Electrochemical Assessment of the Protective Properties for Alkyd Paint Films with Various Thickness

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The aim of this paper was to investigate the influence of the film thickness on the anticorrosive properties of alkyd films. The films were realized in three thickness ranges (20-25, 40-45 and 60-65 μm) on carbon steel substrate. The electrochemical measurements (anodic polarisation and electrochemical impedance spectroscopy - EIS) were used for assessment of the protective properties of alkyd films in acid, neutral and basic solutions at 25^{0}C temperature during a 5000 h period. Porosity, water and ions permeability, adhesion to metallic substrate and efficiency of the films were determined. The experimental results showed that the increase of the film thickness determines the decrease of the dissolution current density of the carbon steel substrate under organic film and moves the corrosion potential in electropositive direction. The interpretation of the impedance spectra (Nyquist and Bode diagrams) with the immitance analysis Equivcrt. Program permitted modelling of the carbon steel/alkyd film interface with electrical equivalent circuits.

Keywords: alkyd film, anticorrosive properties, EIS, polarisation curves, film thickness

The protective properties of the organic films depend on a large number of different parameters as: the kind of the substrate [1-3], the pretreatment of the metallic surface [4,5], the paint composition [6-16], the painting cycles [17-20], the coating adhesion to metal substrate [21,22]. It is important to obtain information about the influence routes of the mentioned parameters on the properties of the metal/coating/electrolyte system. These information are very useful for the prediction of the anticorrosive behaviour of the various coatings in service. The electrochemical measurements can provide such information [23-29]. Among these techniques, the electrochemical impedance spectroscopy is widely used with good results for the characterisation of the organic films on metallic substrates [30-35].

This paper presents the results of the electrochemical measurements (electrochemical impedance spectroscopy - EIS and anodic potentiostatic polarisation) regarding the influence of the thickness of the alkyd coating on the corrosion behaviour of the carbon steel/alkyd film interface in the electrolyte solutions.

Experimental part

The organic films with the alkyd binder were deposited on carbon steel substrate, which previously was mechanical polished and degreased. The films were realised in three thickness ranges: 20-25 μm; 40-45 μm; 60-65 μm.

The experimental tests were carried out in: 0.5N H_2SO_4, 0.5N NaOH, 0.5N NaCl solutions, normally aerated at the 25^{0}C temperature for a total period of up to 5000 h of immersion. All solutions were prepared from reagent chemicals (Merck) and double distilled water.

A conventional electrochemical cell with three-electrodes was used: working electrode (painted carbon steel specimen), reference electrode (saturated calomel electrode -SCE) and counter electrode (platinum).

The electrochemical impedance measurements (EIS) were performed at the open circuit potential using a 5210 EG&G PAR Lock-in Amplifier connected to EG&G 283 PAR Potentiostat. The frequency range was 10 - 50 kHz and the sinusoidal voltage signal was 10 mV for the water penetration studies; for the rest of the determinations the frequency range was 0.1 Hz - 100 kHz and a sinusoidal voltage signal of 7mV was used. The experimental impedance spectra were analyzed on the basis of the equivalent electrical circuits using the fitting software Equivcrt. Program developed by Boukamp [36].

The anodic polarisation curves have been recorded for bare and painted carbon steel electrodes by stepwise polarisation (50mV/5min. step) after various immersion periods. The main electrochemical parameters were determined.

Optical microscopy was used to examine the paint degradation.

Results and discussion

Impedance spectra

The impedance spectra were registered during the immersion period in test solutions. Their evolution as a function of the immersion time in electrolytes shows changes of the impedance characteristics as a consequence of the variations in the dielectric properties of the coatings. These changes accentuated in time due to the electrolyte penetration in the paint film. Spectra have the same modifications in all tested solution (acid, base and neutral media).

