

Corrosion Behaviour of Electrochemically Modified Carbon Steel in 3.5% Sodium Chloride Solution

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Abstract

Carbon steel was electroplated in presence of Ni salt, Diethylenetriamine pentamethylenephosphonic acid (DTPMP) and also ZnSO₄. The various metal specimens are designated as CS, CS + Ni, CS + Ni + DTPMP, and CS + Ni + DTPMP + Zn. Weight loss study was carried by immersing the metal specimens in 3.5% NaCl solution for one day. The order of corrosion resistance is:

CS + Ni + DTPMP + Zn > CS + Ni + DTPMP > CS + Ni > CS

Polarization study was carried out by immersing the metal specimens in 3.5% NaCl solution. The order of corrosion resistance is:

CS + Ni > CS + Ni + DTPMP + Zn > CS > CS + Ni + DTPMP

The difference in corrosion resistance order derived from weight loss method and polarization method may be attributed to the fact that polarization method is an instantaneous method, whereas weight loss method is average method of longer duration, namely, one day. The electrochemically modified electrodes were used to decolourise methyl orange solution (250 ppm). The order of decolorization efficiency is:

CS (100%) > CS + Ni + DTPMP (95%) > CS + Ni + DTPMP + Zn (92%) > CS + Ni (40%)

Keywords: Electroplating, carbon steel, decolourisation, FTIR study, Polarization study.

1. Introduction

Corrosion in a broad sense signifies the whole range of reactions between metals and their environments. The importance of corrosion studies is three fold. The first area of importance is economic, while the second is improved safety and the third is conservation. Economic losses due to corrosion are divided into direct losses and indirect losses.

There are several methods to prevent corrosion of metals. Use of non-metallic materials, cathodic /anodic protection, modification of environment and modification of metal surface, are some of the methods. The metal surface can be modified by electroplating nickel, zinc, chromium etc. through several electroplating industries. It will be useful if there is interaction between electroplating scientists and corrosion scientists to evaluate the corrosion resisting efficiency of the electroplated metal surface. Electro deposition of gold and its alloys has been widely used in the production of new materials that have required specific chemical, physical and mechanical properties [1-3]. Gold deposits containing small amounts of metal ions such as nickel or cobalt have been found to yield consistently bright

alloy electrodeposits with suitable morphology, purity and hardness as well as corrosion resistance [4 – 10]. Nickel has been electroplated on various metals and alloys to modify their properties especially to improve their corrosion resistance [11-20]. Effluents from dyeing industries promote many environmental hazards such as health effects and destroying the wealth of agriculture and aquatic life. Hence scientists are trying to decolorize and degrade the dyes before releasing the effluents. Several methods have been employed to decolorize and degrade dyes. Among them, electrochemical methods [21-27] biochemical methods [28-30] are important. The present work is a case study of small scale electroplating industry. The present work is undertaken

- (i) To electroplate nickel on carbon steel surface with Diethylene triaminepentamethylenephosphonic acid (DTPMP) in the real situation of an electroplating unit using Nickel bath in the presence and absence of zinc sulphate
- (ii) To decolorize methyl orange solution using various electrochemically modified electrodes such as carbon steel (CS), CS+Ni, CS+Ni+DTPMP, and CS+Ni+DTPMP+Zn.

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- (iii) To study the formation of coated protective film by FTIR spectroscopy.
- (iv) To prove the protective film by polarization study.

2. Materials and Methods

2.1. Preparation of the specimen

Carbon steel (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) specimens of the dimensions 1.0 cm × 4.0 cm × 0.2 cm were used in the present study for electroplating and then measuring the corrosion resistivity of the metal surface.

2.2. Electroplating

The chemicals used were of Analytical reagent grade. The process of electroplating of the carbon steel (CS) specimens involve the following steps.

Step – 1

- ✓ Pickling with conc. HCl
- ✓ Distilled water
- ✓ Drying
- ✓ Polishing (nice)
- ✓ Degreasing with cleaning powder containing soda, chalk and nice emery powder
- ✓ Drying
- ✓ Immersed in bath solution

Step – 2

- ✓ Ni-Bath solution

Nickel chloride	-	10g / litre
Nickel sulphate	-	10g / litre
Boric Acid	-	10g / liter
Anode	-	Pure nickel plate
Cathode	-	Carbon steel specimen
Agitation	-	Nil
Temperature	-	Room temperature

Current was passed for 5 minutes. The current density was 2 A/cm².

Step - 3

Carbon steel was electroplated in presence of Ni and DTPMP (5g / 1lit). Current was passed for 5 minutes. The current density was 2 A/cm².

Step – 4

The electroplating was done in presence of ZnSO₄ solution (5g / 1lit). Current was passed for 5 minutes. The current density was 2 A/cm².

