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# Surface Modification of Mild Steel by Orthophenylenediamine and Its Corrosion Study

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An attempt has been made towards the synthesis of strongly adherent orthophenylenediamine (OPD) coating on mild steel substrates, with an objective of using the OPD for corrosion protection of steel in hydrochloric acid medium. In this work, the OPD coatings were obtained by electrochemical reduction of orthonitroaniline (ONA) using dilute sulphuric acid as supporting electrolyte. The characterization of the coating was done by infrared spectroscopic and scanning electron microscopic studies. The non porous nature of the coating was determined by ferroxyl test. The performance of OPD as protective coating against corrosion of mild steel in aqueous hydrochloric acid was assessed by open circuit potential, potentiodynamic polarization, weight loss method. These studies revealed that the OPD coating on mild steel provide very good protection to mild steel against corrosion in hydrochloric acid environment.

**Keywords:** Surface modification; Corrosion inhibition; Mild steel

## 1. INTRODUCTION

Mild steel is extensively used in industry especially for structural applications, but its susceptibility to rusting in humid air and its high dissolution rate in acid media are the major obstacles for its use on larger scale [1]. Inhibitors are widely used for protection of metals from corrosion in acid environments. Usually inhibitors protect the metal by adsorbing on the surface and retard metal corrosion in aggressive media. So selecting the appropriate inhibitor for particular metal is very important [2]. As acidic media HCl and $H_2SO4$ are generally used in the treatment of steel and ferrous alloys, the corrosion inhibition of mild steel in acid media in general and in hydrochloric acid in particular have been reviewed [3]. Most of the well known inhibitors are organic compounds containing nitrogen [4-23], sulphur[7,10,11,17,19,21], oxygen[8,13,15,16,21,]and phosphorous [24-

25] in their functional groups[1,26-30 ]. Some studies have shown that the inhibition of the corrosion process is mainly decided by the formation of donor-acceptor surface complexes between free or π electrons of an inhibitor and vacant d orbital of a metal [3, 26, 27, 29].

Surface modification of the metals with these electro active organic compounds provide good protection to metals against corrosion in these aggressive media [3, 28-30]. It has been found that, during electrochemical reduction or oxidation of electroactive organic compounds, the product of the electrolysis will adsorb on the metal surface and results in the modified surface.

The present paper describes the electrochemical modification of mild steel by orthophenylenediamine during electroreduction of orthonitroaniline. Here an attempt has been made to synthesize strongly adherent OPD coating on mild steel substrate by electroreduction from aqueous sulphuric acid medium and examined the ability of these coatings to serve as corrosion protective coatings on mild steel in hydrochloric acid medium. The results reported in this paper shows that the electroreduction of ONA in aqueous sulphuric acid medium results in the formation of uniform, compact and strongly adherent coating of OPD on mild steel substrate. The evaluation of the corrosion protection performance by weight loss and potentiodynamic polarization studies revealed that the OPD can be considered as a potential surface modifier for mild steel against corrosion in hydrochloric acid medium.

## 2. EXPERIMENTAL PART

Analytical Reagent (AR) grade chemicals (s. d. fine chemicals, Mumbai) were used for the study. The aqueous solution of sulphuric acid was used as the supporting electrolyte. The concentration of sulphuric acid and ONA were kept at 20 %(V/V) and 5% (M/V) respectively.

Mild steel specimen with composition 0.04% C, 0.35% Mn, 0.022%P, 0.036% S and the remainder being Fe were used. Specimens of size 5cm x 1cm x 0.1cm were used for the weight loss method and of 1cm x 1cm (exposed) with a 5cm long stem (isolated with araldite resin) were used for polarization method. These samples were polished with emery papers of different grit size, degreased with trichloroethylene, washed thoroughly with triply distilled water and finally dried. Prior to each experiment, the specimens were treated as described and freshly used with no further storage.

