

CORROSION RESISTANCE OF ORGANOMETALLIC COATING APPLICATED IN FUEL TANKS USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY IN BIOFUEL – PART I

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Abstract

Nowadays, the industry has opted for more sustainable production processes, and the planet has also opted for new energy sources. From this perspective, automotive tanks with organometallic coatings as well as a partial substitution of fossil fuels by biofuels have been developed. These organometallic coated tanks have a zinc layer, deposited by a galvanizing process, formed between the steel and the organometallic coating. This work aims to characterize the organometallic coating used in metal automotive tanks and evaluate their corrosion resistance in contact with hydrated ethyl alcohol fuel (AEHC). For this purpose, the resistance of all layers formed between Zinc and EEP steel and also the tin coated steel, which has been used for over thirty years, were evaluated. The technique chosen was the Electrochemical Impedance Spectroscopy. The results indicated an increase on the corrosion resistance when organometallic coatings are used in AEHC medium. In addition to that, these coatings allow an estimated 25% reduction in tanks production costs.

Keywords: Organometallic coating; Steel fuel tanks; Electrochemical impedance spectroscopy; Resistive medium.

RESISTÊNCIA À CORROSÃO DE RECOBRIMENTO ORGANOMETÁLICO APLICADO EM TANQUES DE COMBUSTÍVEL USANDO A ESPECTROSCOPIA DE IMPEDÂNCIA ELETROQUÍMICA EM BIOCOMBUSTÍVEL – PARTE I

Resumo

Hoje em dia, a indústria tem optado por processos de produção mais sustentáveis, e o planeta tem também optado por novas fontes de energia. A partir desta perspectiva, tanques automotivos com recobrimentos organometálicos assim como a substituição parcial de combustíveis fósseis por biocombustíveis têm sido desenvolvidos. Estes tanques com revestimentos organometálicos têm uma camada de zinco, depositada por um processo de galvanização, interposta entre o aço e o recobrimento organometálico. Este trabalho objetiva caracterizar o recobrimento organometálico usado nos tanques automotivos metálicos e avaliar sua resistência à corrosão em contato com combustível de álcool etílico hidratado (AEHC). Para este propósito, foi avaliada a resistência de todas as camadas formadas entre o zinco e o aço de estampagem extra profunda (EEP) e também o aço recoberto com estanho, que tem sido usado por mais de trinta anos. A técnica escolhida foi a espectroscopia de impedância eletroquímica. Os resultados indicaram um aumento da resistência à corrosão quando os recobrimentos organometálicos são usados no meio de AEHC. Além disso, estes recobrimentos apresentam uma redução estimada de 25% nos custos de produção dos tanques.

Palavras-chave: Recobrimento organometálico; Tanques de combustível de aço; Espectroscopia de impedância eletroquímica; Meio resistivo.

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I INTRODUCTION

From the last decade, the world population has become more aware of the damage caused to the environment due to indiscriminate use of natural resources, leading the consumers to take a more critical attitude concerning their consumer choices. The search for non-toxic, biodegradable and recycled products became a driving force for industries in order to adapt their production processes and remain on the market [1].

Thinking about the biofuels demand in order to minimize environmental impacts, the world began to live the biomass and bioenergy era, with the introduction of a new agriculture model; non feeding, responsible for the production of renewable energy resources. The two main liquid biofuels used in Brazil are: ethanol (extracted from cane sugar) and, in an increasing scale, biodiesel, which is produced from vegetable oils or animal fats [1].

Hydrate ethanol (AEHC) can be used as fuel, or, when anhydrous, added to gasoline in a proportion between 20 and 25%. Law number 11,097 [2] approved a 2% biodiesel addition to automotive diesel (B2). This content was increased to 5% (B5), in January 2010.

To suit the new sustainable market requirements, some automotive manufacturers are now replacing the plastics automotive tanks by coated metal tanks. Metallic tanks are 100% recyclable and are not permeable to fuel, minimizing evaporative losses during their lifetime [3].

