# USE OF INTRINSICALLY CONDUCTIVE POLYMER IN THE ANODIC PROTECTION OF STEEL SAE 1006[1]

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## Abstract

One of the methods to prevent corrosion is the anodic protection, which is characterized by the formation of a protective oxide film, promoting the passivation of metallic material and the slowdown of the corrosion process. The use of intrinsically conductive polymers such as polyaniline (PAni) has been presented as an alternative in protective coating against corrosion because it provides the amplification of the effect of passivation. It is possible through the union of a specific plasticizer and undoped PAni, or emeraldine base, to obtaining films self-supported and against corrosive process in metallic substrates.The coating was produced by mixing the emeraldine base, organic solvent and plasticizer 4-chloro-3-methylphenol. The film obtained was applied to the sheets of carbon steel SAE 1006 with the use of a Spin Coater equipment. The electrochemical tests were carried out from the for techniques cyclic voltammetry, open circuit potential and impedance spectroscopy electrochemistry in an aqueous solution of $H_2SO_4$ 4M. The results showed that the film of emeraldine base has capacity for metal protection against corrosion for a period determined by anodic protection mechanism.

**Key words**: Corrosion; Polyaniline; Coating; Carbon steel.

## USO DE POLÍMERO INTRINSECAMENTE CONDUTOR NA PROTEÇÃO ANÓDICA DE AÇO SAE 1006

## Resumo

Um dos mecanismos de combate à corrosão é o método de proteção anódica, que se caracteriza pela formação de um filme de óxidos protetores, promovendo assim a passivação do material metálico e a desaceleração do processo corrosivo. O emprego de polímeros intrinsecamente condutores, como a polianilina (PAni), tem-se apresentado como alternativa de revestimento protetor contra a corrosão, pois proporciona a amplificação do efeito de passivação do metal. É possível através da união de um plastificante específico e de PAni desdopada ou esmeraldina base, a obtenção de filmes auto-suportados e protetores contra o processo corrosivo de substratos metálicos. O revestimento foi produzido através da mistura da esmeraldina base, solvente orgânico e plastificante 4-cloro-3-metilfenol. O filme obtido foi aplicado em placas de aço carbono SAE 1006 com o uso do equipamento Spin Coater. Os ensaios eletroquímicos foram realizados a partir das técnicas de voltametria cíclica, potencial de circuito aberto e espectroscopia de impedância, em uma solução aquosa de $H_2SO_4$ 4M. Os resultados obtidos demonstraram que o filme de esmeraldina base tem capacidade de proteção do metal contra a corrosão, por um período determinado, através de mecanismo de proteção anódica.

**Palavras-chave**: Corrosão; Polianilina; Revestimento; Aço.

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## 1 INTRODUCTION

The early utilization of protective mechanisms to prevent corrosion of oxidizable metals started in the mid 50s, when the anodic protection was first seen, observing a stainless steel boiler exposed the sulfuric acid solutions. This protection technique provides a reduction in the rate of corrosion in metals effectively, being their main advantages the applicability in highly corrosive solutions and the necessity of low electric current. However, this mechanism is not widely used because it needs electrical equipment of high economic value and, its installation and maintenance are complex. Moreover, there is the sensitivity of the technique, due to the small amplitude of potential tracks that promote the anodic protection. At potentials outside this range may occur, in a destructive way, acceleration of the rate of metal corrosion.(1)

With this, organic coatings have been presented as an alternative for corrosion protection of metallic materials susceptible the passivation or anodic protection, in harsh environments. Since the discovery of intrinsically conductive polymers (PIC) and, their electronic properties, was observed that the oxidation-reduction mechanisms are the base of the efficiency of the metallic coating by ICP. These are presented as a promising constituent of paint or a pre-coating for metal substrates.(2,3)

Polyaniline (PAni), an PCI of the polyamines family, has attracted the attention of researchers due to its environmental characteristics, solubility, processability, ease of doping and undoping and, polymerization. The utilization of polyaniline (PAni) as a protective film, may present the mechanism of spontaneous reduction, i.e oxidation of the metallic surface, which promotes the anodic protection of the metal and, consequently, protection against corrosion.(4)