Figures 1 and 2 present Nyquist, respectively Bode diagrams for carbon steel coated with films of different thickness after 1000 immersion hours in 0.5N NaCl solution. As can be seen from Nyquist spectra the impedance have similar values for 20-25 μm and 40-45 μm thickness, but higher for 60-65 μm thickness of the organic protective films. Bode spectra for the organic protective films with 20-25 μm and 40-45 μm thickness exhibited a maximum that shows the presence of double layer at the metallic substrate/alkyd film interface, namely the beginning of the corrosion process under coating. The organic protective

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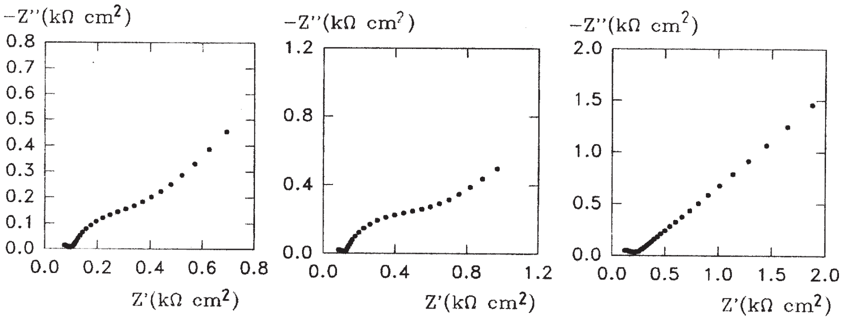
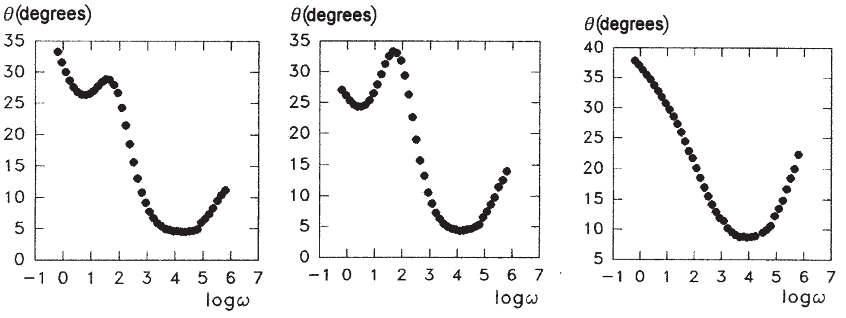


a) b) c)

Fig.1 Nyquist spectra after 1000 immersion hours in 0.5N NaCl solution for carbon steel coated with alkyd films of different thickness: a) 20-25 μm; b) 40-45 μm; c) 60-65 μm



a) b) c)

Fig.2 Bode spectra after 1000 immersion hours in 0.5N NaCl solution for carbon steel coated with alkyd films of different thickness: a) 20-25 μm; b) 40-45 μm; c) 60-65 μm

films with 60-65 μm thickness do not present any maxim proving better protective properties.

The analysis of the experimental impedance spectra on the basis of the fitting software Equivcrt. Program has established the most probable electrical equivalent circuits for tested systems. 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 calculated results.

It resulted that the fitting quality for the simulation of the carbon steel/alkyd film/electrolyte system with electrical equivalent circuits is satisfactory as follows:

- one time constant (fig. 3a) for the alkyd paint film (film capacitance Q_{pf} and film resistance R_{pf}) fitted for the first 100 immersion hours for the organic protective films with 20-25 μm and 40-45 μm thickness and 1500 immersion hours for 60-65 μm thickness films;
- two time constants, one constant characterising the alkyd paint film and other illustrating the reactions at the film/carbon steel interface (double layer capacitance Q_{dl} and charge transfer resistance R_{ct}), fitted for the period of 100-3000 immersion hours for 20-25 μm and 40-45 μm thickness of the organic protective films and for 1500-5000 immersion hours for 60-65 μm thickness films; figure 3b presents such circuit;
- four time constants, in addition the third time constant represents the pore existing in alkyd film (the pore capacitance Q_{por} and the pore resistance R_{por}) and the fourth for the diffusion processes through the alkyd film (the diffusion capacitance Q_{dif} and diffusion resistance R_{dif}), fitted for 3000-5000 immersion hours for 20-25 μm and 40-45 μm thickness of the alkyd paint films; this circuit is illustrated in figure 3b.

The evaluation of the time trends of the electrical paint film capacitance (Q_{pf}) and resistance (R_{pf}) has permitted to determine the protective properties of the alkyd films and the effect of the film thickness on their anticorrosive properties. Figures 4 and 5 present the time trends of these parameters in 0.5N NaCl solution for the tested films.