The electrolysis was carried out in a two comportment H-type cell in which porous frit acts as a separator with mild steel as working electrode, platinum as counter electrode and saturated calomel as reference electrode. The electrolysis was carried out using potentiostat / galvanostat PS-618, Chemilink system, Mumbai. Electrolysis was carried out at an electrode potential of 0.8V vs SCE for different time intervals. The ONA get converted into OPD at the cathode surface and its formation was confirmed by TLC and FTIR spectral analysis. The visual inspection of the mild steel electrode during electrolysis revealed the formation of a brown colored coating of OPD. The thickness of the coating increases with increase in the electrolysis time and after 6 hour of electrolysis, it was noticed that the surface of mild steel was covered with transparent film of OPD. The film was uniform, non-porous and well adhered to the mild steel surface. The non-porous nature of the OPD coating was tested by ferroxyl test [3]. After deposition, the mild steel specimen was removed from the electrolytic bath and rinsed with doubly distilled water, dried and kept in a desiccator.

For the determination of corrosion velocity from weight loss method, the unmodified steel and OPD coated steel was conducted separately in hydrochloric acid of different concentrations. The temperature of the corrosive medium was 303 K. The pure steel and surface treated specimens were immersed in corrosive media and the plates were weighed periodically for every 24 hours in 15 days. The loss in weight was used to determine the corrosion velocity.

The corrosion protection performance of these coatings was investigated in aqueous hydrochloric acid media using open circuit potential (OCP) and potentiodynamic polarization studies. The polarization measurements were performed at 303K for unmodified steel specimens. For the polarization measurements, a conventional three electrode pyrex glass cell consisting of a saturated calomel electrode (SCE), the mild steel specimen and a platinum foil as reference, working and counter electrodes respectively were used. The anodic and cathodic polarization values were measured under galvanostatic conditions. The potential of the working electrode varied from the open circuit potential at the rate of 20mV per min and steady values were noted using as ELICO potentiostat / Galvanostat (Model CL-95). Anodic and cathodic tafel lines were constructed and corrosion rates and percentage efficiencies were calculated.

The fourier transform infrared (FTIR) transmission spectrum of OPD and the compound scrapped from the metal surface was recorded by Shimadzu FTIR 8400 S instrument.

Surface morphology of the modified steel surface before and after corrosion study was recorded using JOEL-JEM-1200 EX-II electron microscope.

## 3. RESULTS AND DISCUSSION

### 3.1. Corrosion rate results

The corrosion rate of unmodified steel showed slight increase in the beginning and remains constant after 50 hours. The OPD coated (8 hour in the electrolytic bath) mild steel specimens were subjected to chemical corrosion in aqueous hydrochloric acid solution and showed no corrosion in the entire 15 days of test duration. This result indicated that OPD coating on mild steel provides good protection to mild steel against corrosion.

### 3.2. Electrochemical results

The OCP of uncoated mild steel and OPD coated mild steel substrates were immersed in aqueous hydrochloric acid of known strength and were measured with respect to time and the corresponding plot are presented in Fig.1a and 1b. In the figure -0.54 and -0.51 V stands for the corrosion potential of bare mild steel in 3 and 5% hydrochloric acid respectively. The initial value of OCP of the OPD coated ( 8 hour treatment ) mild steel; was measured to be as -0.40 and -0.49 V respectively for 3 and 5% hydrochloric acid and it is observed that the OCP decreases slowly with the immersion time and attains a steady value which is still more positive than that of bare mild steel.

