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ELECTRO DEPOSITION OF M-AMINO PHENOL ON LOW CARBON STEEL AND CORROSION PROTECTION STUDIES

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Galvanostatic deposition technique is used to obtain poly m-aminophenol coating on low carbon steel samples in basic hydroalcholic medium. These coatings were characterized by using FTIR spectroscopy and electrochemical methods. The existence of C–O–C etheric and –NH2 groups in the FT-IR spectrum confirms presence of m-aminophenol.Corrosion rate of poly (m-aminophenol) in 3.5 % NaCl is found to be 2.14 mpy which is about two times lower than that of unpainted low carbon steel in neutral medium and coating protects steel by barrier mechanism.

Keywords: Galvanostatic deposition, m-aminophenol, Low carbon steel

1. Introduction

Metals are thermodynamically unstable in their refined form and tend to revert their natural states through the process of corrosion. Corrosion can be defined as the destruction or deterioration of a material because of reaction with its environment [1]. Perhaps, the most corrosion prevention method is the use of inhibitive paint coating containing pigments. The primary films that are intended to have a protective action against corrosion of the substrate are only rarely used if ever non-pigmented. The pigment is incorporated to enhance the barrier action of the basic polymer [2]. These pigments have harmful effects on environment when they are released in substantial amounts. Since basically in all pigments the release of inhibitors is based on leaching, coatings need to be highly pigmented in order to ensure a sufficient pressure of inhibitors over the years. There is a need to replace conventional inhibitive paint contents by environmental friendly and non toxic formulations. Recently, use of phenols and its derivatives have shown the promise in corrosion protection applications. Phenols are aromatic hydroxyl compounds in which the hydroxyl group is directly attached to the benzene ring or aromatic nucleus site [3]. In m-aminophenol, NH_2 is substituted at meta position as shown in figure 1**.**

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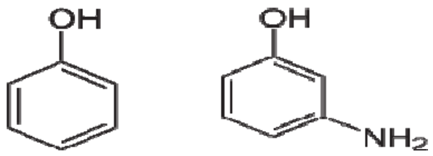

Figure 1.Structure of phenol and m-aminophenol [3]

Amino phenols are interesting electrochemical materials since, unlike aniline and other substituted anilines, they have two groups (–NH_2 and –OH) which can be easily oxidized. Therefore, they can show electrochemical behaviour resembling anilines and phenols [4]. In general these films are very thin, adherent and present low water mobility and low permeability to different ionic and molecular species [5]. This paper is prepared to investigate the possibility of electro deposition of m – amino phenol on low carbon steel and study its corrosion protection aspects.

2. Experimental Procedure

All chemicals required for electro deposition of m-aminophenol on low carbon steel used were analytical reagents (AR Grade, supplied by Loba Chemicals, Mumbai, India) and used as received in Table 1.

Table 1

Chemicals used for coating on steel samples

Chemicals	Formula	Molecular weight
m-Aminophenol	C_6H_7NO	109.13
Sodium hydroxide	NaOH	90.3
Ethanol	C_2H_6O	46.06

The samples for the experiments were cut from the sheet of low carbon steel (AISI 1015). Before each experiment, the specimen was dry polished by using a series of emery papers. The final approximation to a flat scratch free surface was obtained by use of the lapping machine. The specimen was then washed under running water and dried. The electrochemical deposition of m-aminophenol on low carbon steel samples AISI 1015 was carried out at room temperature in a simple one compartment glass cell under galvanostatic conditions. A three electrode geometry were employed during electropolymerization of m-aminophenol on low carbon steel as working electrode (6 cm^2), stainless steel as counter electrode and saturated calomel electrode (SCE) as a reference electrode. The polarization experiment done in hydroalcholic medium of 0.3 M NaOH with water: ethanol (70:30) in which 0.1 M m-aminophenol has added. After getting coating, steel substrate was removed from electrolyte and dried in air. Desiccator was used for storage of samples. Half of the coated samples were damaged by using 0.8 mm drill to simulate defective coating. A Gamry PC3/600 potentiostat/galvanostat/ZRA system (Wilmington, USA) was used for electropolymerization and corrosion studies. This system was interfaced to a personal computer to control the experiments and the data was analyzed using Gamry CMS-300 framework/analysis software. Galvanostatic deposition parameters used for polymerization of m- aminophenol on low carbon steel are included in table 2.

Table 2

Electro deposition parameters

Initial current density	0.5 mA/cm^2
Final current density	8 mA/cm^2
Final time	600 sec

3. Results and Discussion

3.1 Galvanostatic Deposition of poly (m-aminophenol) coatings on low carbon steel in basic aqueous medium

Galvanostatic deposition, at high current density, is a key method for obtaining coatings in less time. Therefore, poly(m-aminophenol) coatings on low carbon steel were obtained using this technique. Passivation of low carbon steel is possible when the potential of steel surface and the pH of an aqueous medium are sufficiently high. Relationship between current and time recorded during galvanostatic synthesis of m- aminophenol coating on low carbon steel at current density 8 mA/ cm^2 for 600 seconds is shown in the figure 2.