The films produced based on polyaniline in the oxidized conductive state or protonated emeraldine (PAni EP), present difficulty in forming self-sustaining films, with enough cohesion to form a protective coating against corrosion. So the use of PAni in the oxidized and non-conductive state (undoped) or base emeraldine (PAni EB) in the formation of films, has been presented as an option to corrosion inhibition, through its ability to form self-supported films and enabling a greater time of corrosion protection of oxidizable metallic materials. Production of the coating must occur by a chemical process, where is associated with PAni EB, organic solvent and plasticizer low molecular weight.(5,6)

This study aims to analyze the electrochemical capacity electrochemical of carbon steel SAE 1006, coated with film based on PAni EB, composed of a component of cohesion, plasticizer 4-chloro-3-methylphenol (CMF), and an organic solvent used to disperse the polymer and, adjust the drying time of the binder. The observations will be performed from electrochemical tests of Cyclic Voltammetry (CV), Open Circuit Potential (OCP) and Electrochemical Impedance Spectroscopy (EIS), conducted in a $H_2SO_4$ 4M solution. And from these observations, present the formation of passivating oxide induced film of PAni EB on the metal surface, thereby promoting anodic protection of carbon steel SAE 1006.

## 2 MATERIALS AND METHODS

Materials and methods were divided according to the stages of application, production and electrochemical tests, in order to analyze the effectiveness of protection of carbon steel, by the PAni EB, film against corrosion in $H_2SO_4$ 4M solution.

## 2.1 Production and Application of PAni EB Film

The protective coating was produced with using of the ratio by weight of 1:2 of PAni EB and CMF, respectively. Besides of the addition organic solvent, chloroform ($CHCl_3$), with the objective of to control the drying time and to dissolve PAni EB in the CMF. These components were homogenized for 6 hours at high speed disperser Dispermat Model N1.(3,6,7)

The work electrode used was carbon steel SAE 1006, composed with maximum in the 0.08% C, between 0.25%-0.40% Mn, max 0.040% P and in the maximum 0.050%S. Was performed in alkaline degreasing process using the degreaser Saloclean 619L, the steel was subsequently washed (in water) and dried by applying hot air jets. This process aims to obtain metal parts with chemically clean surface, being applied the immersion of the part at a temperature of 45°C, in concentration of 5% w/v, with the immersion time of 15 minutes.(2,4) After these processes, the coating was applied with the aid of the equipment Spin Coater KW-4, with the rotation speed set to 100 rpm, shown in Figure 1.(4,8)

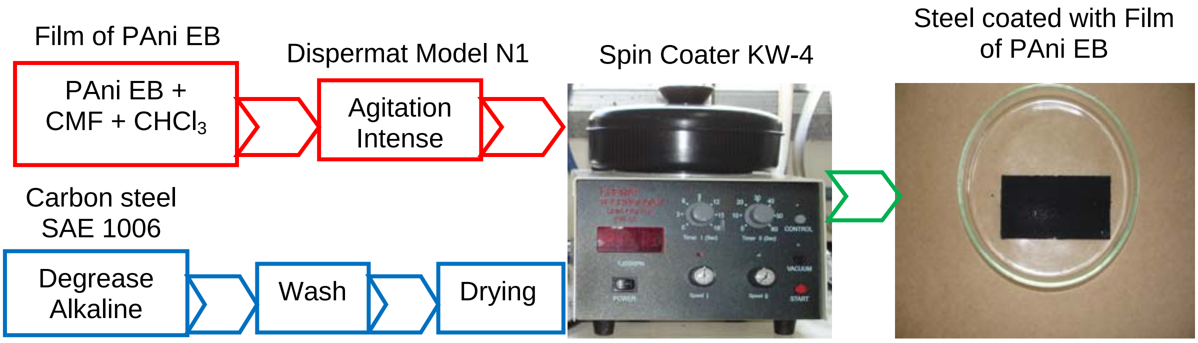

**Figure 1**: Schematic representation of the preparation, by chemistry, the film of PAni EB and its application on steel SAE 1006.