There are two major types of coating used to minimize corrosion process of metal tanks in contact with fuels: tin coatings and organometallic coatings. The latter have a zinc layer, deposited by hot-dip galvanizing process (*galvannealed*), formed between the extra deep drawing steel and the organometallic coating. Zinc forms intermetallic layers with steel, which are responsible for better adhesion of the organometallic coating. The tin coating is applied directly to the EEP steel and, after steel forming, the outside surface is painted by cathodic electrodeposition process - KTL. It is estimated that the cost of the organometallic coated tanks is around 25 % less than the tin coated tanks cost, once they have a cleaner production process, because they do not need to be painted after the tanks manufacture. This fact reduces production costs and generates less waste; therefore, they become more sustainable [4].

In evaluating the coating corrosion resistance, it is important to verify their ability to form an effective barrier in order to prevent metal corrosion when it is exposed to a corrosive environment. Among the various techniques for evaluating the corrosion resistance, Electrochemical Impedance Spectroscopy (EIS) has been widely used in electrolytic means. According Bierwagen *et al.* [5], the EIS technique is an excellent method to examine the protection corrosion properties of organic coatings. EIS combined with other accelerated tests, it is a very good

procedure to estimate the lifetime of corrosion protection coatings.

When EIS is used in a very resistive media, such as fuels and biofuels, Nyquist and Bode diagrams suffer deformations, making the results difficult to be analyzed. Brossia and Kelly [6] state that a low conductivity medium makes electrochemical tests difficult to be executed, due to high ohmic drop and also because the usual ohmic drop compensation is not always successful, as a result of the environment instability. They also point out that the reference electrodes developed for aqueous medium should not be used in organic resistive media, because they promote the organic medium contamination with water and electrolytes. In this case, according to Brett [7], the use of a quasi-reference electrode (EQR) is appropriate to prevent the organic medium contamination and to decrease the ohmic drop in a low conductivity media.

Studies on the ethanol corrosiveness are being carry out since the 80s. Souza *et al.* [8] studied the ethanol corrosion with and without corrosion inhibitors using the EIS technique. The results pointed to the use of two electrodes cells, with large area electrodes and small distance between them. This configuration showed to be more efficient for electrochemical impedance measurements in resistive media than the use of three electrodes configuration.

Santos *et al.* [9] studied the carbon steel corrosion in the ethanol medium, using a “Tait” electrochemical cell type with counter electrode and quasi-reference electrode (EQR) of AISI 316 stainless steel. The results showed that the electrochemical impedance technique was appropriate to be used in an ethanol electrolyte, but the results interpretation should be taken carefully. Also, significant differences from the metals behavior in conductive media were found.

Jakab *et al.* [10] used EIS to study the carbon steel corrosion resistance in biodiesel and diesel/biodiesel blends using a two carbon steel electrodes system, in which the electrodes are separated by a very small distance. The authors found that the results are influenced by the mixtures conductivity, so that, the conductivity is so low that no corrosion rate can be determined.

Aquino [11] presented the difficulties in evaluate the phenomena occurring in the metal/biodiesel interface, using the technique of EIS, due to the high medium resistance. As Souza *et al.* [8], Jakab *et al.* [10] verified that the electrochemical cell arrangement using two electrodes, with large area and small distance between them, is more suitable for resistive media than the three electrodes electrochemical cell. Then, the results obtained are used only to assess the quality of biodiesel.

In 1995, Bonora *et al.* [12] used EIS to evaluate the corrosion occurring in different types of organic coating deposited on metals, using an electrolytic medium. They proposed various equivalent electrical circuits for each system studied, in which it was possible to evaluate, from

the impedance results, the influence of the substrate type and the defects in the organic coating.

