Studying of Corrosion inhibition on Low Carbon Steel by Aqueous Solution Diammonium Phosphate Fertilizer Solution

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Abstract

The aim of the present work is study the corrosion behavior of low carbon steel in aqueous diammonium phosphate (DAP) fertilizer solution with and without inhibitors' addition in different concentrations (5% & 35%) in different temperatures (25, 35, and 50 °C) by using polarization method and take an optical microscope with (600 X) for samples after testing. The inhibitors used in this work are thiourea 20 ppm in concentration, and(20ppm thiourea + 20ppm hexamine) in concentration.

The results show that the adding of the thiourea (20 ppm in 5% and 35% DAP solution respectively)causes increasing the inhibition efficiency to 63% and 60% at room temperature(25 °C), but at 50 °C it is be 35% and 32% . Also the results improve that the current density decreases while inhibition efficiency for both hexamine and thiourea (in 5% and 35% DAP solution respectively) be 70% and 75% at room temperature and 62% and 64% at 50°C respectively.

الخلاصة

يهدف البحث الحالي الى دراسة السلوك التآكلي لمادة الفولاذ الواطئ الكاربون في المحلول المتعادل لسماد ثنائي فوسفات الأمونيوم مع وبدون اضافة المثبطات وبتراكيز مختلفه(5%و35%) في درجات حرارة محتلفة(50و35,25)°م باستخدام طريقة الآستقطاب وكذلك استخدام التصوير بالمجهر الضوئي بقوة تكبير(600X) لفحص اسطح العينات بعد التاكل . المثبطات التي استخدمت في هذا العمل هي الثايويوبا بتركيز 20 ppm ،وايضا (الهكسامين بتركيز20ppm + الثايويوريا بتركيز20ppm) .

اظهرت النتائج التي تم التوصل اليها عند اضافة الثايويوريا(في 5% و35%) على التوالي ان كثافة التيار قد انخفضت وبكفاءة تثبيط تصل الى63% و 60% في درجة حرارة الغرفه وللتراكيز أعلاه بينما في درجة حراره 50°م وصلت 35% و ز32% عند اضافة كل من الهكسامين و الثايويوريا وفي نفس التراكيز للمحلول فان كثافة التيار قد انخفضت وبكفاءة تثبيط تصل الى70% و 75% في درجة حرارة الغرفه وللتراكيز أعلاه بينما في درجة حراره 50°م وصلت 62 % و 64%.

1- Introduction

Corrosion is one of the most destructive agents and perhaps the greatest consumer of metals known to man. It is the deterioration of a metal through an unwanted chemical or electrochemical attack by its environment starting at the surface.**(Khurmi *etal.*,1995)**

The low carbon steel have carbon concentration between about(0.002 and 0.25wt%). Applications include railway wheels and tracks, gears, crank shafts, and other machine parts and high strength structural components calling for a combination of high strength, wear resistant and toughness. **(Callister *et al.*, 2007)**

Also low carbon and low alloy steels applied for production of metal construction, conveyor belts, collective vessels, etc. **(Shluger, 1981)**

Ammonium phosphate fertilizer is chemical given to plants with intention of promoting growth. It is has two types according to manufactured chemical process. these are monoammonium phosphate (MAP)($NH_4H_2Po_4$) and diammonium phosphate (DAP)($(NH_4)_2HPO_4$).

DAP is used in this work ,are the most popular phosphate fertilizers worldwide because of their high analysis and good physical properties.**(Vasant Gowariker, 2009)**.

Also DAP can lead to increased corrosion via hydrolysis to acids(i.e. a fall in pH).**(Eker *etal.*, 2005)**

Very large work are done in this field one of them used low carbon steel in aqueous solution of ammonium sulfate mineral fertilizer (1-40%, 20-60 C°)by gravimetric, potentiodynamic polarization and optical – microscopic methods. It has been established that the corrosion rate grows two times by increasing the concentration from 1 to 40% and by enhancement the temperature from 20 to 60C°-4 to 7 times. **(Fachikov, 2006)**

The effect of inhibitor content and inhibitor type associated with a temperature of corrosive environment on corrosion behavior of AISI 1020 carbon steel in 3.5 wt% NaCl solution by electrochemical technique. The results show that corrosion resistance of AISI 1020 carbon steel gradually increases with the amount of CaGL at 35C°.**(Paranard, *etal.*,2010)**.

The present work aims to study the corrosion behavior of low carbon steel in aqueous solution of ammonium phosphate fertilizer at various concentration and temperatures with and without using inhibitors using optical microscope method in order to investigate sample microstructure in different stage.