## 2.2 Equipment for Electrochemical Studies

The electrochemical tests were performed with the aid of equipment Potentiostat/Galvanostat Autolab PGSTAT302 Ecochemie and, with using a conventional three electrodes cell. The auxiliary electrodes as 99.99% Pt wire (counter electrode) and reference electrode Ag/AgCl, beyond work electrode, the carbon steel SAE 1006 with or without coating. Thus, with this equipment can be evaluated the corrosion protection, by electrochemical tests of CV, EIS and OCP in $H_2SO_4$ 4M solution, observed in Figure 2.

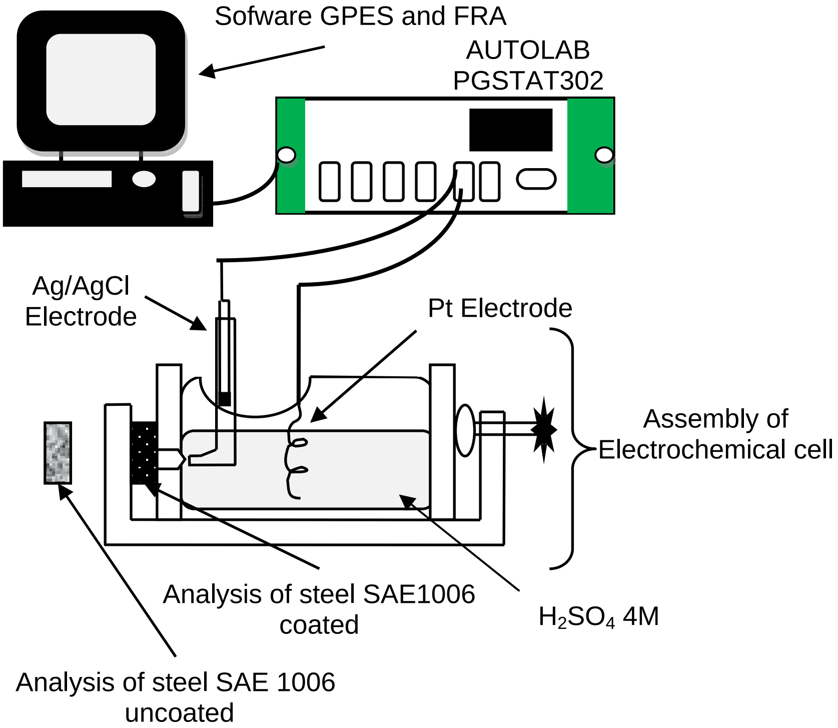

**Figure 2**: Schematic representation of equipment used in electrochemical tests in the sample with and without coating.

To interpretate the data obtained with the CV and OCP assay, was used the software GPES, and for the results obtained from EIS tests, was used the software FRA. These tests aim to get answers from the analysis of regions anodic, cathodic and passivation, and of electrical resistance of the samples.

## 3 RESULTS AND DISCUSSION

The electrochemical techniques performed (CV, OCP, EIS) used as electrolyte, sulfuric acid $H_2SO_4$ 4M and carbon steel SAE 1006 as work electrode, with and without coating. The Results and discussions were divided according to the electrochemical techniques used to observe the protective capability against the corrosion.