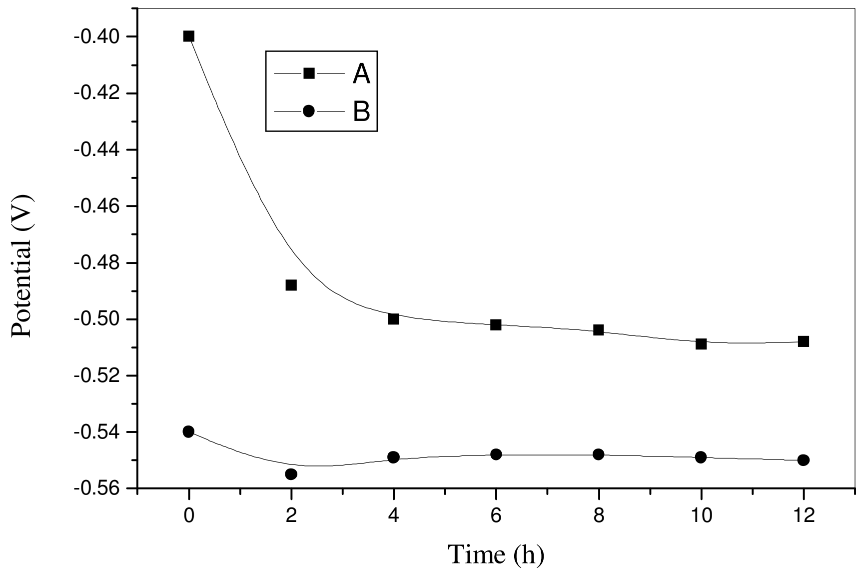

**Figure 1a.** Plot of OCP for OPD coated mild steel and bare mild steel in aqueous 3% HCl. (A) OPD coated mild steel, (B) bare mild steel.

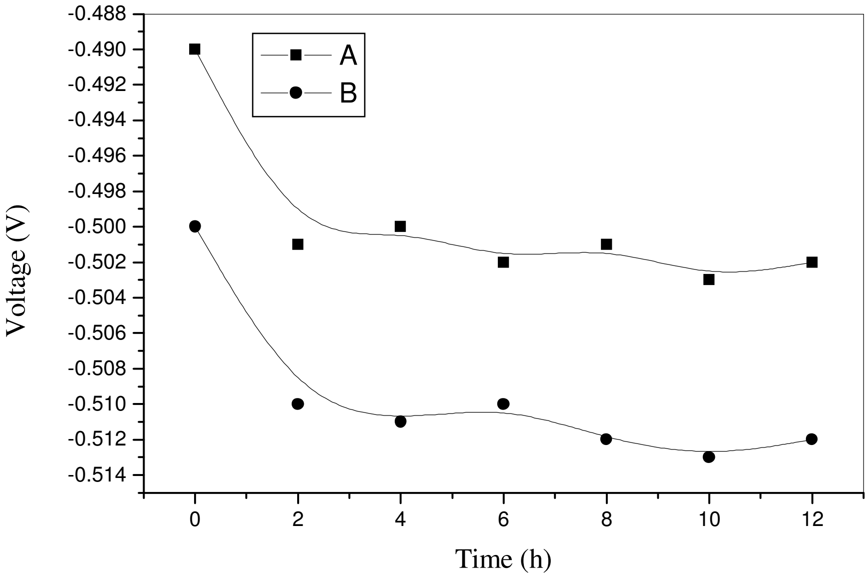

**Figure 1b.** Plot of OCP for OPD coated mild steel and bare mild steel in aqueous 5% HCl. (A) OPD coated mild steel, (B) bare mild steel.

It was observed that the OCP value of the coated specimen does not drop to the value of the OCP of bare metal. Instead the OCP of the OPD coating remains fairly constant over 40 hours. The variation of OCP of bare mild steel and OPD coated mild steel in 3 and 5% aqueous hydrochloric acid is shown in Fig.1a and 1b respectively.