2-Experimental Work

2-1 Sample Preparation

Samples cut from a shaft of a commercial low carbon steel which get from engineering college workshop in Babylon University.

The chemical composition of the medium carbon steel used in this investigation is shown in **table (1)**. Which investigation in general company mechanical industries in Alskendiriya, Babylon.

The samples dimensions are 20 mm in diameter and 3 mm in thickness with drill hole diameter 2 mm. Firstly, the samples were polished by silicon carbide with grindiny 100, 400, 800 for removing all coarse scratches and contaminations. The samples were then rinsed by distilled water, and dried before testing. Exposed areas of the samples were fixed for 0.816 cm^2.

2-2Apparatus and equipment

Fig. (2) Shows the apparatus and equipments used in this work which include 1) Ammeter 2) Power supply 3) variac resistance 4) voltmeter and 5) the test cell.

The test cell included the low carbon steel specimen as a working electrode, corrosive solution in which the specimen was to be tested and saturated calomel electrode (SCE) as a reference electrode as well as Platinum electrode as an auxiliary electrode.

2-3Corrosive solution

The working media are prepared from diammonium phosphate (DAP) ($(NH_3)_2PO_4$) which get from local market in two concentration (5 %, 35%) dissolved tap water. Experiments have been down with absence and presented inhibitors at different temperatures (room temperature, 35 °C and 50 °C).

The samples tests were immersed in 250 ml corrosive solution without and with 20 ppm hexamine and (20 ppm hexamine and 20 ppm thiourea). Polarization curves were plotted with potential against current on semi log. scale.

The cathodic polarization is under activation control in the corrosion potential through the temperate and concentration ranges used in this work. This increasing in corrosion rate is attributed to the increasing of oxygen mass transfer and effected the activation polarization.

3-Results and Discussions

The electrochemical behavior of low carbon steel in (5 %, 35%) of diammonium phosphate fertilizer solution at (room temperature, 35 °C and 50 °C) which was studied on the basis of change in corrosion potentials (Ecorr) with corrosion current.

3-1 The results without inhibitors

The results of polarization curves of all tested low carbon steel are shown in figures (3-8). The values of corrosion current density and efficiency shown in table (2 and 3). It is obvious that as the temperature increases the corrosion rate increases and the corrosion potential become slightly more negative.

The cathodic polarization is under activation control in the corrosion potential through the temperature and concentration ranges used in this work. This increasing in corrosion rate is attributed to the increasing of oxygen mass transfer and effected the activation polarization.**(Joseph Riskin, 2009).**

$$\mathbf{2H^+ + 2e^- \longrightarrow 2H\ (ads.)}$$

The corrosion process governed by the cathodic reduction of dissolved oxygen might be expected to be wholly controlled by concentration polarization because of low solubility of oxygen especially in concentration salt solutions. Temperature is complex in that the diffusively of oxygen increases, but solubility decreases with temperature increase. **(Coway B. E.**,**etal. ,1976)**

3-2 Inhibitors effect

Figures (9-20) shown the effect of adding (20 ppm) thiourea and mixed of (20 ppm) thiourea + (20 ppm) hexamine. However, these are obvious that the inhibitors have an influence on an increasing of the corrosion potentials (less negative).

The inhibitors classed as anodic inhibitors, since they operate by producing a passivating oxide film primarily at these parts of the surface where matel cautions are formed at the anodes. **(West, 1965)**

The relationship between organic adsorption and hydrogen evolution on the medium carbon steel is still in the early state of understanding. In the case of medium steel this relationship is more complicated by hydrogen permeation into the metal. **(Nestor Perez, 2004)**

Over and above this inhibitor adsorption leads to the following general effects:

1- Simple blocking of the metal surface.
2- Variation in the free energy of adsorption of hydrogen.
3- Change in the potential drop at the outer Helmhottz layer.

The relative importance of each effect may depend on the surface species of the inhibitor.

Corrosion current density increasing and its inhibition efficiency decreases with the rise of temperature for the each types of inhibitors, it is suggested that ferrous adsorption at metal surface, the oxygen atom in the hydroxyl groups being the electron donor.

The adsorption of an organic molecule on the surface of the low steel is regarded as substitution of adsorption process between the organic compound in the aqueous phase (org_{aq}) and the water molecules adsorbed on the steel surface (H_2O) ams.

$$Org_{aq} \quad + \quad XH_2O \rightleftarrows org_{ams} \quad +XH_2Oaq$$

Where :

X: the size ratio, in terms of the number of water molecules replaced by adsorbate molecules. When the equilibrium of the process described in the above equation is reached it is possible to obtain different expression of the adsorption isotherm potls. **(A.K.Dubey, etal., 2007)**

From tables (2-3) show that the types of inhibitor efficiency be decreasing with increasing temperature and concentration. Also the second type decreases with increasing the concentration of slat.

