



Electrochemical stability and surface analysis of a new alkyd paint with low content of volatile organic compounds

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ABSTRACT

This paper presents the results regarding the electrochemical stability and surface analysis of a new alkyd paint with low content of volatile organic compounds in comparison with a conventional alkyd paint. The alkyd films were realized on carbon steel substrate. Dry films thickness in 30–35 μm range was obtained. The experimental tests were carried out in 3% NaCl solution at the 25 °C temperature. The electrochemical techniques (electrochemical impedance spectroscopy (EIS), potentiodynamic and Tafel polarization) and surface analysis techniques (AFM, SEM, EDX) were used to evaluate protective properties of the tested paint films. The correlation of all experimental results established that the new alkyd paint with low content of volatile organic compounds presents better protective performances and lower permeability than conventional alkyd paint. AFM, SEM and EDX indicated a compact, homogenous, non-porous and adherent coating.

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1. Introduction

The organic coatings are an important group of protection materials and they are widely used. Their role is to act as a barrier between environment and the metallic substrate and it has been described as the combination of a physical barrier, chemical inhibitor and electrical resistor [1]. Electrochemically, the protection by the organic coatings consists of a resistance polarization (due to the high electrical resistance of the coating), a cathodic polarization (due to the restricted permeation of the oxygen through the coating) and a concentration polarization of the anodic reaction (due to the restricted migration of the metal ions out through the paint film) [2–6].

From all organic anticorrosive coatings, the paints represent 80–90%, resulting the importance of this domain. The paint coatings are generally not impervious barriers to corrosive reactants such as water, water vapours, oxygen and ions. Their permeability depends on: the paint composition [7–16], the deposition technique of the coating [8,17,18], its thickness [19,20] and the adhesion to the substrate [21–24].

The conventional paints with volatile organic solvents have a detrimental influence on the environment and are considered as

hazardous to health. Their use will be prohibited, even if they present high protective performance. Therefore, it is necessary to develop new anticorrosive paints with low content of volatile organic compounds.

For an efficient development of new paints, the rapid evaluation of the anticorrosive performance is very important. This is possibly due to the electrochemical techniques, which can characterize the quality and the performances of paint films in a short time [25–36]. Among these techniques, the electrochemical impedance spectroscopy (EIS) is considered to be very important because both the dielectric properties of the film and the corrosion processes at the interface metal/film can be investigated [37–55]. Therefore, in the last years the electrochemical impedance spectroscopy was widely used with good results for the characterization of the paint films on metallic substrates.

The application of another new electrochemical technique – the electrochemical noise analysis (ENA) for the same purposes has become of interest [56,57]; the low cost of the equipment and the ease of the data collection seem to be the main attraction of this technique. Kwiatkowski and Bednarkiewicz [58] have monitored the degradation of organic coatings by tensammetry (alternating current voltammetry). This method may be helpful in comparison of the coatings durability in corrosive environments as well as for mechanistic considerations. Application of scanning electrochemical technique to the study of the anticorrosive characteristics of the coated metals appears to be very promising in elucidating the

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Table 1

The tested films.

Film symbol	Binder type	VOC content (%)	Dry film thickness (μm)
CA	Conventional alkyd resin	45–46	30–35
MA	Modified alkyd resin	4–5.5	30–35

complex processes occurring in the interaction of the metal/coating system with corrosive environments [59–61].

This paper presents the results of the electrochemical measurements (electrochemical impedance spectroscopy; potentiodynamic and Tafel polarisation) and of the surface analysis (AFM, SEM and EDX) regarding the protective performance of a new alkyd paint with low content of volatile organic compounds (VOC) in comparison with a conventional alkyd paint.

2. Experimental details

2.1. The paint films

The protective films were realized from alkyd resin. Table 1 presents the tested films.

The carbon steel support was previously polished and degreased. No primer was used. For the application of paints, it was used the brushing for to induce defects in films and so, to study the corrosion processes through and under paint films.

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 results was obtained.

2.2. Solutions

The experimental tests were carried out in a normal aerated 3% NaCl solution at the 25 °C temperature for a total period of up to 600 h of immersion.

2.3. Experimental cell

A conventional glass electrochemical cell with three-electrodes was used. The working electrodes were the coated carbon steel specimens, exposing a circular painted area (3.5 cm²) to the electrolyte solution. An Ag/AgCl reference electrode and a platinum counter electrode were employed.

2.4. Testing procedure

The electrochemical impedance measurements (EIS) were performed at the open circuit potential using Autolab equipment with its software. The frequency range was 10–50 kHz for the water penetration studies and 0.1 Hz to 100 kHz for the rest of the determinations; sinusoidal voltage signal of 10 mV was used. The experimental impedance spectra were analysed on the basis of the equivalent electrical circuits using the Autolab fitting software. The number of time constants 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 paint film capacitance (Q_{pf}) and resistance (R_{pf}) were monitored with the immersion time. Their time dependences have permitted to establish the water permeability of the paint film and the movement of ions through film. Time trend of the double layer capacitance (Q_{dl}) and the charge transfer resistance (R_{ct}) were determined. These