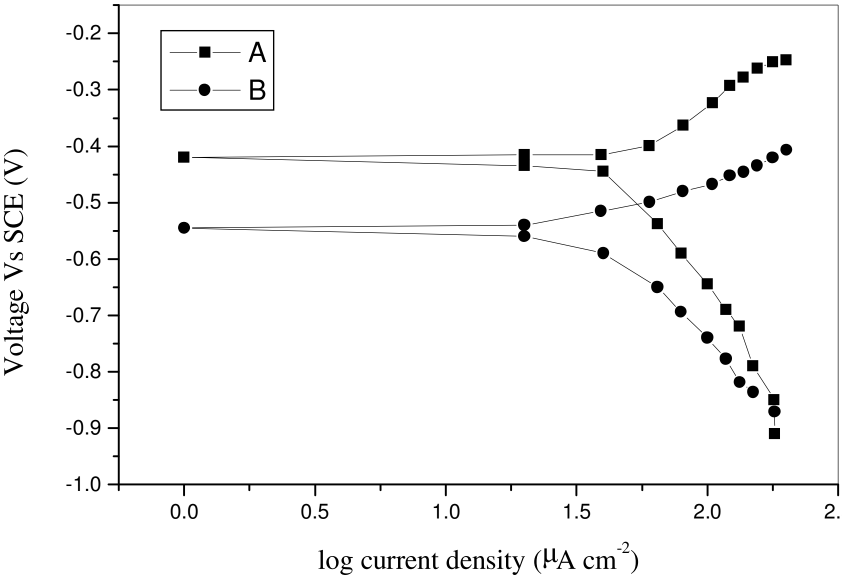

**Figure 2a.** Potentiodynamic polarization curves in 3% Hcl solution. (A) Bare mild steel, (B) OPD coated mild steel

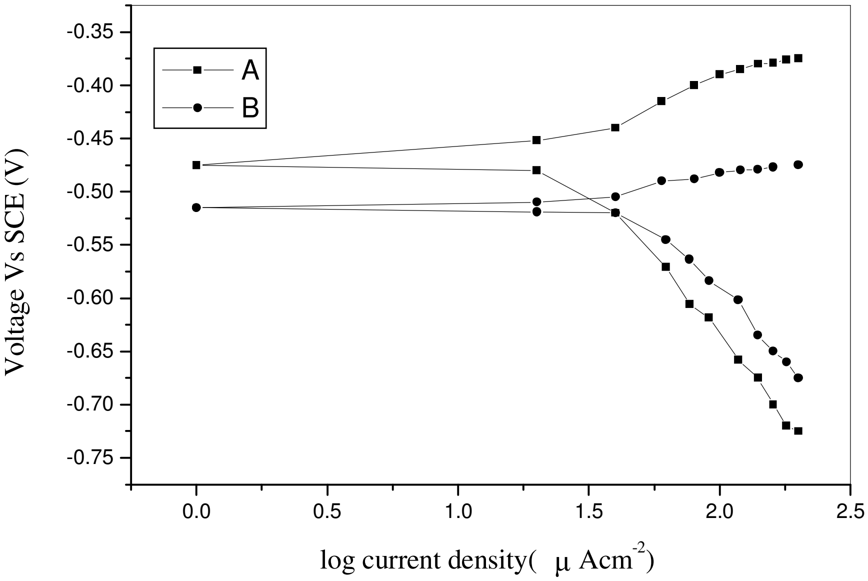

**Figure 2b.**. Potentiodynamic polarization curves in 5% HCl solution. (A) Bare mild steel, (B) OPD coated mild steel

The Fig. 2a and 2b shows the anodic and cathodic potentiodynamic polarization curves for bare and OPD coated mild steel in hydrochloric acid of 3 and 5% strength. The specimens were first polarized in cathodic direction upto a maximum shift from OCP. For anodic polarization, the specimens were again kept at OCP value for about 10 min to attain equilibrium and then anodic polarization were carried out in a similar manner. The corrosion current density ($I_{corr}$) and corrosion potential ($E_{corr}$) were determined by extrapolating the anodic and cathodic tafel lines of the plots of potential Vs log current density by their intersection. The cathodic curves are more polarized than anodic curves and the OPD coating is comparatively more effective on cathodic sites. The decrease in anodic and cathodic current densities indicates that the OPD coating suppresses both the anodic and cathodic reactions. The tafel extrapolations show that the OPD coating caused a appreciable shift in the corrosion potential, relative to the values of bare mild steel. The positive shift in $E_{corr}$ confirms the best protection of the mild steel when its surface is covered with OPD coating.

**Table 1.** Potentiodynamic polarization measurement results

| Sample | $-E_{corr}$ (mV) | $I_{corr}$ ($mAcm^{-2}$) | %IE (η) |
|---|---|---|---|
| Corrosive solution = 3% HCl | | | |
| Bare mild steel | 500 | 158 | |
| OPD Coated mild steel (2 hour) | 480 | 100 | 36 |
| OPD Coated mild steel (4hour) | 470 | 56 | 64 |
| OPD Coated mild steel (6hour) | 470 | 28 | 82 |
| OPD Coated mild steel (8hour) | 440 | 25 | 84 |
| Corrosive solution = 5% HCl | | | |
| Bare mild steel | 520 | 177 | |
| OPD Coated mild steel (2 hour) | 475 | 100 | 43 |
| OPD Coated mild steel (4 hour) | 480 | 63 | 64 |
| OPD Coated mild steel (6 hour) | 500 | 31 | 82 |
| OPD Coated mild steel (8hour) | 490 | 19 | 84 |