### 3.1 Electrochemical CV Assay

The CV test for the electrode without coating was performed by applying potential of $25mV.s^{-1}$ for sweep from -0.50 to $2.0V_{Ag/AgCl}$, shown in Figure 3. It was observed from the potential from $-0.5V_{Ag/AgCl}$ an active region until around $-0.37V_{Ag/AgCl}$, where is verified a cathodic region. After, the potential reaches $0.45V_{Ag/AgCl}$ which is characterized as a peak of corrosion (anodic).(5,9)

The potential range between $0.45V_{Ag/AgCl}$ to $1.75V_{Ag/AgCl}$ is attributed to the region of passivation of the metal, where there is the formation of ferric oxides. In the potential region above $1.75V_{Ag/AgCl}$, occurs the transpassivation process with increasing current and, release of oxygen from the electrolyte. The reverse scan showed the same anodic and cathodic regions described in the initial scan.(10,11)

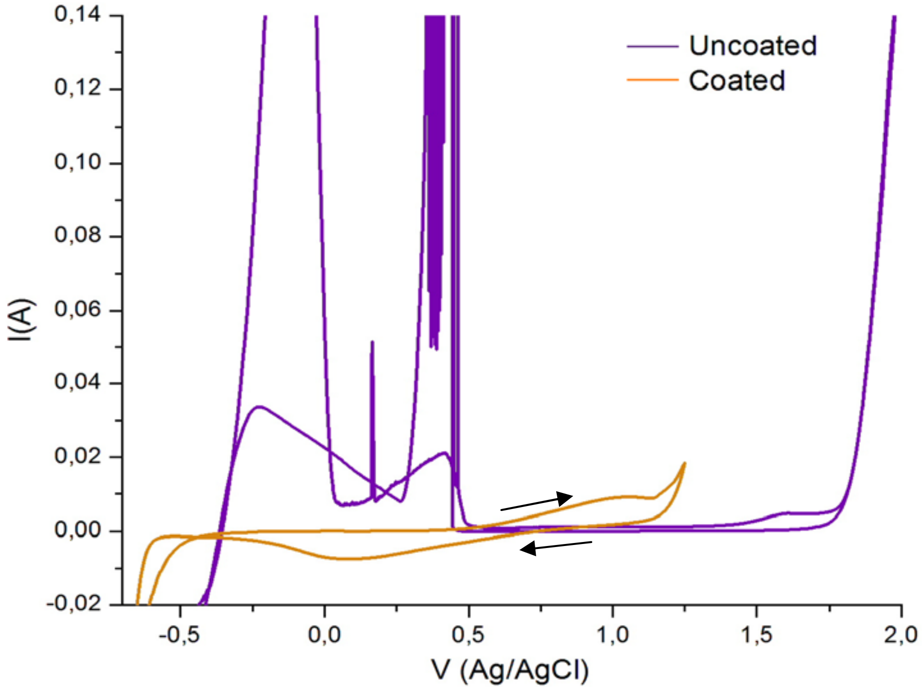

**Figure 3**: CV analysis of steel SAE 1006 with and without coating.

The carbon steel coated with the film of PAni EB, presented a voltammogram from of the application of potential $25mV.s^{-1}$ between -0.75 and $0.50V_{Ag/AgCl}$, where was found, conform Figure 3, a (active) cathodic region (reduction), which was stabilized in $0.45V_{Ag/AgCl}$ potential. From this potential was observed (active) anodic region (oxidation), attributed to the reduction of PAni EB and the subsequent oxidation of the metal. The scan reverse presents the region of oxidation of PAni EB next of potential $0.74\ V_{Ag/AgCl}$, consistent with the passivation region of the work electrode.(11,12) With that, one can infer the presence of a redox couple in the region $0.45V_{Ag/AgCl}$ (reduction) and $0.74V_{Ag/AgCl}$ (oxidation), characteristic of PAni EB and, within region the passivation of the work electrode without coating, resulting in the formation protectives oxides against corrosion, and the consequent anodic protection of the metal.(12,13)

## 3.2 Electrochemical OCP Assay

The OCP technique was performed with immersion of the electrode with and without coating, in $H_2SO_4$ 4M, for a predetermined period of 1000 seconds.(11) The Figure 4, presents the analysis test data generated by the assay OCP of carbon steel without the coating, which has a initial abandonment potential of $1V_{Ag/AgCl}$. The abandonment potential was used in an attempt to equalize the start of testing in order to inhibit the possible influence of impurities on the surface of ET that could alter the results in early analysis.