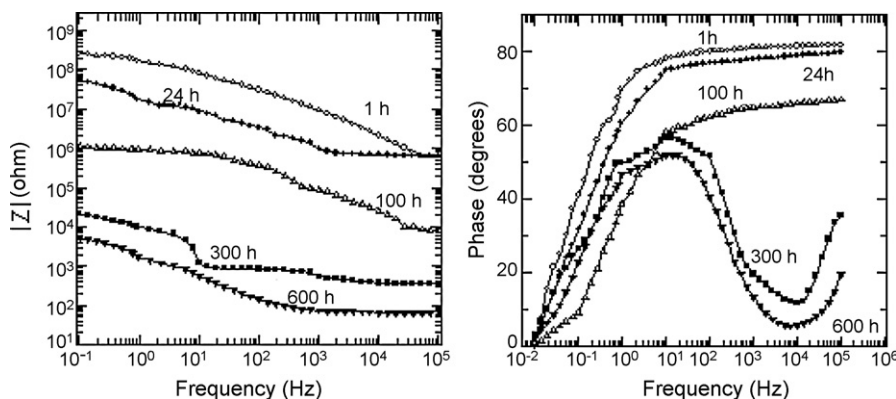


Fig. 1. Bode diagrams for MA painted carbon steel after different immersion periods in 3% NaCl solution.

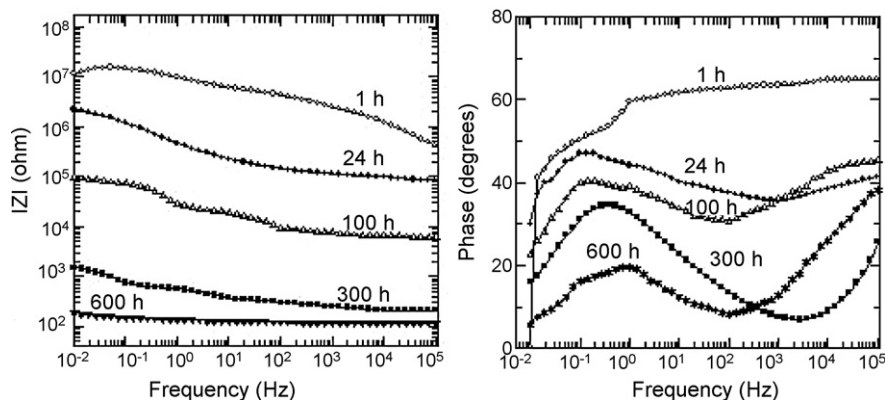


Fig. 2. Bode diagrams for CA painted carbon steel after different immersion periods in 3% NaCl solution.

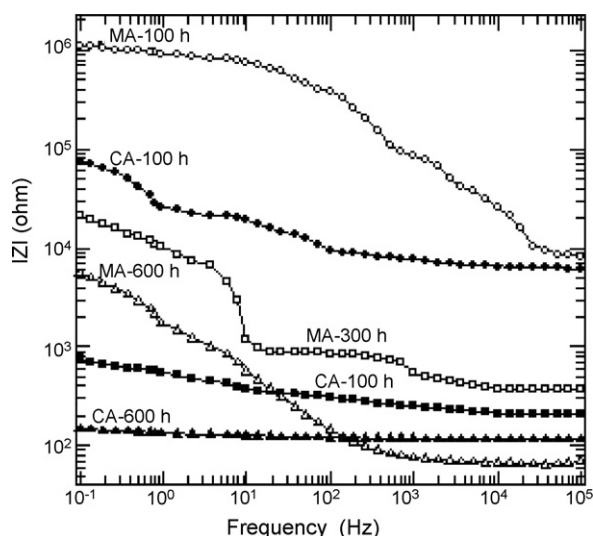


Fig. 3. Bode diagrams for MA and CA painted carbon steel after different immersion periods in 3% NaCl solution.

dependences permitted the assessment of the electrochemical processes at the carbon steel/coating interface.

The cyclic potentiodynamic polarisation was applied beginning from -0.9 V to $+0.5$ V (vs. Ag/AgCl) using a scan rate of 2 mV/s. The polarisation curves have been recorded for bare and coated carbon steel electrodes after various immersion periods; the electrochemical set-up consisted a potentiostat/galvanostat Autolab equipment with its software.

Tafel polarisation method was applied for ± 150 mV around the open circuit potential with a scan rate of 2 mV/s. The main electrochemical parameters: E_{corr} – corrosion potential, i_{corr} – corrosion current density, R_p – polarisation resistance and V_{corr} – corrosion rate were determined. The same Autolab equipment was used.

The equipment for the surface analysis with atomic force microscopy (AFM) was an electrochemical atomic force microscope from APE Research, Italy. The contact mode AFM was used.

The coatings were also characterized for their morphology, composition and microstructure by scanning electron microscopy (SEM) with the Field Environmental SEM Philips XL30, with pressure in the chamber to 0.7 Torr, and an Energy Dispersive (EDX) module. The spectrometer used for analysis is EDX Sapphire with ultra thin window (UTW). The surface of detector is 10 mm².

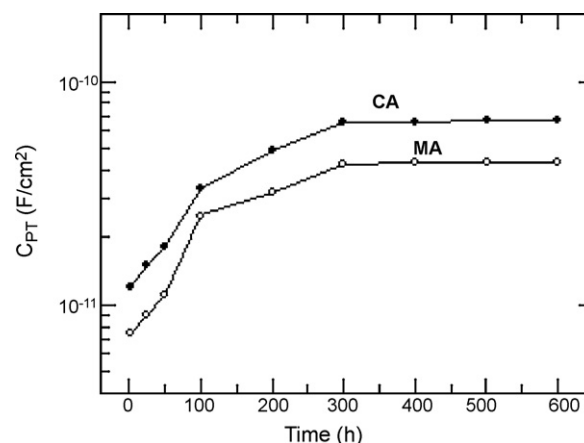


Fig. 5. Time dependence of the film capacitance in 3% NaCl solution.