3-3Effect of temperature

The corresponding results are given in table (2-3), the change of limiting current with the temperature is plotted in fig (21&22). We note that the corrosion rate density increase with increasing temperature

R is amenable to rate expression

$$K= Ae^{-E/RT}$$

Where:
A: the pre-expontial factor.
E: activation energy
K: gas constant
T: temperature. **(West, 1965)**

3-4Optical microscope test

Figures (23-28) shows the microscope test for specimens surface after immerged in DAP solution .At 50° C the corrosion causes a high crystal precipitated on the surface and this increase with increasing concentration while this effect decrease by using inhibitors especially at mixed inhibitor.

4-Conclusion

1-the corrosion behavior of low carbon steel in aqueous solution of diammonium phosphate fertilizers has shown that the steel pass into a state of cathodic polarization.

2- The corrosion current increasing and the inhibitor efficiency increasing as the DAP concentration increasing.

3-The corrosion current increasing and the inhibitor efficiency decreasing with increasing temperature.

4-the efficiency of the second type inhibitor decreases with increasing concentration.

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Table 1. Chemical composition of low carbon steel

C%	Cr%	Mn%	Si%
0.09	0.04	0.50	0.07

Table 2.limition current density and inhibition efficiency of low carbon steel in 5% DAP aqueous solution containing thiourea and (thiourea + hexamine) as inhibitors in different temperatures.

T (C°)	T (k)	1/T (K^{-1})	1/T ($C^{\circ -1}$)	i_o without inhibitor	i with one inhibitor	Ί %= (i_o-i)/i_o	i_L with two inhibitors	Ί %= (i_o-i)/i_o
20	293	0.0034	0.05	2.45	0.857	65	0.735	70
35	308	0.0033	0.0286	4.899	2.327	53	1.837	63
50	323	0.0031	0.02	7.958	9.799	35	3.061	62

Table 3.limition current density and inhibition efficiency of low carbon steel in 35% DAP aqueous solution containing thiourea and (thiourea + hexamine) as inhibitors in different temperatures.

T (C°)	T (k)	1/T (K^{-1})	i_o without inhibitor	i with one inhibitor	Ί %= (i_o-i)/i_o	i_L with two inhibitors	Ί %= (i_o-i)/i_o
20	293	0.0034	3.67	1.4698	60	0.919	75
35	308	0.0033	12.243	7.349	40	4.28	65
50	323	0.0031	23.273	13.929	32	8.574	64

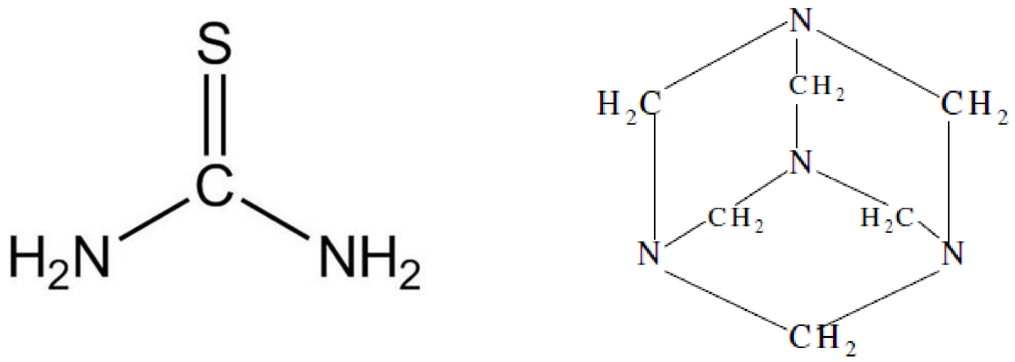


Fig. 1 Chemical structures of (a) Thiourea (b) Hexamine (Finar I L, 1959)