After 5s was detected the decay of the potential $0.20V_{Ag/AgCl}$ to $-0.40V_{Ag/AgCl}$ where the rate remained almost constant for the entire period of analysis, being characterized with the potential for corrosion of metal.

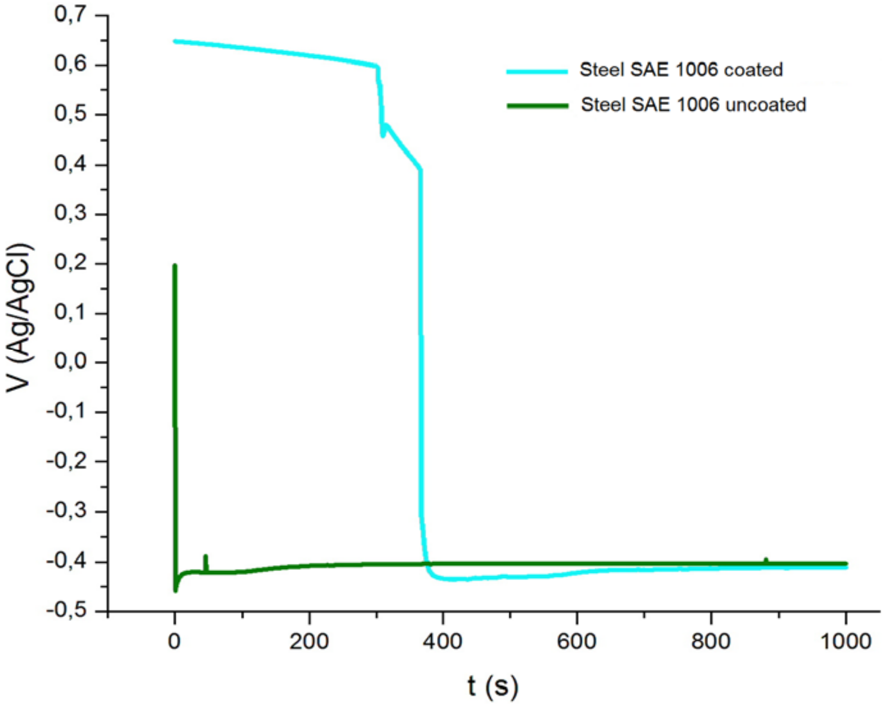

**Figure 4**: OCP test of SAE 1006 steel with and without coating.

Figure 4 shows the assay of OCP of carbon steel coated with a film of PAni EB, having as potential of abandonment 1$V_{Ag/AgCl}$. After 5s, was presented a curve which was initiated at a potential of 0.68$V_{Ag/AgCl}$, for a period of 370 seconds and, posteriorly had a drastic decrease to levels similar to the curve of the uncoated electrode, i.e at the corrosion potential.

According to the results of OCP of SAE 1006 steel, it was observed that the extra potential provided by redox couple characteristic of PAni EB to the system, results in the formation of its protective oxide layer, making a metal, before vulnerable to corrosion, capable of withstand the corrosive environment by the action of anodic protection produced by PIC.(10,14)

### 3.3 Electrochemical EIS Assay

The EIS technique was employed with the representation in the Nyquist diagrams, with frequency sweep from 100 kHz to 10 mHz, with immersion of the samples (0.60 $cm^2$) with and without coating, in $H_2SO_4$ 4M, for a period of 5 min. The Figure 5(a) presents the Nyquist diagram of the uncoated sample, revealed an arc with resistance values of about 4(Ohm).$cm^2$. These spectra reveal that the corrosion process is already installed in the sample, where the falls potential to values in the order for potential for corrosion of steel SAE 1006, possibly the potential values of -0.40$V_{Ag/AgC}$.(3,15)