3. Results and discussion

3.1. Electrochemical impedance spectroscopy

The impedance spectra were registered during the immersion period in 3% NaCl solution. Figs. 1 and 2 present Bode plots (logarithm of the impedance modulus and the phase angle as function of the logarithm of the frequency) for both tested alkyd films for a period up to 600 immersion hours.

The evolution of EIS spectra as a function of the immersion time in electrolytes for MA film shows some changes of the impedance characteristics as a consequence of the variations in the dielectric properties of the paint coatings. These changes accentuated in time due to the electrolyte penetration in the film. The film impedance decreases with the immersion time; important changes take place in the first 300 h of immersion, after that no significant variation is observed (the coating is saturated with electrolyte). The phase angle remained close to 80° for 100 immersion hours and then, two phase angles at about 50° and 60° were obtained, revealing two processes at the interface carbon steel/film.

For CA film, the impedance had lower values than MA film and the impedance decreased very much in time, denoting a defective coating. Phase angles exhibited two values at about 45° and 20° after 24 h of immersion, showing a diffusion process through film, therefore, a degradation process of this coating.

The alkyd film with low COV content has a better behaviour: higher impedance values and slower variations (Fig. 3).

Analysis of the experimental impedance spectra has established the most probable electrical equivalent circuit (Fig. 4a) for tested systems. It resulted that the fitting quality (Fig. 4b) for the sim-

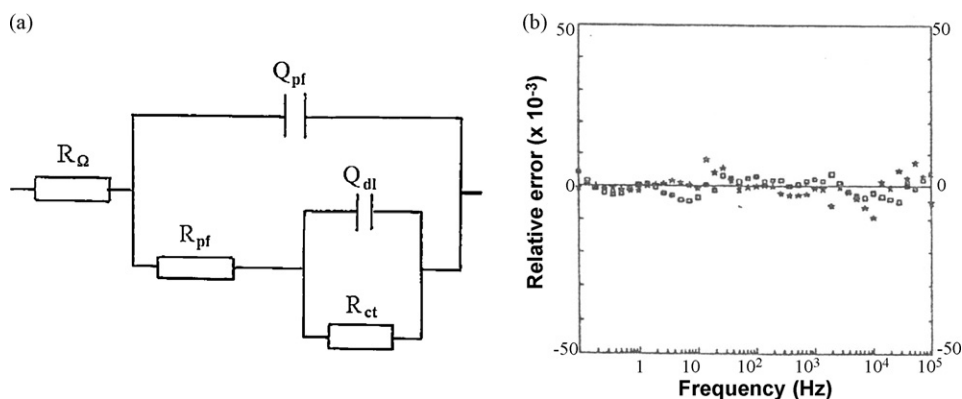


Fig. 4. Electric equivalent circuit with two time constants (a) and its fitting quality (b): (Δ) real relative error; (*) imaginary relative error.

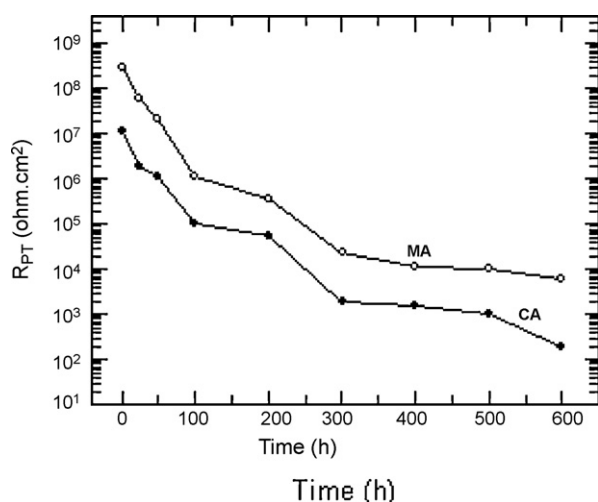


Fig. 6. Time dependence of the film resistance in 3% NaCl solution.

ulation of the carbon steel/alkyd film/electrolyte system with two time constants electrical equivalent circuit is satisfactory. One time constant represents the paint film (film capacitance Q_{pf} and film resistance R_{pf}) and other constant illustrate the reactions at the film/carbon steel interface (double layer capacitance Q_{dl} and charge transfer resistance R_{ct}).

The evaluation of the time trends of the electrical film capacitance (Q_{pf}) and resistance (R_{pf}) has permitted to determine the protective properties of the alkyd films. Figs. 5 and 6 present the time trends of these parameters in 3% NaCl solution.

The capacitance evolution includes two different stages (Fig. 5): an initial period up to 150 h with a significant increase due to the water uptake (capillary water) and a second one (150–300 h) where slight variation is observed (into polymer water); after that, the film is saturated with water. The time trend of the film resistance (Fig. 6) presents the same stages; its decrease in time is due to the conductive pathways that develop in film.

The water uptake changes the dielectric constant of the polymer and therefore, the capacitance of the film. So, supposing the homogeneous water dispersion, the lack of water–polymer chemical interaction and the absence of the swelling process, the volume fractions of water (Φ_t) in the paint films were calculated from the time dependence of the film capacitance following the Brasher and Kinsbury's formula [62]:

$$\Phi_t = \frac{\log C_t / C_0}{\log 80} \quad (1)$$

where C_t is the coating capacitance at time t , C_0 is the coating capacitance at time $t = 0$ and 80 is the relative permittivity of water.