Miskovic-Stankovic *et al.* [13] evaluated, by EIS, the influence of epoxy coating deterioration, deposited on metal with different coating thicknesses, after several immersion days in a 5% w/v NaCl solution. They concluded that, the longer the corrosive medium exposure time, the greater is the pores increase on the coating surface, in other words, the greater is the corroded area. The corroded area extension was also evaluated by the reduction in charge transfer resistance and the increase in the electric double layer capacitance. Thicker films presented lower degradation rate.

The objective of this research is to perform the coating layers chemical characterization of the organometallic coated tanks used in automotive manufacture industry, as well as, to study these layers corrosion resistance when in contact with hydrated ethyl alcohol fuel (AEHC), using the Electrochemical Impedance Spectroscopy (EIS) technique and compare the results with the tin coating, commonly used in metal tanks.

2 MATERIAL AND METHODS

Initially, the chemical characterization of each coating layer deposited on EEP steel, which is steel used on the manufacture of organometallic coated metallic automotive tanks, was performed, through the scanning electron microscopy (SEM) technique, coupled with X-ray energy dispersive spectroscopy (EDS). The equipment used was FEG Scanning Electron Microscope - FEI Quanta 200.

The corrosion resistance evaluation of each layer deposited on the steel extra deep drawing (EEP) was performed by EIS, using a potentiostat IVIUM Compactstat. The electrochemical cell was assembled with the following elements: quasi-reference silver/silver chloride electrode, platinum counter electrode and study samples, as working electrode. The experiments were performed at corrosion potential, with potential amplitude of 500 mV. The frequency used for data acquisition ranged from 5.0×10^{-3} Hz to 5.0×10^4 Hz. Before the EIS measurements were taken, the open circuit potential was measured after the systems stabilization with minimum of 3600 seconds periods of time. The electrolytic medium studied was hydrated ethyl alcohol fuel (AEHC).

The quasi-reference electrode used for data acquisition was constructed in the laboratory by silver chloride deposition on a silver wire surface. The samples have an exposure area of 1 cm^2 each. Except for the studied surface, these electrodes were protected with "Colacoat" paint, resistant to fuels media, to avoid any interference on the results.

Initially, coatings that are in direct contact with the AEHC: organometallic and tinned coatings were studied.

To study the layer located just below the organometallic coating (*galvannealed* steel), entire organometallic coating was removed by mechanical friction, using cotton soaked in P.A. acetone. After tested, the zinc layer was solubilized by immersing each specimen in a 0.1 mol/L HCl solution, until de solution stop to bubble. This bubbling is due to the reaction that occurs between the acid and zinc, releasing hydrogen gas while zinc oxidizes. This procedure allows the removal of all coatings from the EEP steel surface.

To evaluate the AEHC potential aggressiveness, pH and conductivity parameters were measured. The pH test was performed according to NBR 10891 standard [14], in which the Ag/AgCl electrode is immersed in the sample fuel for a two minutes period of time. The equipment used was a pH meter model NTPHM TecnoPON MS coupled to an Ag/AgCl electrode. The electrical conductivity test was performed according to NBR 10547 [15]. The cell was immersed into fuel sample for a two minutes period, after which, the result was recorded. The equipment used was a conductivity Digimed DM32 model and results expressed in $\mu\text{Siemens.m}^{-1}$. All tests were performed in triplicate.

3 RESULTS AND DISCUSSION

Organic metallic coated sample profile micrograph was performed, according to Luciano [4], in order to visualize the deposited layers on EEP steel. In Figure 1, it can be noticed on the substrate (region 1), and above it, the existence of two thin layers (regions 2 and 3). Each of these regions had their chemical composition determined by EDS analysis.

Figure 2 shows that the region 1, attributed to the EEP steel, has a very strong iron element electronic transition when compared with other elements electronic transitions present: zinc, nickel, aluminum and carbon.