2.3. Measurement of corrosion resistance of the electroplated metal surface

The following studies were used to measure the corrosion protective nature of the film formed on the carbon steel surface after electroplating.

2.4. Immersion in chloride environment

The metal specimens in triplicate were immersed in 100 ml of an aqueous solution containing 3.5% NaCl for a period of one day. After one day the corrosion product, if formed, were cleaned with Clarke's solution. The inhibition efficiency (IE) was calculated using the equation.

$$IE = 100 [(W_1 - W_2)/W_1]\%$$

Where W_1 = Corrosion rate before electroplating
 W_2 = Corrosion rate after electroplating

2.5. Decolourisation process

Decolourisation of a dye such as methyl orange was attempted using various electrodes such as carbon steel, carbon steel electroplated with nickel etc. The optical density of the methyl orange solution before and after decolourisation was measured by the instrument photoelectric colorimeter – 112(Systronics). The electrodes were immersed in the solution containing 250 ppm of methyl orange (100 ml). The solution was subjected to electrochemical decolourisation process after addition of 8gm of NaCl. Graphite was used as cathode carbon steel or electroplated carbon steel was used as anode. The electrolysis was carried out in an undivided cell with a stirring bar.

2.6. Surface Analysis of FTIR Spectroscopic Study

The film formed on the surface of the CS+Ni+DTPMP system was scratched carefully, and it was thoroughly mixed with KBr and made into a pellet. FTIR spectrum was recorded. Similarly, the film on the CS+Ni+DTPMP+Zn system was analysed. It was recorded using Perkin – Elmer 1600 Spectrophotometer.

2.7. Potentiodynamic polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, model 660A. A three electrode cell assembly was used. The working electrode was carbon steel or any one of the electrochemically modified metal specimen. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{cor}), corrosion current (I_{cor}) and Tafel slopes (anodic and cathodic) were calculated.

3. Results and Discussion

3.1. Analysis of weight – loss study

Carbon steel was electroplated with

- (i) Ni
- (ii) Ni in presence of DTPMP
- (iii) Ni in presence of DTPMP and ZnSO₄

The metal specimens were immersed in an aqueous solution containing 3.5% NaCl. The corrosion rates and corrosion protective efficiency (CPE) obtained by weight-loss method are given in Table 1.

Table 1. Corrosion rates of metal specimens immersed in an aqueous solution containing 3.5% NaCl and corrosion protective efficiency (CPE) obtained by weight-loss method

Sample	NaCl %	CR mdd	CPE %
CS	3.5	30.00	--
CS+Ni	3.5	6.00	80
CS+Ni+DTPMP	3.5	2.40	92
CS+Ni+DTPMP+Zn	3.5	0.600	98

It is evident from Table 1 that when the nickel plated carbon steel (CS+Ni) is immersed in 3.5% NaCl solution for the period of one day, the corrosion protective efficiency is 80%. But the CS -Ni-DTPMP system immersed in 3.5% NaCl solution, shows better CPE (92%). The CS-Ni-DTPMP-Zn system showed excellent CPE (98%). This is due to the fact that DTPMP and Zn are also electroplated with nickel on CS. This accounts for very high corrosion protective efficiency.

3.2. Decolouration process

3.2.1. Decolouration using carbon steel

Uncoated carbon steel anode and graphite cathode were immersed in the solution to be decolourised (methyl orange solution). Current was passed for 10 minutes with out addition of NaCl. There was no decolorization. The experiment was repeated after addition of 8 g of NaCl. Current was passed. The current density was 0.4 A/cm² and the potential was 1.5 volt. Methyl orange was completely decolorized within 4 minutes. The efficiency of decolourisation was 100%.

3.2.2. Decolouration using carbon steel – nickel specimen

The experiment was repeated by using carbon steel electroplated with nickel after addition of 8 g of NaCl. Current was passed. The current density 0.3A/cm² and the potential was 2.2 volt. Methyl orange solution was decolourised within 4 minutes (OD value 0.20). The efficiency of decolourisation was only 40%. The solution turned green due to the formation of nickel chloride and also ferrous chloride. This indicates that first the nickel film dissolves in chloride medium giving Ni²⁺, and also iron dissolves giving Fe²⁺. Moreover, because of the presence of protective film on carbon steel surface, electron transfer from the metal specimen to the dye solution was restricted. This accounts for low decolourisation efficiency. This also indicates that nickel film is formed on the CS surface.

3.2.3. Decolouration using CS+Ni+ DTPMP system

The experiment was repeated by using carbon steel electroplated with nickel, DTPMP and Zn after addition of 8 g of NaCl. Current was passed. The current density 1.04A/cm² and the potential was 3 volts(OD value 0.01). The efficiency of decolourisation was 95%. The solution turned green due to the formation of nickel chloride and also ferrous chloride.