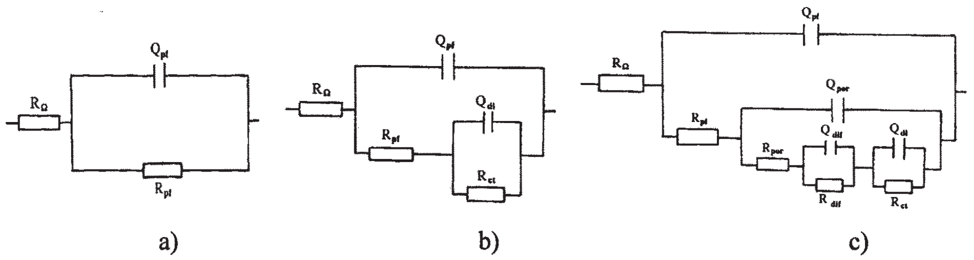
The capacitance evolution includes two different stages. An initial period up to 100 h with a significant increase due to the water uptake (capillary water) and a second one (100 – 500 h) where slight variation is observed (into polymer water); after that, the film is saturated with water. The time trend of the film resistance presents the same stages, but it decreases in time, because the conductive pathways develop in the film.

For acid and basic solution the time evolution of the film capacitance and resistance show the same behaviour.

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 the 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 [37].

The movement of the ions through films was estimated from the total area of conductive pathways, A_t [37].

Table 1 summarise the calculated values for the two uptaked water phase: "capillary water" and "into polymer water", as well as the saturation water for all tested films and total area of the conductive pathways. Data from this



a) b) c)

Fig. 3 Electrical equivalent circuits with: a) one time constant; b) two time constants; c) four time constants

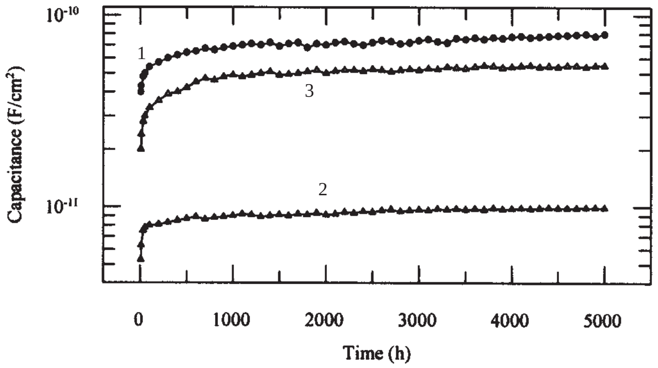


Fig. 4. Time dependence of the film capacitance after immersion in 0.5N NaCl solution for tested films:
1 - 20 - 25 μm; 2- 40 - 45 μm; 3 - 60 - 65 μm

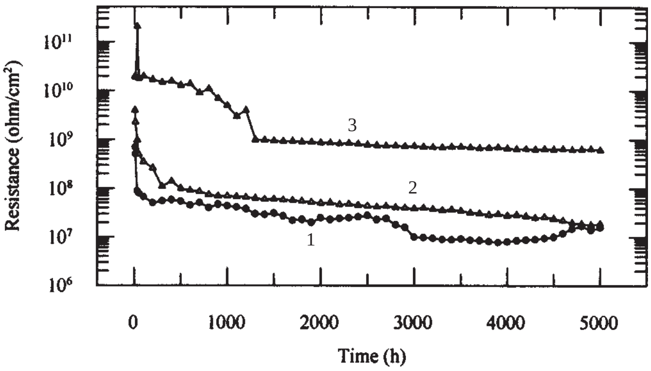


Fig. 5. Time dependence of the film resistance after immersion in 0.5N NaCl solution for tested films: 1 - 20 - 25 μm; 2- 40 - 45 μm; 3 - 60 - 65 μm