The percentage protection efficiency (η) were determined from the equation

$$\eta = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \text{ X } 100$$

Where $I^0_{corr}$ and $I_{corr}$ are the corrosion current densities of bare mild steel and OPD coated mild steel respectively. The values of tafel measurements clearly shows that the substantial decrease in corrosion current density ($I_{corr}$) for OPD coated mild steel than compared to bare mild steel. Calculated polarization results like corrosion potential, corrosion current density and % protection efficiency (η) in aqueous hydrochloric acid of known strength are listed in Table 1. These data show that corrosion current density decreases with increase in electrolysis time and it is lowest for the OPD coated specimen modified in the electrolytic bath for 8 hours. This indicates that as the electrolysis time increases, the thickness of the OPD on the mild steel specimen increases which offer good protection to mild steel against corrosion. The % protection efficiency for OPD coated mild steel is 84 in 3% and 5% hydrochloric acid respectively. Thus these results reveal the capability of OPD coating to act as a corrosion protective layer on mild steel and its thickness significantly affects the corrosion protection properties. The corrosion protection efficiency may be attributed to the presence of π electrons in the aromatic ring and lone pair of electrons on the nitrogen leads to the effective surface modification of mild steel.

The protection offered by OPD coating on mild steel is almost same as the concentration of hydrochloric acid increased. So the OPD coating provide good protection to corrosion of mild steel even in higher concentration of acid.

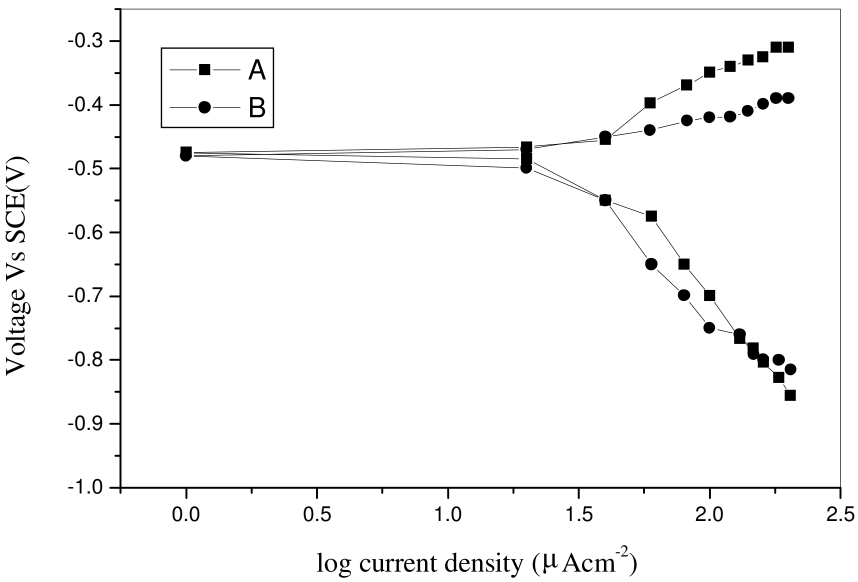

**Figure 3.** Potentiodynamic polarization curves (A) freshly prepared and (B) after storing in air for 15 days at $30^0$ C recorded in aqueous 3% HCl solution

The potentiodynamic polarization study was also carried out using the OPD coated mild steel (8 hour electrolysis) substrates after storing them in air at $30^0$ C for 15 days and the polarization curves are shown in Fig.3. Figure also shows the potentiodynamic polarization curves of freshly prepared OPD coated mild steel, these two curves clearly indicates that no appreciable change in the corrosion protection efficiency of the OPD coating. Thus the coating of OPD shows high chemical as well as physical stability. The same trend was also observed in the weight loss measurements.

## 4. SURFACE MORPHOLOGY STUDIES

To establish the formation of protective layer on the mild steel surface, scanning electron microscopic images were taken (Fig. 4). Fig.4a is the SEM image of the bare mild steel specimen obtained after anodic polarization in aqueous hydrochloric acid, which shows the deterioration of metal surface due to the attack of corrosive solution. Fig. 4b is the SEM image of OPD coated mild steel which shows the uniform growth of organic compound on the metal surface, leads to greater corrosion protection efficiency. Fig. 4c is the SEM image of OPD coated mild steel obtained after anodic polarization in 3% HCl solution. Very small amount of corrosion products were observed on the surface and rest will carry the similar morphology as Fig. 4b.