The region 2 was associated with the zinc coating (*galvannealed*), once it has more intense zinc electronic

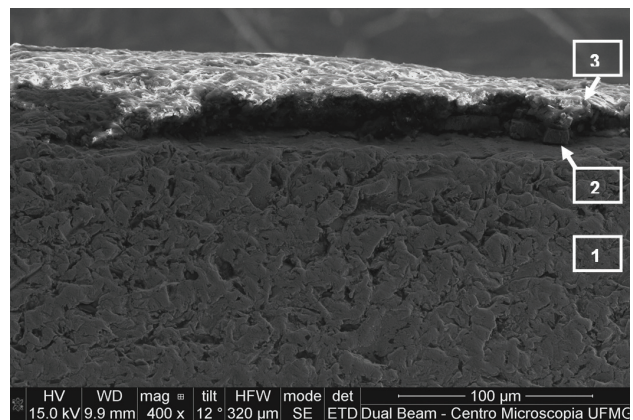


Figure 1. Micrograph of the organometallic coated metal sample profile.

transitions than iron electronic transitions, characteristic of the Fe-Zn intermetallic layer formation, which occurs during the galvanizing process (Figure 3).

In region 3, Figure 4, the high intensity of the carbon, oxygen and aluminum electronic transitions, and less intense magnesium, phosphorus and silicon electronic transitions indicate the presence of a compound with excellent covering ability. This fact can be proven by the absence of iron or zinc elements electronic transitions, obtained by EDS analysis.

Table 1 shows the results of pH and electrical conductivity of the electrolyte media used - AEHC as well as their limits for quality assurance according to ANP [16].

By analyzing the pH parameter, it was observed that the AEHC sample has high acidity, standing above of the standard specification [16]. The low value found for electrical conductivity parameter shows that this electrolyte is very resistive, making EIS technique measurements very difficult [8, 10, 11].

After knowing the AEHC quality parameters, the coating layers corrosion resistance, of different coatings used in automotive metallic tanks, was evaluate. For this, were acquired Nyquist and Bode diagrams (-phase (Φ) versus $\log(f)$) were obtained from EIS results, according to the methodology described in section 2. Nyquist diagrams are shown in Figures 5a and 5b.

In all Figure 5 diagrams, it is observed a capacitive arc formation, at high frequency regions. The increase in phase angle above about 10^4 Hz is probably due to the connecting cables capacitance and not related to any electrochemical process. The studied systems Bode diagrams in AEHC are presented in Figure 6

For tin coating (Figure 5a) and EEP steel (Figure 5b) systems, one time constant can be identified at low frequencies (between 1 and 10^{-3} Hz) related to electrochemical phenomena occurring at the metal/AEHC interface.

From Figure 6, the presence of only one more time constant, at low frequencies, can be observed. For each of these two systems, an equivalent electric circuit (Figure 7) was associated with electrolyte resistance (R_m) in series with the charge transfer from the metallic surface resistance (R_{ct}) and in parallel with a constant phase element (CPEI) from the electric double layer, represented by the Q_1 and n_1 parameters. Table 2 shows the numerical results attributed to each electric circuit element presented on Figure 7.

Analyzing the Bode plot (Figure 6), it can be seen that the maximum phase angle for tin coated steel is approximately 60° , and for the EEP steel is around 10° . These results indicate that the tin coated steel has a more capacitive behavior and EEP steel has a more resistive behavior. This can be confirmed by the analysis of the Q parameters, which is related to the coating non-ideal capacitance, as well as by the electric charge transfer impedance, R_{ct} (Table 2). The tin coating has higher values of R_{ct} compared with EEP steel, indicating a higher corrosion resistance in the AEHC medium.

