 300 h the general corrosion was formed and the coatings were damaged.

The results of the cyclic polarisation, linear polarisation, EIS and salt spray tests are in the very good agreement

Material	Immersion time (h)	i_{corr} ($\mu A/cm^2$)	V_{corr} (mm/year)	R_p (Ω)
Bare carbon steel	0	26.4	0.204	$0.864x10^3$
AK+MF painted carbon steel	190	0.56	0.0043	$33.23x10^3$
	220	0.93	0.0072	$23.27x10^3$
	250	1.31	0.010	$10.7x10^3$
	300	1.87	0.0174	$8.31x10^3$
PU painted carbon steel	190	0.65	0.005	$22.9x10^3$
	220	0.93	0.0072	$23.04x10^3$
	250	1.35	0.0105	$19.79x10^3$
	300	1.99	0.0155	$8.66x10^3$

Table 5
CORROSION PARAMETERS OBTAINED FROM TAFEL PLOTS

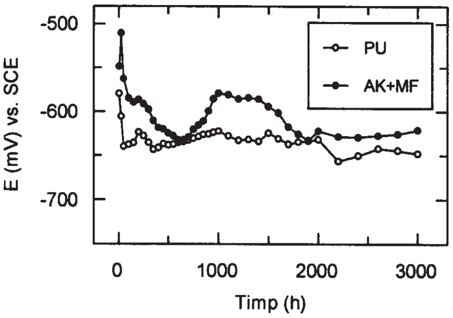

Fig. 4. Monitoring of open circuit potentials in 3% NaCl solution

Table 6
DEGREE OF THE PAINT RUSTING IN THE SALT SPRAY CHAMBER

System	Exposure time (h)			
	190	220	250	300
PU	9	8 - S	5 – many S	4 - G
AK+MF	9	8 - S	5 – many S	4 – G

S – spot rusting; G – general rusting

and show that the protective properties of the studied coatings are very good for a period of 8 years of exposure in the ambient environment.

Conclusions

An electric equivalent circuit with two time constants representing the barrier characteristics of the intact organic coating, and the corrosion process occurring at the substrate/paint interface was fitted.

Parameters of the electric equivalent circuit with two time constants show that the both studied films (polyurethane – PU and alkyd+melamine-formaldehyde – AK+MF) are able to offer protection up to 190 h of immersion in 3% NaCl solution.

Cyclic polarisation curves exhibited passive regions both for PU and AK+MF coatings in the first 190 exposure hours, confirming the EIS data, showing the very good protective properties of the coatings for this immersion period.

For 190 immersion hours in 3% NaCl solution, the both coatings reveal very good protective properties, assuring a very good resistance for about 8 years in the ambient environment.

According to the salt spray tests, the both studied coatings remained about intact with a rate of damage of 0.1% for 190 hours, corresponding to 8 years of exposure in atmosphere.

Acknowledgements: This research was supported by the Romanian PNCDI II, contract no. 31-003/2007-2010.