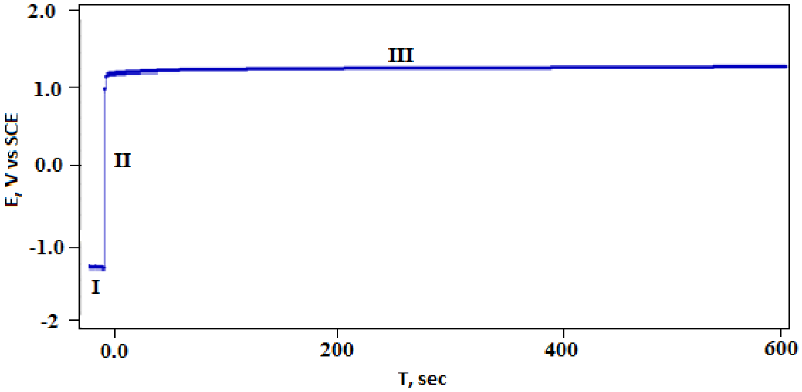

Figure 2.Galvanostatic growth of poly (m-aminophenol) on low carbon steel

The nature of the figure 2 shows that the growth of poly(m-aminophenol) coating on steel at room temperature occurs in three stages :

1. Stage I: In the early stages of polarization, the potential value of the electrode is negative
2. Stage II: At the end of the first stage, the potential increases rapidly to a positive potential.
3. Stage III: At the end of the second stage, the electrode potential reaches to a steady state value. It implies polymerization of m- aminophenol on steel sample.

3.2 Characterization

The FTIR spectra of poly(m-aminophenol) coating is shown in figure 3.

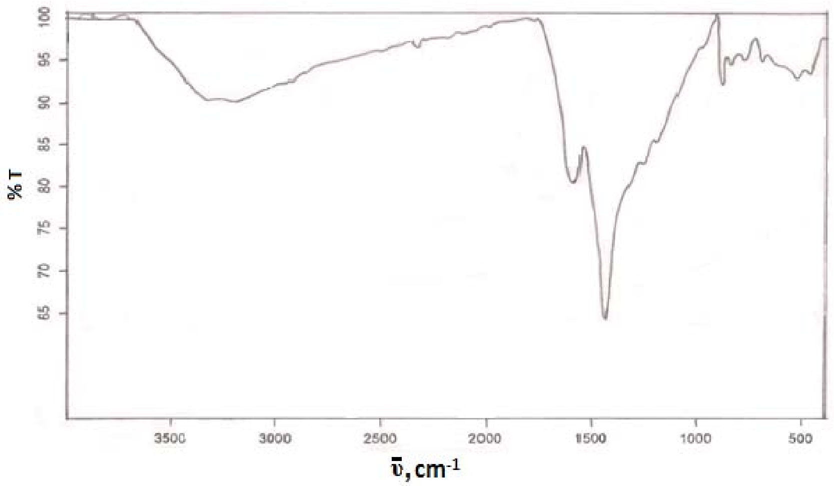

Figure 3.FTIR Spectroscopy of m-aminophenol

Two positive bands at 1427 and 1252 cm^{-1} are clearly observed in the figure 3. The band at 1427 cm^{-1} can be assigned to the C=C stretching vibration of the aromatic ring and the band at 1252 cm^{-1} to the C–O stretching vibration of an alcohol group. The band at 1585cm^{-1} can be assigned to NH_2 bending of amine. The appearance of strong absorption band at 1147.71 cm^{-1} and at 1188.42 cm^{-1} may be assigned to C-O-C starching vibration which revels the presence of ether linkages. The band at 3319 cm^{-1} can be assigned to N-H stretching of aromatic amine. Free O-H stretching occurs at 3600 – 3650 cm^{-1} .The existence of C–O–C etheric and –NH_2 groups in the FT-IR spectrum confirms presence of m-aminophenol [7].

Table 3

Wavelength and corresponding stretching and vibration

Wavelength (cm^{-1})	Stretching and vibration
686.773, 872	*Meta* substituted rings
1188.42	C-O-C starching vibration
1260 – 1000	C-O stretching
1252	C–O stretching vibration of an alcohol group
1427	C=C stretching vibration of the aromatic ring
1585	NH_2 bending of amine
3319	N-H stretching of aromatic amine
3600 – 3650	Free O-H stretching

3.3 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopic study of m-aminophenol coated samples with intact and damaged coating at just after immersion was carried out and shown in terms of Bode and Nyquist plots as depicted in figures 4 and 5.