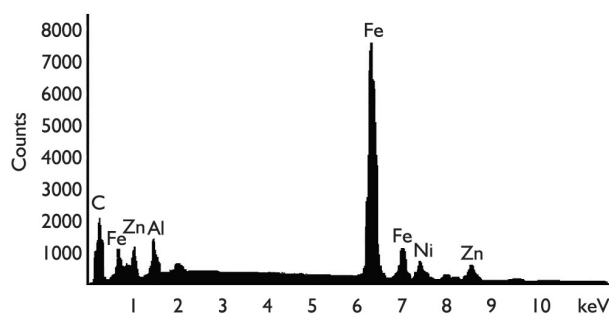


Figure 2. Region 1 chemical characterization - EEP steel.

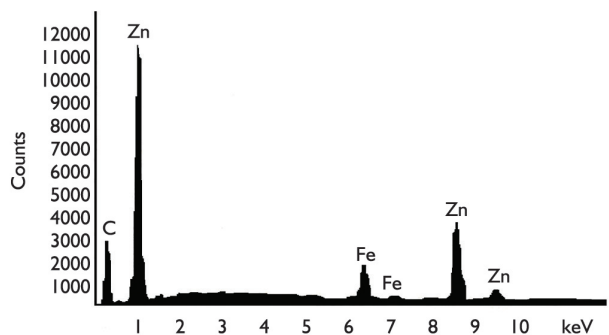


Figure 3. Region 2 chemical characterization - galvanealead.

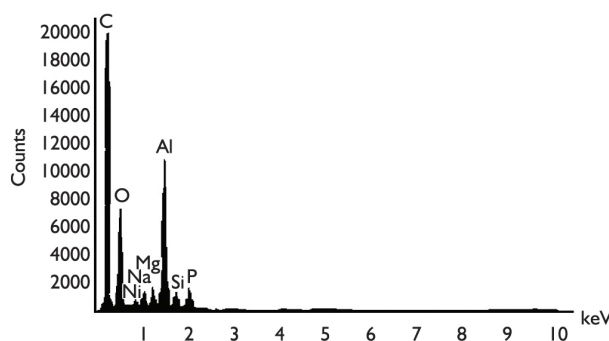


Figure 4. Region 3 chemical characterization - organometallic coating.

Table 1. AEHC quality parameters values

Parameters	Results	Limit Values	Standard
pH	4.9 ± 0.1	6 at 8	NBR 10891
electrical conductivity ($\mu\text{Siemens.m}^{-1}$)	187 ± 20	389	NBR 10547

The relative errors of the values found for each equivalent circuit element, in which the data were fit, were small, and the equivalent circuit has a physical significance relative to the studied systems.

Regarding to the zinc coating behavior, it is possible to observe a flattening in the second capacitive arc (Figure 5b) and the presence of two time constants at low frequencies, in the Bode plot (Figure 6). The increased surface porosity, the presence of corrosion products or