References

1. TOLNAY, G., SAJO, I., NAGY, P., PAVAI, M., HOLCZER, E., KOZAN-NAUMESCU, A., KORMOS, F., KALMAN, E., Rev. Chim. (Bucharest), **61**,no. 2, 2010, p. 238
2. POPA, M.V., DROB, P., VASILESCU, E., SANTANA LOPEZ, A., MIRZA ROSCA, I., VASILESCU, C., Rev. Chim. (Bucharest), **54**, no.11, 2003, p. 880.
3. POPA, M.V., DROB, P., VASILESCU, E., ANGHEL, M., MIRZA ROSCA, I., SANTANA LOPEZ, A., Rev. Chim. (Bucharest), **54**,no.2, 2003, p. 135
4. POPA, M.V., DROB, P., VASILESCU, E., MIRZA ROSCA, I., SANTANA LOPEZ, A., ANGHEL, M., Rev. Chim. (Bucharest), **52**, 2001, no. 12, p. 718
5. VASILESCU, E., DROB, P., POPA, M.V., ANGHEL, M., VASILESCU, C., Rev. Chim. (Bucharest), **51**, no. 7, 2000, p. 502
6. DROB, P., VASILESCU, E., POPA, M.V., ANGHEL, M., MIRZA ROSCA, I., GONZALEZ, J.E., SERBAN, R., Rev. Chim. (Bucharest), **50**, no. 11, 1999, p. 777
7. ROUT, T. K., Corros. Sci., **49**, 2007, p.794
8. GONZALEZ-GARCIA, Y., GONZALEZ, S., SOUTO, R. M., J. Adhession Sci. Technol., **14**, 2005, p. 1141
9. SAKHRI, A., PERRIN, F. X., ARAGON, E., LAMOURIC, S., BENABOURA, A., Corros. Sci., **52,** 2010, p. 901
10. SOUTO, R. M., GONZALEZ-GARCIA, Y., GONZALEZ, S., Progress. Org. Coat., **65**, 2009, p. 435
11. SATHIYANARAYANAN, S., KARPAKAM, V., KAMARAJ, K., MUTHUKRISHNAN, S., VENKATACHARI, G., Surf. Coat. Tech., **204**, 2010, p. 1426
12. HAMMOUDA, N., BOUDINAR, Y., TOUIKER, M., BELMOKRE, K., Mater. Corros., **57**, 2006, p. 338r
13. SOUTO, R. M., GONZALEZ-GARCIA, Y., GONZALEZ, S., Corros. Sci, **47**, 2005, p. 3312
14. GONZALEZ, S., GIL, M. A., HERNANDEZ, J. O., FOX, V., SOUTO, R. M., Progress. Org. Coat., **41**, 2001, p. 167
15. YAGAN, A., PEKMEZ, N. O., YILDIZ, A., Corros. Sci, **49**, 2007, p. 2905
16. LIN, C. H., DUH, J. G., Surf. Coat. Tech., **204**, 2009, p. 784
17. CAKMAK, E., TEKIN, K. C., MALAYOGLU, U., SHRESTHA, S., Surf. Coat. Tech., **204**, 2010, p. 1305
18. ITAGAKI, M., ONO, A., WATANABE, K., KATAYAMA, H., NODA, K., Corros. Sci, **48**, 2006, p. 3802
19. SHI, X., NGUYEN, T. A., SUO, Z., LIU, Y., AVCI, R., Surf. Coat. Tech., **204**, 2009, p. 237
20. GONZALEZ-GARCIA, Y., GONZALEZ, S., SOUTO, R. M., Corros. Sci, **49**, 2007, p. 3514
21. SKALE, S., DOLECEK, V., SLEMNIK, M., Corros. Sci, **49**, 2007, p. 1045
22. GONZALEZ, S., MIRZA ROSCA, I. C., SOUTO, R. M., Progress. Org. Coat., **43**, 2001, p. 282
23. BOUKAMP, B., Solid State Ionics, **21**, 1986, p. 31
24. POPA, M.V., DROB, P., VASILESCU, E., MIRZA ROSCA, J., SANTANA LOPEZ, A., VASILESCU, C., Rev. Roum. Chim., **51**, 2006, p. 1079
25. POPA, M.V., DROB, P., VASILESCU, E., ANGHEL, M., MIRZA ROSCA, I., SANTANA LOPEZ, A., Mater. Corros., **53**, 2002, p. 91
26. POPA, M.V., DROB, P., VASILESCU, E., MIRZA ROSCA, J., SANTANA LOPEZ, A., VASILESCU, C., DROB, S.I., Mater. Chem. Phys., **100**, 2006, p. 296
27. MANSFELD, F., KENDIG, M. W., TSAI, S., Corrosion, **47**, 1991, p. 952
28. KENDIG, M. W., MANSFELD, F., Corros. Sci., **23**, 1983, p. 317.
29. BALACEANU, M., BRAIC, M. V., BRAIC, M., KISS, A., ZOITA, C.N., VLADESCU, A., DROB, P., VASILESCU, C., DUDU, D., MURESANU, O., Surf. Coat. Tech., **202**, 2008, p. 2384.
30. BRAIC, M., BRAIC, V., BALACEANU, M., KISS, A., COTRUT, C., DROB, P., VLADESCU, A., VASILESCU, C., Plasma Process. Polym., **4,** 2007, p. S171
31. VLADESCU, A., KISS, A., BRAIC, M., COTRUT, C.M., DROB, P., BALACEANU, M., VASILESCU, C., BRAIC, V., J. Nanosci. Nanotechn., **8**, 2008, p. 733

Manuscript received: 18.05.2010