Table 2 summarises the calculated values for the two water phase: “capillary water” and “into polymer water”, as well as the saturation water for the tested films [62–65]. Data from table

Table 2

Water permeability of the tested alkyd films.

Parameter	Alkyd film	
	MA	CA
Capillary water (%)	6.3	8.1
Into polymer water (%)	0.9	1.2
Saturation water (%)	7.2	9.3

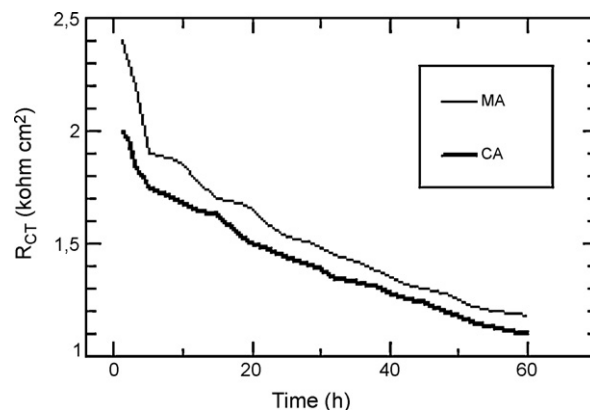


Fig. 7. Time dependence of charge transfer resistance – R_{ct} for the tested alkyd paint films on carbon steel in 3% NaCl solution.

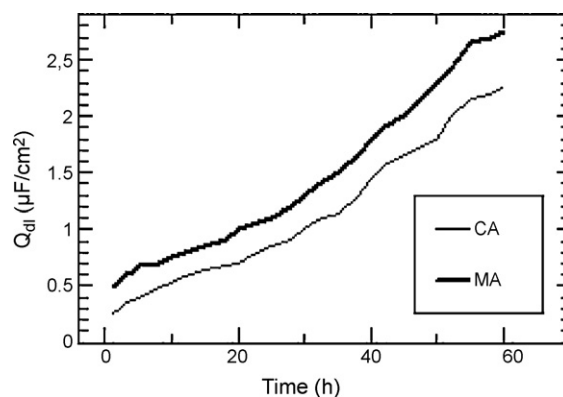


Fig. 8. Time dependence of double layer capacitance – Q_{dl} for the tested alkyd paint films on carbon steel in 3% NaCl solution.

emphasise that the alkyd film with reduced VOC content has lower water permeability.

The movement of the ions through coating was estimated from the coating surface with the conductive pathways ($S_{CP}\%$):

$$S_{CP}\% = \frac{A_{CP}}{A_T} \cdot 100 \quad (2)$$

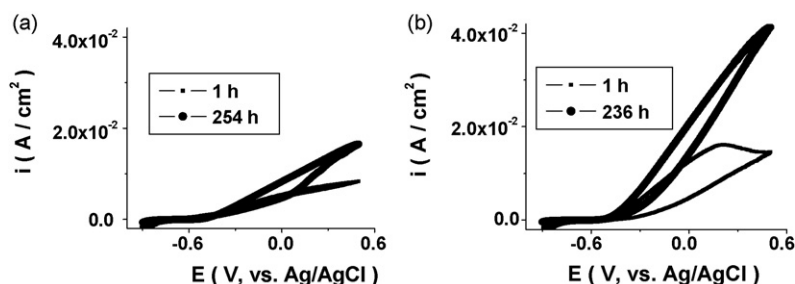


Fig. 9. Cyclic voltammograms for painted carbon steel (a – MA film; b – CA film) after different immersion periods in 3% NaCl solution.

Table 3

Ionic transport through the tested alkyd films.

Parameter	Alkyd film	
	MA	CA
Area of conductive pathways ($\text{cm}^2/1 \text{ cm}^2$ film)	5.1×10^{-8}	1.8×10^{-7}
Percentage surface with conductive pathways (%)	5.1×10^{-6}	1.8×10^{-5}

where A_T is the total coating area exposed to the electrolyte solution and A_{CP} is the area of conductive pathways, which develop in the protective coating between the metallic substrate and the bulk electrolyte. A_{CP} was calculated using the Walter's formula [66]:

$$A_{CP} = \frac{l}{k \cdot R_{pf}} \quad (3)$$

where l is the average length of the pathways (\approx film thickness), k is the conductivity of the pathways (\approx the conductivity of the solution) and R_{pf} is the coating resistance.

Data calculated with (2) and (3) formula are included in Table 3. These data show that the ionic transport in the alkyd film with reduced VOC content is lower than of the conventional alkyd film.

The time trend of the double layer capacitance (Q_{dl}) and the charge transfer resistance (R_{ct}) were respectively determined. These dependences permitted the assessment of the electrochemical processes at the carbon steel/coating interface. The charge transfer resistance is inversely proportional to the corrosion rate and the active area of the metal substrate [65]. The double layer capacitance is related to the area of metal surface in contact with the electrolyte and therefore interested by the swelling and detachment processes [67].