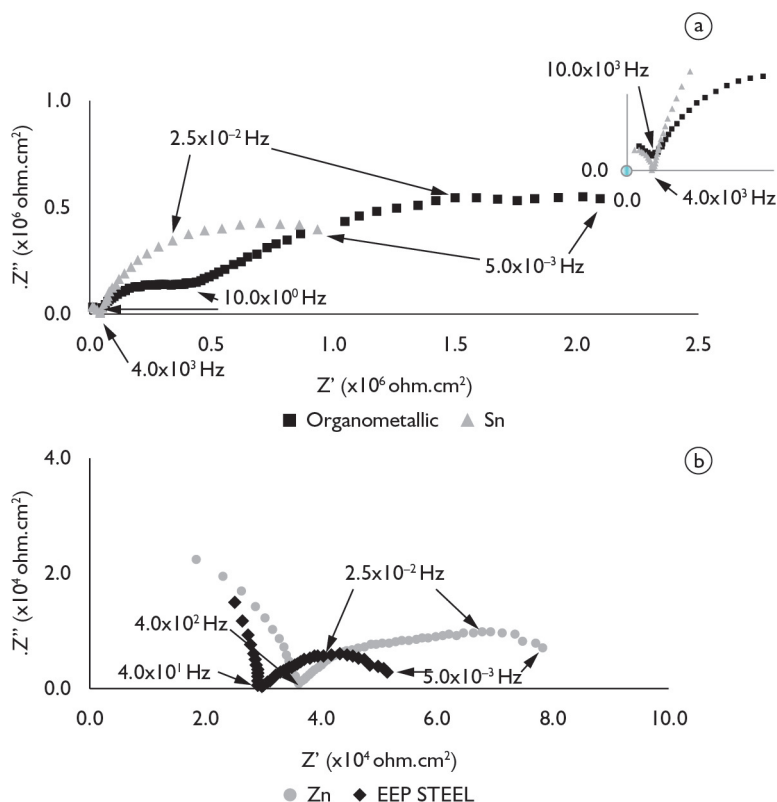


Figure 5. (a) Organometallic coated steel and tin coated steel Nyquist diagrams in AEHC medium; and (b) Galvannealed steel and EEP steel Nyquist diagrams in AEHC medium.

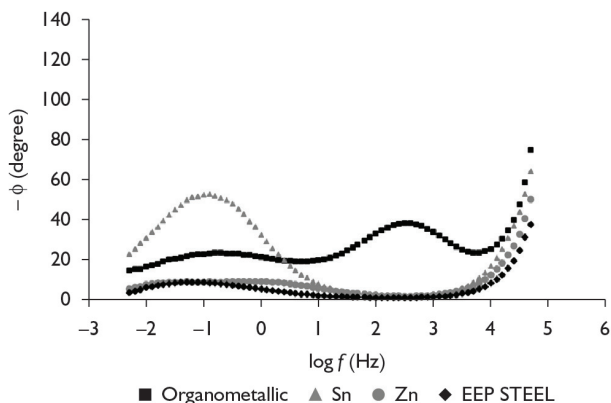


Figure 6. Studied systems Bode diagrams in AEHC solution.

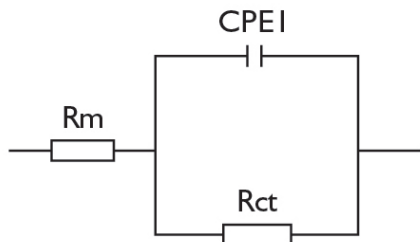


Figure 7. Equivalent electrical circuit associated with the systems formed by EEP steel and the tin coated EEP steel, in AEHC.

the presence of several Fe-Zn phases in the coating may be related to the existence of close time constants at low frequencies.

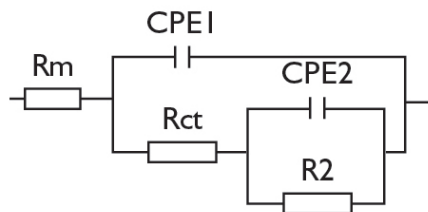
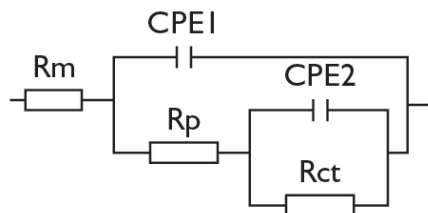
For this system, an equivalent circuit (Figure 8) was associated with the electrolyte resistance (R_m), in series with a first loop, where the charge transfer resistance (R_{ct}) is determined, and the electric double layer constant phase element ($CPE1$). The second circuit may probably be correlated with the diffusion processes caused by the presence of corrosion products (R_2 and $CPE2$), or a process at the pores bottom [12]. The results are shown in Table 2.

In AEHC medium, the phase angle associated with the zinc coated steel is as low as the phase angle for the EEP steel, indicating a more resistive behavior. The galvannealed steel impedance, in alcohol media, was of the same magnitude order than the one of the steel without coating, and was lower than the one of the steel without coating, and was lower than the Sn and organometallic coated steels impedance. An inefficiency of the use of zinc as the only protective barrier to corrosion caused by AEHC in metal fuel tanks was identified.