Figure 5 (b) presents the EIS spectra obtained by the sample covered with PAni EB, film, during the potential of 0.68$V_{Ag/AgCl}$, this was divided into three regions: a semicircle in highs frequencies (1), a straight with frequencies medium with and a maximum slope of 45° (2) and a vertical straight at the limit of low frequencies (3). The presence of the semicircle (1) at high frequencies is characterized by the interfacial process of transfer charge between the coating and metallic substrate, i.e reducing of the polymer and oxidation of the steel. The region (2), in medium frequencies, is attributed to an ionic diffusion, due to transport of ions $HSO_4^-$ of the solution into the film, leading to the oxidation of PAni EB. The straight vertical region (3) shows that the diffusion was halted in the system film/electrode, which is characterized with a passivation region, with presence of iron oxides which increase the electrical resistance of the system and, consequent protection of carbon steel.(3,15,16)

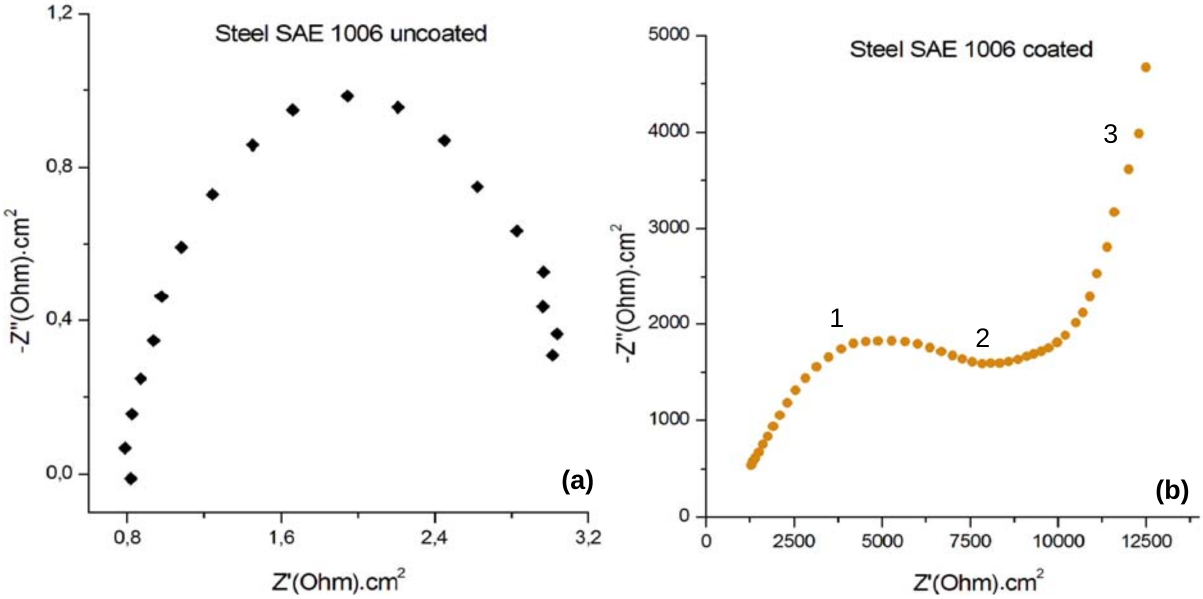

**Figure 5:** EIS Nyquist representation in (a) uncoated and (b) coated Film PAni EB, the potential of OCP for 5 min immersion in $H_2SO_4$ 4M.

## 4 CONCLUSION

Conform the objectives of this study, the utilization of PAni EB and CMF as components of an anticorrosive resin, presented results that promote the anodic protection carbon steel SAE 1006, because through electrochemical assay (CV, OCP and EIS), there was a distancing from the potential of corrosion of the electrolyte ($H_2SO_4$ 4M)/electrode(carbon steel) system for a period of 370s, doing with that the metal, in question, behave so as a more noble, through of forming a passivation layer, which represents the protection action of the metallic electrode by anodic mechanism, beyond of possible barrier effect this coating should provide.

With that, the utilization of plasticizer CMF and of the PAni EB, in the form of functional resin, showed with a new option in the line of research of anti-corrosives resins, which promote anodic protection of steels oxidizable.

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