Fig. 7 presents the time evolution of the charge transfer resistance for the studied paint coatings. The decrease of the charge transfer resistance emphasizes the presence of the electrochemical reactions at the coating/carbon steel interface. Comparing the values of this parameter with those for an uncoated sample resulted that the electrochemical reactions at the coating/metal interface were slowed down (≈ 50 times for the alkyd paint

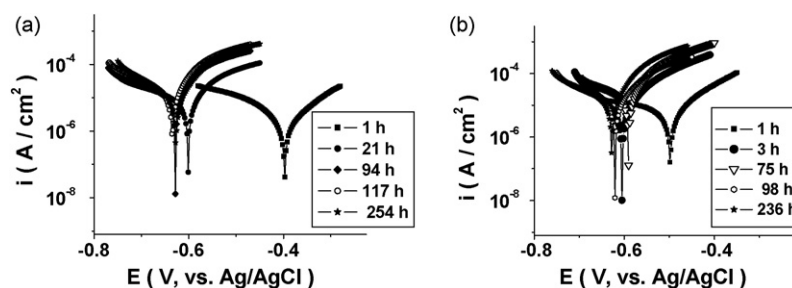


Fig. 10. Tafel diagrams for painted carbon steel (a – MA film; b – CA film) after different immersion periods in 3% NaCl solution.

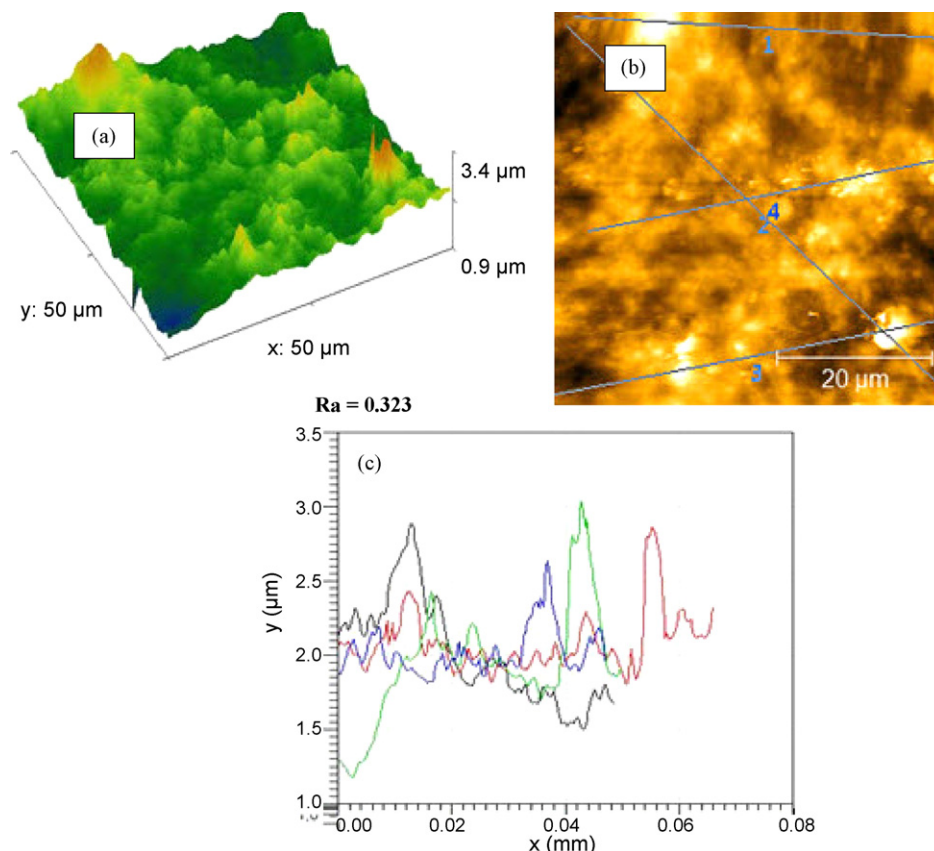


Fig. 11. Three-dimensional images (a), topography (b) and surface profile ($50 \mu\text{m} \times 50 \mu\text{m}$) (c) for MA paint film.

Table 4
Electrochemical parameters of painted carbon steel.

Paint film	Immersion time (h)	E_{corr} (V)	i_{corr} (A/cm ²)	R_p (Ω)		V_{corr} (mm/year)
				From Tafel plots	From EIS plots	
MA	10	−0.397	5.91×10^{-7}	5.046×10^3	5.35×10^3	1.659×10^{-3}
	50	−0.401	1.143×10^{-6}	8.910×10^2	8.85×10^2	3.207×10^{-3}
	100	−0.482	2.547×10^{-6}	6.760×10^2	6.35×10^2	3.275×10^{-3}
	300	−0.505	2.832×10^{-6}	6.034×10^2	5.98×10^2	7.942×10^{-3}
	600	−0.527	3.69×10^{-6}	5.550×10^2	5.47×10^2	1.036×10^{-2}
CA	10	−0.498	1.033×10^{-6}	1.399×10^3	1.49×10^3	2.896×10^{-3}
	50	−0.563	1.73×10^{-6}	5.735×10^2	5.68×10^2	4.850×10^{-3}
	100	−0.601	2.79×10^{-6}	5.608×10^2	5.33×10^2	7.820×10^{-3}
	300	−0.618	3.09×10^{-6}	5.528×10^2	5.12×10^2	8.670×10^{-3}
	600	−0.635	4.106×10^{-6}	4.675×10^2	4.33×10^2	1.152×10^{-2}

with low content of VOC and ≈ 45 times for alkyd conventional paint).

Fig. 8 shows the time trend of the double layer capacitance after immersion in electrolyte solution. As can be seen in figure, the double layer capacitance increases during immersion period showing the presence of the double layer under coating. Comparing these values with those measured on a bare sample it resulted a significant decrease a wet area of metallic substrate in the coating presence (≈ 60 times for the alkyd paint with low content of VOC and ≈ 50 times for alkyd conventional paint).