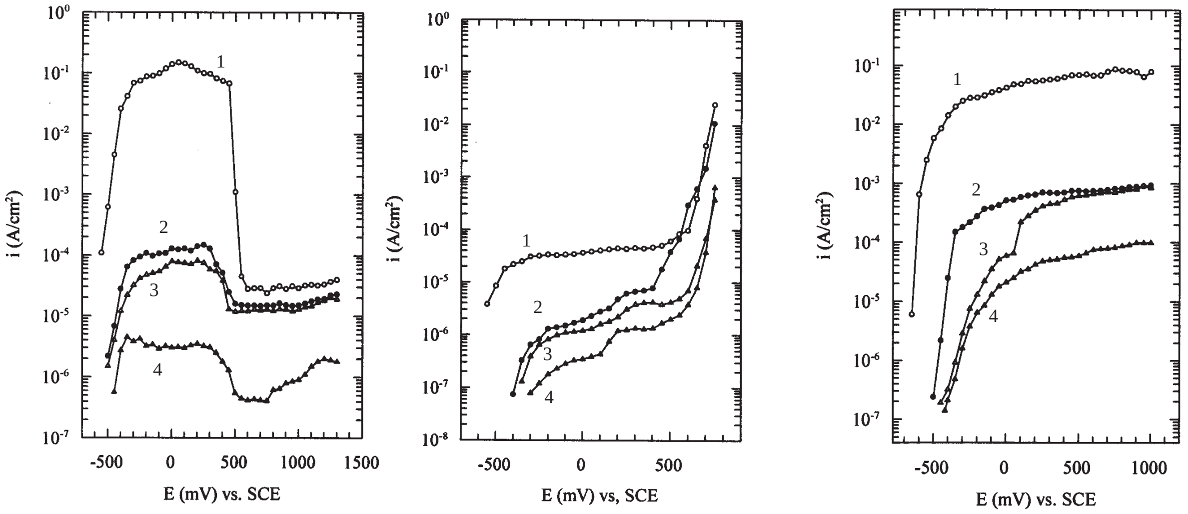
table show that the increase of the film thickness has a beneficial effect and reduces very much the water permeability of the alkyd film. The most intense ionic transport takes place in the alkyd film with the 20 - 25 μm thickness and the lowest transport is in that with 60 - 65 μm thickness.

Polarisation curves

The polarization curves offered supplementary information about the corrosion behaviour of the tested painted specimens, but these depended on the exposure time in the electrolyte solution before the polarization. Figure 6 illustrates the anodic polarization curves recorded

Table 1
WATER UPTAKE AND CONDUCTIVE PATHWAYS IN THE TESTED ALKYD FILMS

Solution	Parameter	Film thickness (μm)		
		20 - 25	40 -45	60 - 65
0.5N H_2SO_4	Capillary water (% in volume)	9.3	8.5	2.2
	Into polymer water (% in volume)	5.8	3.7	1.5
	Saturation water (% in volume)	15.1	12.2	3.7
	Total area of conductive pathways, A_t (cm^2/1 cm^2 coating)	$8.9x10^{-4}$	$6.7x10^{-4}$	$1.5x10^{-6}$
0.5N NaOH	Capillary water (% in volume)	8.9	8.2	1.9
	Into polymer water (% in volume)	4.8	2.5	1.3
	Saturation water (% in volume)	13.7	10.7	3.2
	Total area of conductive pathways, A_t (cm^2/1 cm^2 coating)	$9.1x10^{-4}$	$5.8x10^{-4}$	$1.5x10^{-6}$
0.5N NaCl	Capillary water (% in volume)	8	7.5	1.2
	Into polymer water (% in volume)	4	1.5	0.3
	Saturation water (% in volume)	12	11.3	1.5
	Total area of conductive pathways, A_t (cm^2/1 cm^2 coating)	$9.2x10^{-5}$	$4.3x10^{-5}$	$1.5x10^{-6}$



a) b) c)

Fig, 6. Anodic curves for bare (1) and coated carbon steel (2 - 20 - 25 μm; 3- 40 - 45 μm; 4 - 60 - 65 μm) after 1500 immersion hours in: a) 0.5N H_2SO_4; b) 0.5N NaOH; c) 0.5N NaCl