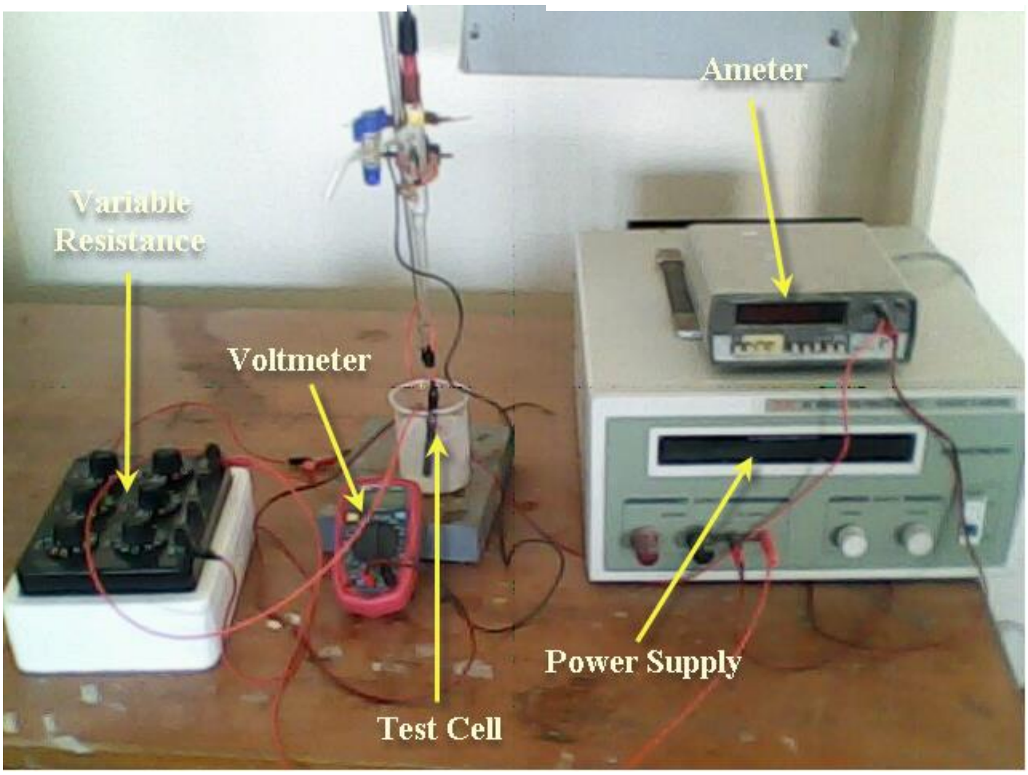


Fig.2 Electrochemical polarization circuit

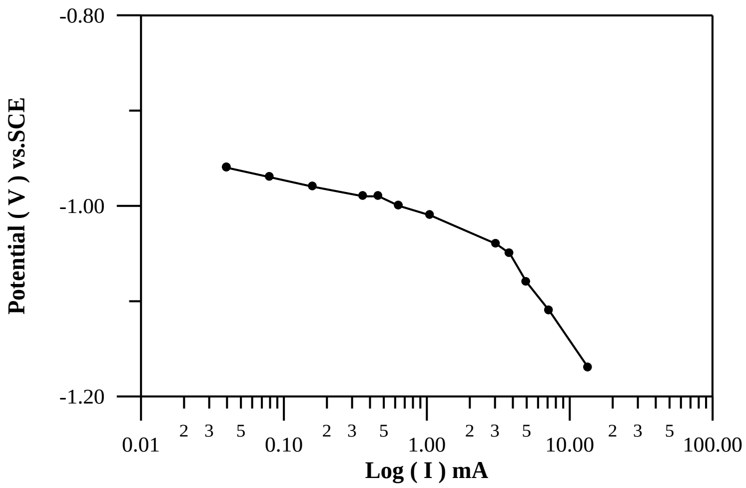


Fig.(3) Cathodic polarization curve of low carbon steel specimen in 5% DAP solution at room temperature

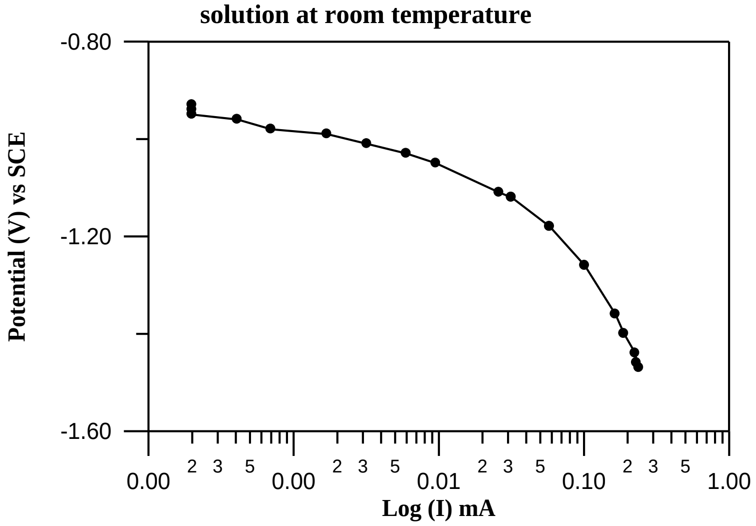


Fig.(4) Cathodic polarization curve of low carbon steel specimen in 5% DAP solution at T= 35 C °