3.2. Potentiodynamic polarisation

The cyclic polarization curves offered supplementary data about the protective properties of the tested painted specimens, but these depended on the exposure time in the electrolyte solution before

the polarization. Fig. 9 illustrates the curves recorded after different immersion hours in test solution for the alkyd painted carbon steel.

The specimens coated with the alkyd films with low content of VOC can be characterized by a marked tendency to limit the corrosion of the carbon steel substrate. The polarization curves show a decrease of the dissolution current density of the painted steel with MA alkyd film in comparison with CA alkyd film.

3.3. Tafel plots

Tafel plots (Fig. 10) permitted the determination of the electrochemical parameters. Table 4 summarizes the values of corrosion potential (E_{corr}), corrosion current density (i_{corr}), polarisation resistance (R_p) and corrosion rates (V_{corr}) of the tested films for an immersion period of 600 h. The values of these main electrochemical parameters slightly change in time in comparison with the

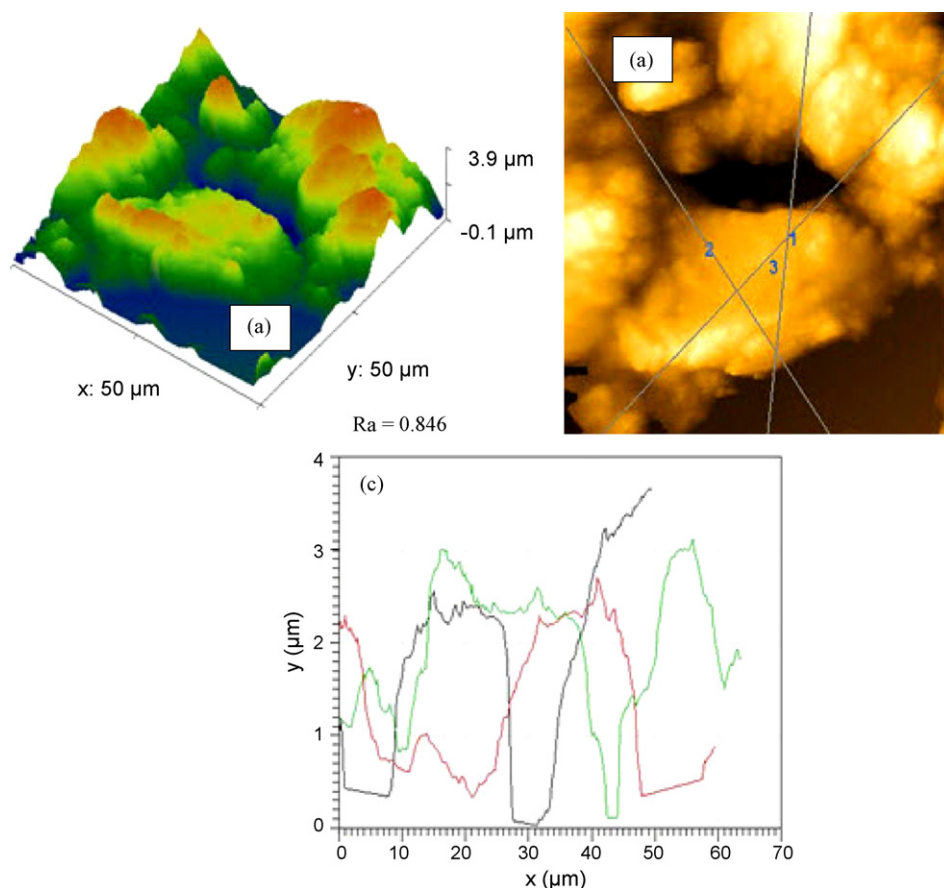


Fig. 12. Three-dimensional images (a), topography (b) and surface profile (50 $\mu\text{m} \times 50 \mu\text{m}$) (c) for CA paint film.

un-painted specimen. It resulted that the films with low content of VOC presented the best behaviour; the carbon steel substrate exhibited the lowest corrosion rates under this paint film. Polarisation resistance R_p obtained from Tafel plots decreased in time, showing a slight increase of the corrosion rate; the about same values presented polarisation resistance obtained from EIS plots (Table 4), revealing a slow increase of the film permeability to ions and water. Therefore, a good concordance between Tafel and EIS data resulted for long exposure time.

Comparing the corrosion rate of the painted substrate with the corrosion rate of the bare substrate, the efficiency ($\eta_p\%$) of the protective films were calculated [25]:

$$\eta_p\% = \left[\frac{V_{\text{corrb}} - V_{\text{corrc}}}{V_{\text{corrb}}} \right] \cdot 100, \quad (4)$$

where V_{corrb} is the corrosion rate for bare carbon steel and V_{corrc} is the corrosion rate for coated carbon steel.

Table 5 presents the efficiency values for both studied paint films. It results that the alkyd film with low VOC content presents better performances.

3.4. Surface analysis by AFM

Figs. 11 and 12 present three-dimensional images, topography and surface profile ($50 \mu\text{m} \times 50 \mu\text{m}$) for non-exposed samples. These revealed: a compact coating without pores with low roughness for alkyd paint film with low VOC content (Fig. 11) and a non-uniform coating with pores and with higher roughness for paint film with conventional alkyd resin (Fig. 12).

Table 5

The efficiency of the studied paints.

Paint film	Immersion time (h)	Efficiency (%)
MA	10	99
	50	98
	100	97
	300	95
	600	90
CA	10	97
	50	95
	100	93
	300	90
	600	85

3.5. SEM and EDX measurements

Figs. 13 and 14 present SEM micrographs (obtained from a cross-section) of the samples surface before and after 600 immersion hours in 3% NaCl solution. It is observed that, before immersion the MA coating is homogenous and adherent (Fig. 13a). After 600 immersion hours did not appear important changes (Fig. 13b).