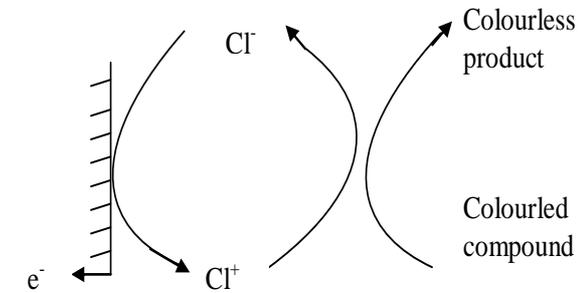
3.2.4. Decolouration using Nickel plated with DTPMP & Zn²⁺

The Experiment was repeated by using carbon steel electroplated with nickel after addition of 8 g of NaCl. Current was passed. The current density 1.36A/cm² and the

potential was 3 volts(OD value 0.02). The efficiency of decolourisation was only 90%. The solution turned green due to the formation of nickel chloride and also ferrous chloride.

3.3. Mechanism of decolourisation

When NaCl solution is electroplated, the active species produced is Cl⁻ [31, 32]. This oxidized the coloured material into colourless product. This is shown in scheme 1 [33].



Scheme 1. Electrochemically regenerated Cl⁻.

The chemical reactions taking place at the surface of a corrosion resistant anode, during electrolysis in the presence of NaCl electrolyte are explained below.



At acidic conditions free chlorine is the main oxidizing agent, while in slightly alkaline conditions hypochlorite predominates. These two strong oxidizing agents, cause the decolorization of the dye solution.

3.4. Analysis of the FTIR spectra

The FTIR spectrum of the film on Ni-DTPMP plate is shown Figure 1a. The P-O stretching frequency of DTPMP appears at 1115 cm⁻¹[34]. This indicates that Diethylenetriaminepentamethylenephosphonic acid (DTPMP) was electroplated with nickel on CS surface. The FTIR spectrum of the film on CS-Ni-DTPMP-Zn plate is shown Figure 1b. The P-O stretching frequency appears at 1114 cm⁻¹. The band at 1387 cm⁻¹ results from Zn coated on the nickel plate. The FTIR study reveals the presence of DTPMP and Zn on the CS surface coated with nickel.

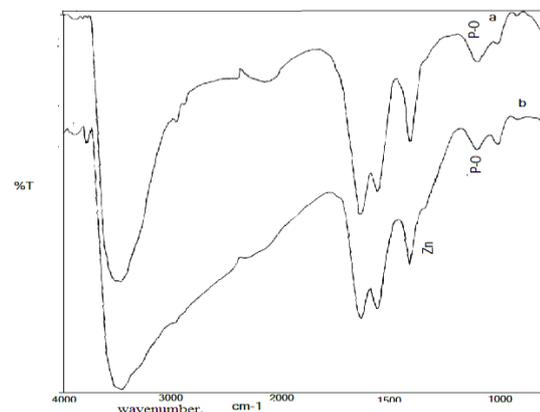


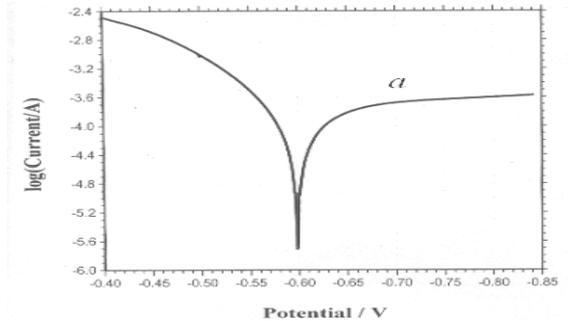
Fig. 1. FTIR Spectra (KBr Technique)

- a) Carbon steel electroplated with Ni and DTPMP (CS + Ni + DTPMP)
- b) CS + Ni + DTPMP + Zn

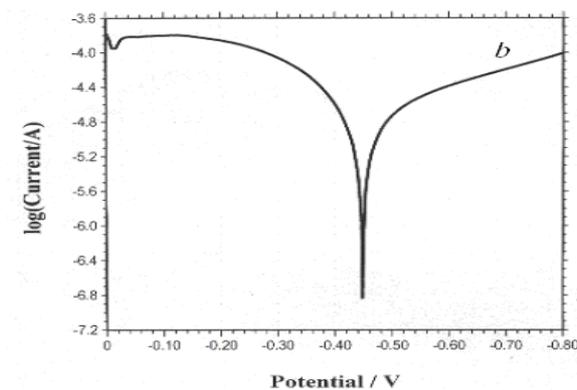
3.5. Analysis of potentiodynamic polarization study