Analyzing Nyquist diagram for the system compound by organometallic coating in AEHC (Figure 5a), it is possible to observe two capacitive arcs beyond the capacitive arc associated with equipment cables. The Bode diagram (Figure 6) confirms the presence of these two capacitive arcs, with a time constant between 100

Table 2. Electrochemical parameters of EEP, tin coated, galvanized and organometallic coated steels in AEHC medium

	Elements	EEP Steel	Zn	Sn	Organometallic
	Rm (ohm)	2.997×10^4	3.585×10^4	4.387×10^4	2.086×10^4
	error (%)	0.005	0.013	0.076	0.887
	Rct (ohm)	2.540×10^4	2.564×10^4	1.252×10^6	2.500×10^6
	error (%)	0.024	0.216	0.024	0.064
	R2(ohm)	---	2.561×10^4	---	--
	error (%)	---	0.266	---	--
	Rp (ohm)	--	--	--	4.524×10^5
	error (%)	--	--	--	0.175
	Rtot (ohm)	2.540×10^4	5.125×10^4	1.252×10^6	2.952×10^6
CPE1	Q1(ohm.cm ² .s ⁿ)	6.201×10^{-8}	7.397×10^{-9}	1.491×10^{-7}	9.07×10^{-13}
	error (%)	0.432	1.703	0.293	3.097
	n1	0.57	0.60	0.76	0.59
	error (%)	0.076	0.308	0.000	0.402
CPE2	Q2(ohm.cm ² .s ⁿ)	---	1.833×10^{-6}	---	3.035×10^{-12}
	error (%)	---	2.881	---	1.394
	n2	---	0.66	---	0.51
	error (%)	---	0.381	---	0.187

**Figure 8.** Equivalent electric circuit associated with the system formed by zinc coated EEP steel in AEHC.**Figure 9.** Associated electrical circuit equivalent to the system formed by galvanized EEP steel with organometallic coating in AEHC.

and 1000 Hz and a time constant at lower frequencies (0.1 Hz), which is associated to electrochemical reactions occurring on the zinc coating surface, due to the flaws in the organometallic coating.

Bonora *et al.* [12] proposed a similar equivalent electric circuit to be applied in the study of epoxy coatings in electrolyte medium. The equivalent electrical circuit proposed in Figure 9 [13] is similar to that proposed for zinc; Rp is the ionic impedance of the organometallic coating impregnated with the electrolyte and CPE1 is the non ideal coating capacitance. The second series circuit with Rp can be correlated to the charge transfer resistance (Rct) and the constant phase element (CPE2) of the

electrical double layer at the organometallic coating/zinc coating interface. The results are shown in Table 2.

The organometallic coated steel polarization resistance was two orders of magnitude higher than the galvanized steel polarization resistance and twice the value of the tin coated steel resistance.

The association of the organometallic coating with galvanized EEP steel is very advantageous, because in addition to having a lower cost of production and generate less waste to be treated at the end of the production process, they are even more resistant to corrosion than tin coated steel tanks.

4 CONCLUSIONS

The use of silver/silver chloride quasi-reference electrode and the application of a large potential amplitude allowed to evaluate the corrosion resistance of metal surfaces and organometallic coated steel used in automotive steel tanks industry, in a resistive medium (AEHC), through the Electrochemical Impedance Spectroscopy technique. The results interpretation was only possible due to previous knowledge of the organic resistive solutions electrochemical behavior.

The organometallic coated steel polarization resistance was two orders of magnitude higher than the galvanized steel polarization resistance, and twice the value of the tin coated steel resistance.

Acknowledgements

The authors thank the Fuel Testing Laboratory (LEC) of Federal University of Minas Gerais, the Microscopy Center of Federal University of Minas Gerais, and Petrobras.

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Received: 11 Nov. 2013

Accepted: 16 June 2014