SEM micrographs for CA coating revealed that, before immersion this film is adherent and homogenous (Fig. 14a). After 600 immersion hours, SEM images showed that the electrolyte have penetrated the film, have accumulated under it and the coating have begun to detach from metallic substrate (Fig. 14b).

Chemical elemental analysis by EDX (Figs. 15 and 16) confirms SEM observations.

For MA coating it was detected the same constituent elements both before immersion (Fig. 15a) and after 600 immersion hours

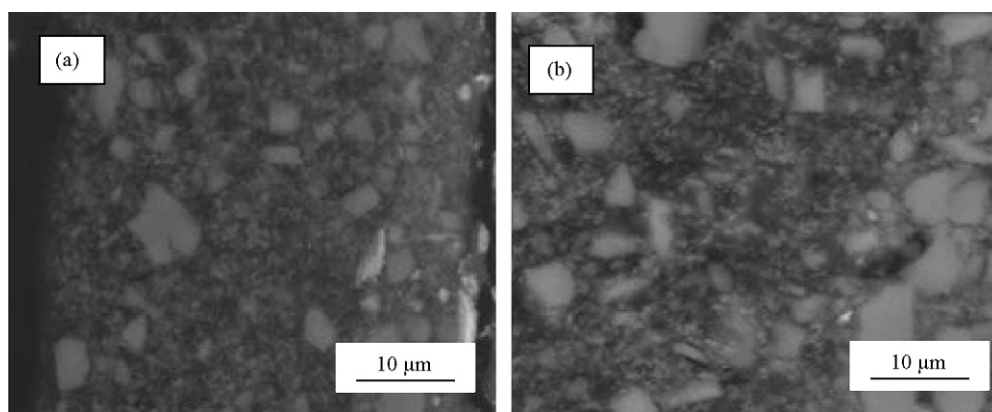


Fig. 13. SEM micrographs for MA coating before (a) and after 600 immersion hours (b) in 3% NaCl solution.

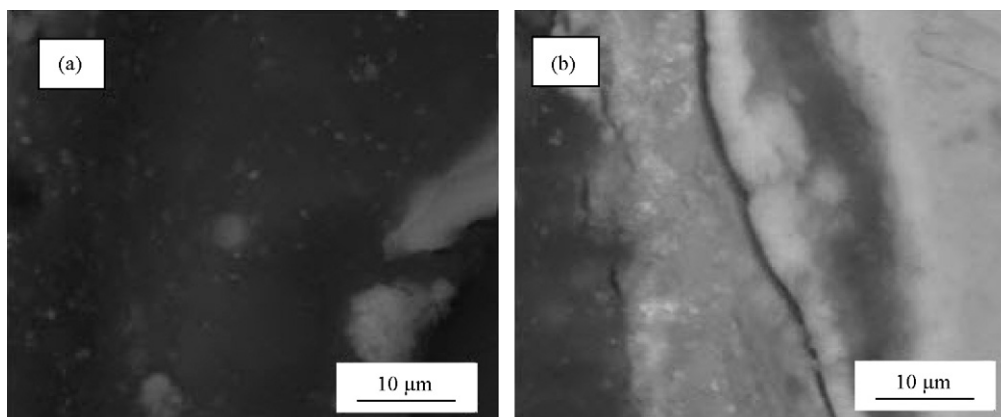


Fig. 14. SEM micrographs for CA coating before (a) and after 600 immersion hours (b) in 3% NaCl solution.

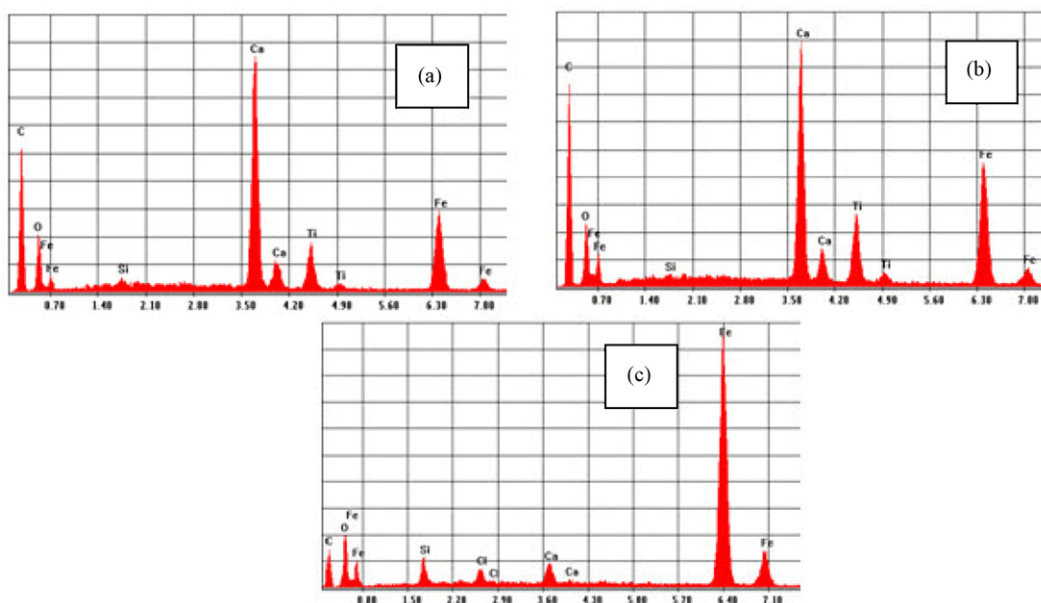


Fig. 15. EDX analysis for MA coating: (a) before immersion; (b) after 600 immersion hours; (c) at metal/paint interface after 600 immersion hours in 3% NaCl solution.