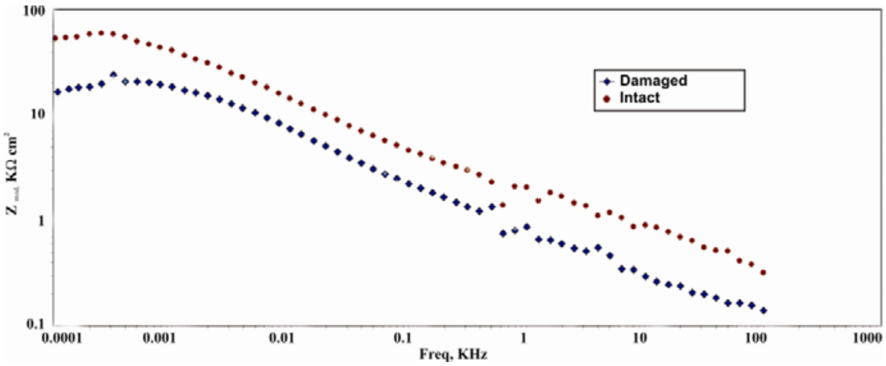

Figure 4.Bode plot of poly(m-aminophenol) coated low carbon steel with intact and damaged coating

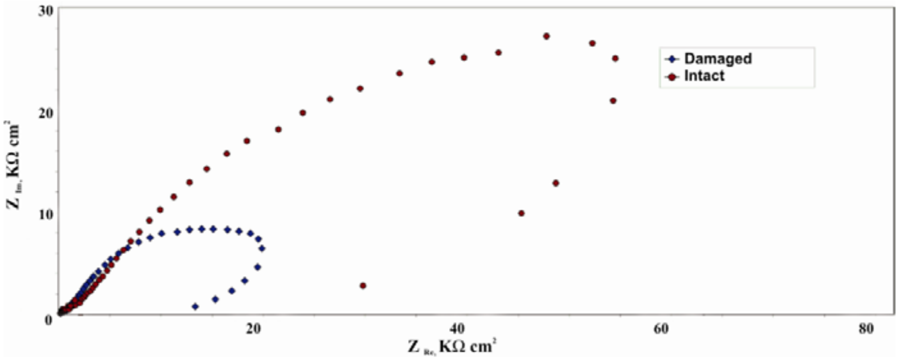

Figure 5.Nyquist plot of poly(m-aminophenol) coated low carbon steel with intact and damaged coating

The Bode plot show combined capacitive and resistive behavior and the Nyquist diagram show capacitive loop obtained just after immersion for intact and damaged coating. This can be attributed to corrosion prevention by barrier mechanism. The plots shown in the figures 4 and 5 were analyzed by using equivalent circuit shown in figure 6.

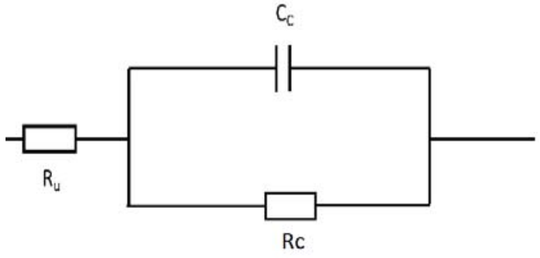

Figure 6.Equivalent circuit used for modeling the impedance curves

The Equivalent circuit , shown in the figure 6, consists of the electrolyte resistance (R_u), the coating resistance (R_c) and the coating capacitance (C_c). The values of these parameters were found by using Gamry software and recorded in table 4.

Table 4

Impedance Parameters

Coating	**Z_{real} (ohm)**	**Z_{mod} (ohm)**	**R_{ct} (ohm/cm^2)**	**C_c (μF)**
Intact	8913	6000	8880	0.912
Damaged	2729	1997	4180	1.23

A decrease is observed in impedance and charge transfer resistance values for damaged coating with increase in coating capacitance. This can be attributed to the uptake of saturated electrolyte in coated film.

3.4 Potentiodynamic Polarization Study

Potentiodynamic polarization behavior of un coated low carbon steel and m-aminophenol coated sample in 3.5 wt % NaCl solution is shown in figures 7 and 8 respectively.