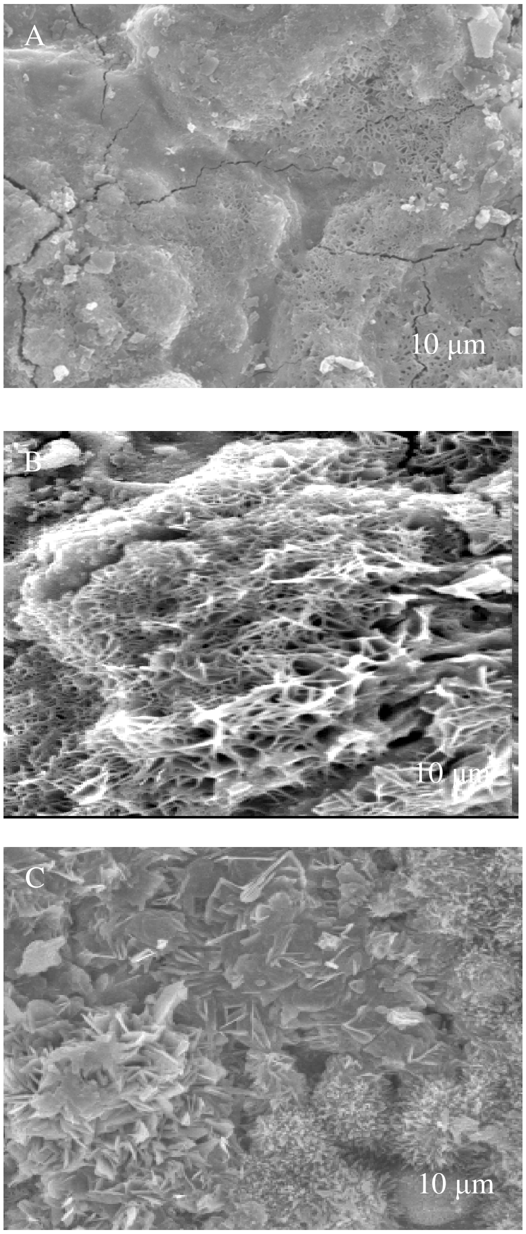

**Figure 4.** SEM images of steel samples A) Unmodified steel sample after polarization B) Modified steel before polarization C) Modified steel after polarization

## 5. IR SPECTRAL STUDIES

The FTIR spectrum of OPD obtained after electrolysis and the compound adsorbed on the mild steel surface was recorded. These spectrums exhibit the following features. The appearance of two bands at 3386 and 3365 $cm^{-1}$ corresponds to the asymmetric and symmetric stretching vibration of –NH of aromatic primary amine. A band at 1635 and 1274 $cm^{-1}$ corresponds to –NH bending and –CN stretching vibrations. The appearance of these bands confirms the formation of OPD from ONA. The FTIR spectrum of OPD coating scrapped from the metal surface shows the band at an absorption frequency 3452 $cm^{-1}$ corresponds to –NH stretching of aromatic amine. A peak at 1636 and 1276 $cm^{-1}$ corresponds to –NH bending and –CN stretching vibrations. The appearance of these bands in the IR spectrum of coating confirms the formation of a layer of OPD on the mild steel surface.

## 6. CONCLUSIONS

The following conclusions have been drawn from the present work:

- The OPD coating on mild steel surface was obtained by the electrooreduction of ONA, the coating was uniform, non-porous and well adhered to the mild steel surface.
- The formation of OPD from ONA was confirmed by the FTIR spectrum
- Weight-loss, OCP and potentiodynamic polarization measurements revealed the corrosion protection property of OPD coating.
- FTIR spectrum of compound collected from the mild steel surface confirms the adsorption of OPD on the mild steel.
- SEM images of the mild steel specimens confirms the formation of passive layer on the metal surface.

The study reveals that the OPD coating has good corrosion protection properties and it inhibit the corrosion of mild steel in hydrochloric acid.

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