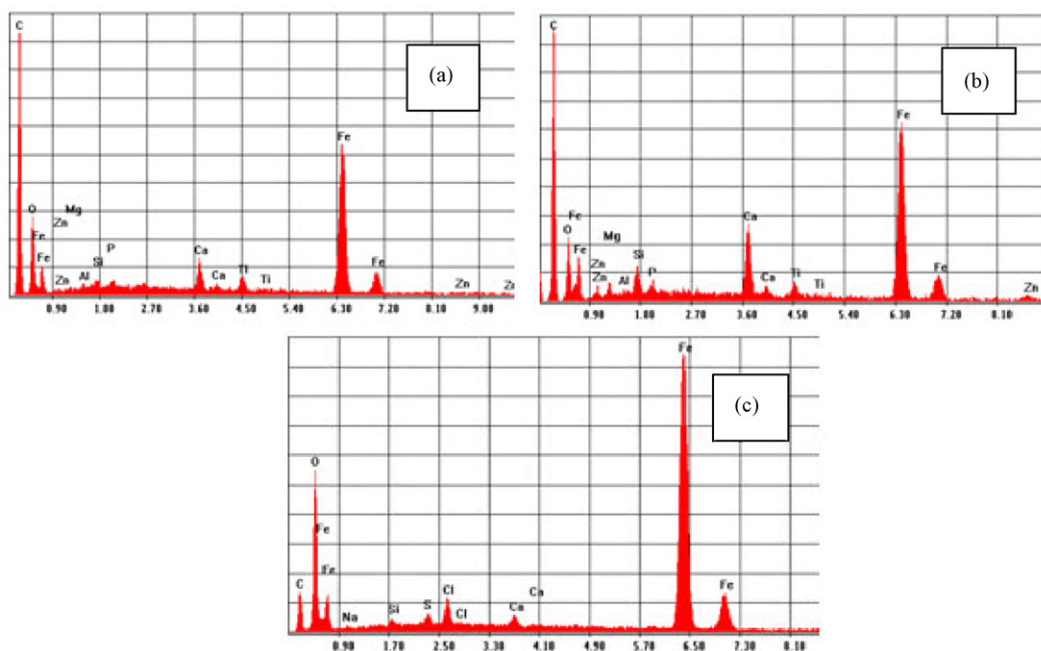


Fig. 16. EDX analysis for CA coating: (a) before immersion; (b) after 600 immersion hours; (c) at metal/paint interface after 600 immersion hours in 3% NaCl solution.

(Fig. 15b), proving that the paint film is resistant and did not degrade. The iron content slightly increases after 600 h (Fig. 15b) denoting transport process of iron ions through film. EDX analysis at the metal/coating interface after 600 immersion hours (Fig. 15c) revealed that the iron quantity increased; correlating with the impedance data (Section 3.1) that showed the presence of the double layer at this interface, it result that the corrosion process starts under film.

EDX elemental analysis performed on the CA coating detected about the same composition both before immersion (Fig. 16a) and after 600 immersion hours (Fig. 16b) in 3% NaCl solution, revealing some changes in this paint film. The quantity of oxygen and iron at the metal/coating interface after 600 immersion hours (Fig. 16c) increased very much due to the corrosion development under film and the formation of the iron oxides. It can be concluded that

the CA coating is more permeable to water and oxygen than MA coating.

4. Conclusion

1. The carbon steel/alkyd film/electrolyte system can be satisfactory simulated with two time constants: one time constant characterizing the organic coating and the other time constant concerning the metal surface.
2. For the characterization of the coatings, the physical properties obtained from the principal elements of the equivalent electrical circuits were used:
 - the evolution of the water absorption process in the alkyd coatings was established from the time dependence of the coating

- capacitance; the saturation value of the water uptake emphasizes a lower water permeability of the alkyd paint with low content of VOC;
- the ionic transport in the coatings was determined from the time trend of the coating resistance; it resulted a more reduced ionic transport in the alkyd paint with low content of VOC than for the alkyd conventional paint;
 - the corrosion processes at the carbon steel/coating interfaces were evaluated using the charge transfer resistance and the double layer capacitance; time evolution of the double layer capacitance showed that the wet metal area under coating is more reduced for the alkyd paint with low content of VOC; time trend of the charge transfer resistance stood out that the electrochemical reactions at this interface were slightly slowed down for the alkyd paint with low content of VOC than for alkyd conventional paint.
3. The results of the potentiodynamic and linear polarization were in concordance with the EIS results and offered supplementary information about the corrosion behaviour of the tested alkyd painted carbon steel. They confirmed the good performance of the alkyd paint with low content of VOC; its efficiency does not decrease in time below 90%.
 4. The alkyd paint with low content of VOC present a good adhesion to the carbon steel substrate; during the exposure period (600 h) no degradation or delamination process could be observed; surface analysis by AFM revealed a compact coating without pores; SEM micrographs showed that, before immersion the coating is homogenous and adherent and after 600 immersion hours did not appear important changes; EDX elemental analysis detected the same constituent elements both before immersion and after 600 immersion hours, proving that the paint film is resistant and did not degrade.

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