Table 2
ELECTROCHEMICAL PARAMETERS OF SAMPLES AFTER 24 AND 5000 IMMERSION HOURS

Solution	Parameter	Time (h)	Painted carbon steel			Bare carbon steel
			20-25 μm	40–45 μm	60-65 μm	
0.5N H_2SO_4	E_{corr} (V)	24	-0.48	-0.45	-0.42	-0.50
		5000	-0.52	-0.51	-0.47	-0.55
	i_{max} (A/cm^2)	24	$9.2x10^{-5}$	$5.8x10^{-5}$	$1.8x10^{-6}$	$7.5x10^{-2}$
		5000	$2x10^{-4}$	$9x10^{-5}$	$4.2x10^{-6}$	$2x10^{-1}$
	i_p (A/cm^2)	24	$9x10^{-6}$	$8.2x10^{-6}$	$2.5x10^{-7}$	$1.5x10^{-5}$
		5000	$1.5 x10^{-5}$	$1.1x10^{-5}$	$4x10^{-7}$	$5.2x10^{-5}$
0.5N NaOH	E_{corr} (V)	24	-0.40	-0.35	-0.30	-0.55
		5000	-0.44	-0.38	-0.32	-0.60
	i_{max} (A/cm^2)	24	$3.2x10^{-6}$	$1.5x10^{-6}$	$6.8x10^{-7}$	$1.5x10^{-5}$
		5000	$5x10^{-6}$	$3 x10^{-6}$	$8x10^{-7}$	$4x10^{-5}$
0.5N NaCl	E_{corr} (V)	24	-0.48	-0.45	-0.40	-0.7
		5000	-0.55	-0.48	-0.42	-0.72
	i_{max} (A/cm^2)	24	$4.4x10^{-4}$	$2.3x10^{-4}$	$8.9x10^{-5}$	$7x10^{-2}$
		5000	$1.2x10^{-3}$	$8.2x10^{-4}$	$1.1x10^{-4}$	$6.5x10^{-2}$

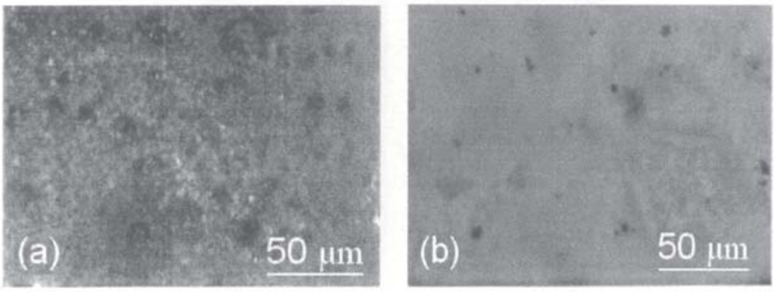


Fig. 7 Surface aspect of carbon steel samples coated with alkyd film after 5000 immersion hours in 0.5N H_2SO_4 solution for: a) 20 – 25 μm thickness; b) 40 – 45 μm thickness

after 100 immersion hours in all test solutions for the bare and painted carbon steel.

The specimens coated with the films can be characterized by a marked tendency to limit the corrosion of the carbon steel substrate. The corrosion potential of the coated specimens is nobler than the corrosion potential of the uncoated carbon steel samples and remains almost stable over time. The polarization curves show a decrease of the dissolution current density of the painted steel in comparison with the bare carbon steel. The main electrochemical parameters of the tested painted specimens slightly change in time (table 2). It resulted that the films with 60 – 65μm thickness present the best behaviour.

The microscopic assessment established that the film porosity decreases with the increase of the film thickness. The films with 20 – 25 μm thickness and 40 – 45 μm thickness present degradation in time in tested solutions. Microscopic studies emphasized the phenomenon of the blister formation, as an important stage in the degradation process of the coatings. So, after 500 h of immersion the blisters appear; these blisters increase in time, conducting at delaminated areas under coatings. The corrosion reactions start in these areas and the corrosion products appear on the outside film surface (fig. 7a and b).

The film adhesion to metallic substrate is very good for the films with 60 – 65 μm thickness; the samples coated with these films do not show corroded or delaminated areas during the whole immersion period.

Conclusions

By using the EIS measurements and polarisation curves, the influence of the organic film thickness on the protective properties of the alkyd films has been investigated.

The experimental results established that the film thickness has a significant influence on the water and ions permeability of the alkyd films. The best protective properties were obtained for the alkyd film with 60 – 65 μm thickness.

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