The polarization curves of carbon steel, before and after electroplating in presence of different additives, immersed in 3.5% NaCl solution are shown in Figure 2. The corrosion parameters are given in Table 2. In general, when corrosion protection efficiency is high, the linear polarization resistance (LPR) increases and corrosion current (I_{corr}) decreases. Based on the concept, the decreasing order of corrosion resistance of different systems are:

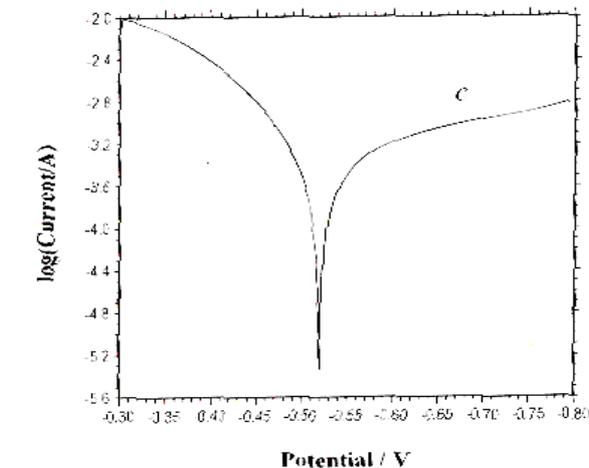
$$CS + Ni > CS + Ni + DTPMP + Zn > CS > CS + Ni + DTPMP$$



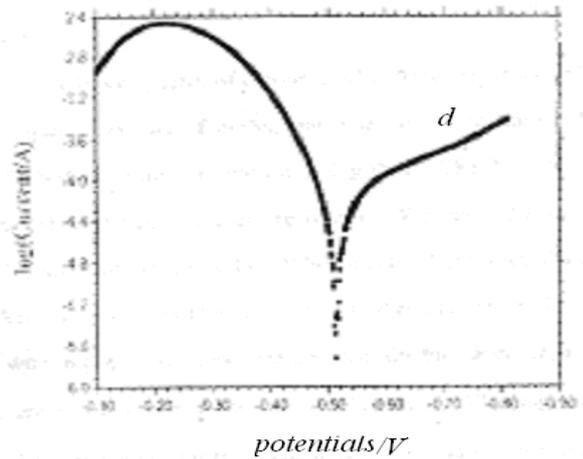
a. Carbon steel



b. Carbon steel + Nickel



c. Carbon steel + Ni + DTPMP



d. Carbon steel + Ni + DTPMP + Zn

Fig. 2 : Polarization curves of metal specimens immersed in an aqueous solution containing 3.5% NaCl.

Table 2. Corrosion parameters of metal specimens immersed in 3.5% NaCl solution, obtained from polarization study

Sample	E_{corr} mV vs SCE	b_a mV / decade	b_c mV / decade	LPR ohm cm^2	I_{corr} A/ cm^2
CS	-598	137	742	2.242×10^2	2.245×10^{-4}
CS + Ni	-448	221	335	2.170×10^3	2.675×10^{-5}
CS + Ni + DTPMP	-520	143	410	7.704×10^1	5.99×10^{-4}
CS + Ni + DTPMP + Zn	-513	366	124	4.592×10^2	8.742×10^{-5}

Thus, it is inferred that CS + Ni system is the best system. It is more corrosion resistant than other systems.

4. Conclusions

- ✓ Carbon steel was electroplated in presence of Ni salt, DTPMP and also $ZnSO_4$.
- ✓ The various metal specimens are designated as CS, CS + Ni, CS + Ni + DTPMP, and CS + Ni + DTPMP + Zn.
- ✓ Weight loss study was carried by immersing the metal specimens in 3.5% NaCl solution for one day.
 The order of corrosion resistance is :
 $CS + Ni + DTPMP + Zn > CS + Ni + DTPMP > CS + Ni > CS$
- ✓ Polarization study was carried out by immersing the metal specimens in 3.5% NaCl solution.
 The order of corrosion resistance is
 $CS + Ni > CS + Ni + DTPMP + Zn > CS > CS + Ni + DTPMP$
- ✓ The difference in corrosion resistance order derived from weight loss method and polarization method may be attributed to the fact that polarization method is an instantaneous method, whereas weight loss method is average method of longer duration, namely, one day.
- ✓ The electrochemically modified electrodes were used to decolourise methyl orange solution (250 ppm).
 The order of decolorization efficiency is :

CS (100%) > CS + Ni + DTPMP (95%) > CS + Ni + DTPMP + Zn (92%) > CS + Ni (40%)

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