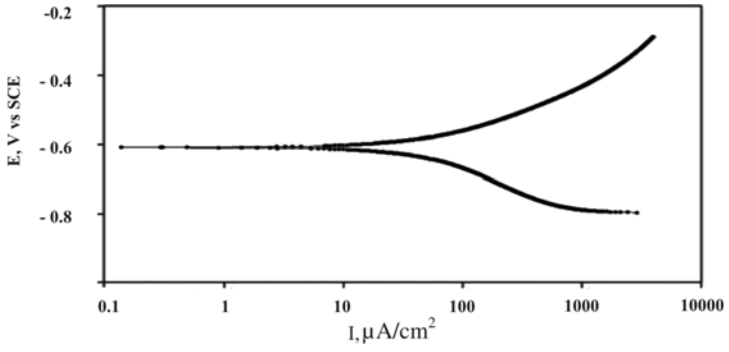

Figure 7.Tafel plot for uncoated low carbon steel sample in 3.5 wt% NaCl

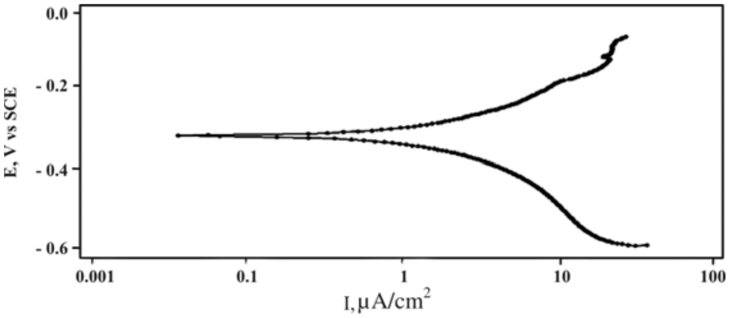

Figure 8.Tafel plot for m-aminophenol coated low carbon steel in 3.5 wt % NaCl solution

The values of the corrosion potentials, corrosion current densities and corrosion rates obtained from the figures 7 and 8 are recorded in Table 5. The thickness of the coating before immersion was found to be 10 microns. Tafel plot method was used to find corrosion rate.

Table 5

Corrosion rates for uncoated and Poly (m-aminophenol) coated low carbon steel

Sample	E_{corr} (mV)	I_{corr} (μA/cm^2)	Corrosion rate (mpy)
Uncoated low carbon steel	-680.0	87	5
Poly (m-aminophenol) coated low carbon steel	-303.0	1.34	2.14

Corrosion potential is found to be increased from – 680 mV for uncoated low carbon steel to –303 mV for poly (m-aminophenol) coated low carbon steel showing anodic protection. It should also be noted that the corrosion rate is substantially reduced due to decrease in current density from 87 μA/ cm^2 to 1.34 μA/ cm^2 for poly (m-aminophenol) coated steel. The corrosion rate of poly (m-aminophenol) coated low carbon steel in 3.5 wt% NaCl is 2.14 mpy which is about 2 times lower than that of uncoated low carbon steel.

3.5 Protection mechanism of m-aminophenol coating

Mechanism for the corrosion of low carbon steel in NaCl solution can be described as follows. Anodic reaction starts with the diffusion of Cl$^-$ ions through film and produce soluble iron compounds.

$Fe^{2+} + 2H_2O + 2Cl^- \rightarrow Fe(OH)_2 + 2HCL$
$\mathrm{FeOOH} + H_2O \rightarrow Fe^{3+} + 3OH^-$
$\mathrm{FeOOH} + Cl^- \rightarrow \mathrm{FeOCl} + OH^-$
$\mathrm{FeOCl} + H_2O \rightarrow Fe^{3+} + Cl^- + 2OH^-$

On the other hand, due to low permeability of m-aminophenol films oxygen diffusion is hindered, which in turn reduces the rate of the oxygen reduction reaction given below [7].

$$O_2 + 2H_2O + 4e^- \rightarrow OH^-$$

Cathodic protection effect of m-aminophenol arises from the barrier effect for diffusion. Thus, it can be said that m-aminophenol coating prevents corrosion of low carbon steel in 3.5 wt% NaCl by barrier mechanism.

4. Conclusions

1. It is possible to obtain adherent poly (m-aminophenol) coating on low carbon steel samples in basic hydroalcholic medium using galvanostatic deposition technique.

2. The existence of C–O–C etheric and $-NH_2$ groups in the FT-IR spectrum confirms presence of m-aminophenol.

3. The corrosion rate of poly (m-aminophenol) coated low carbon steel in 3.5 wt% NaCl is found to be 2.14 mpy which is about 2 times lower than that of uncoated low carbon steel in the same medium.

4. The coating resistance of poly (m-aminophenol) intact coated and damaged coated steel just after immersion is 8880 ohm/cm^2 and 4180 ohm/cm^2 respectively. The coating capacitance of poly (m-aminophenol) intact coated and damaged coated steel just after immersion is 0.91 μF and 1.23 μF respectively. This revels that corrosion resistance of poly (m-aminophenol) intact coating is higher than that of the m-aminophenol damaged coating.

5. The poly (m-aminophenol) coating prevents corrosion of low carbon steel in 3.5 wt% NaCl by barrier mechanism.

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