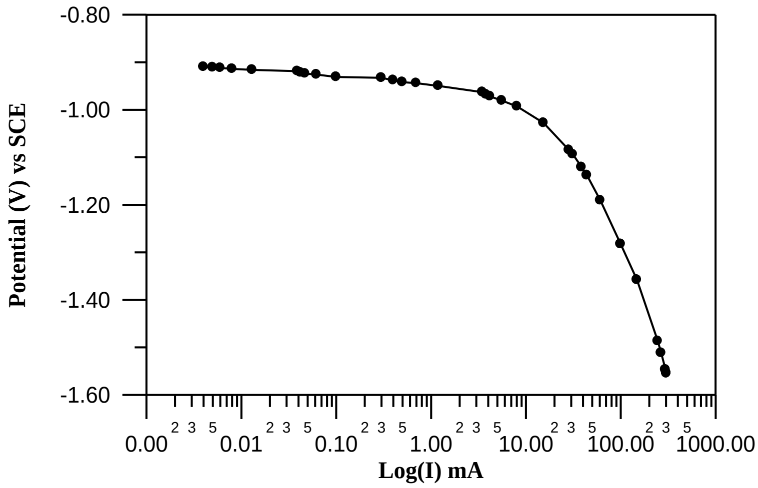


Fig.(5) Cathodic polarization curve of low carbon steel specimen in 5% DAP solution at T= 50 C °

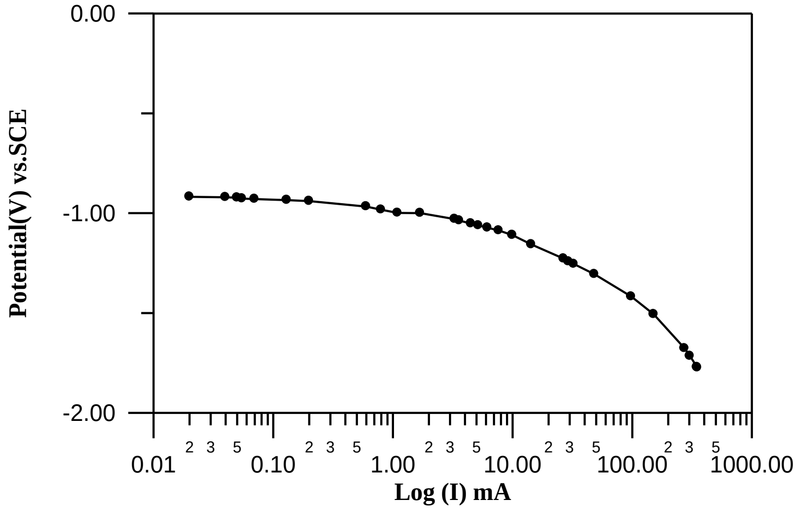


Fig.(6) Cathodic polarization curve of low carbon steel specimen in 35% DAP solution at room temperature

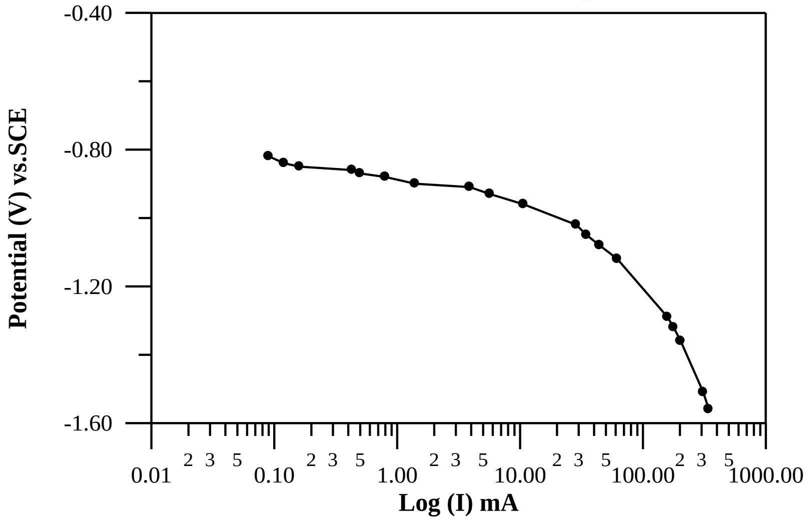


Fig.(7) Cathodic polarization curve of low carbon steel specimen in 35% DAP solution at T= 35 C °

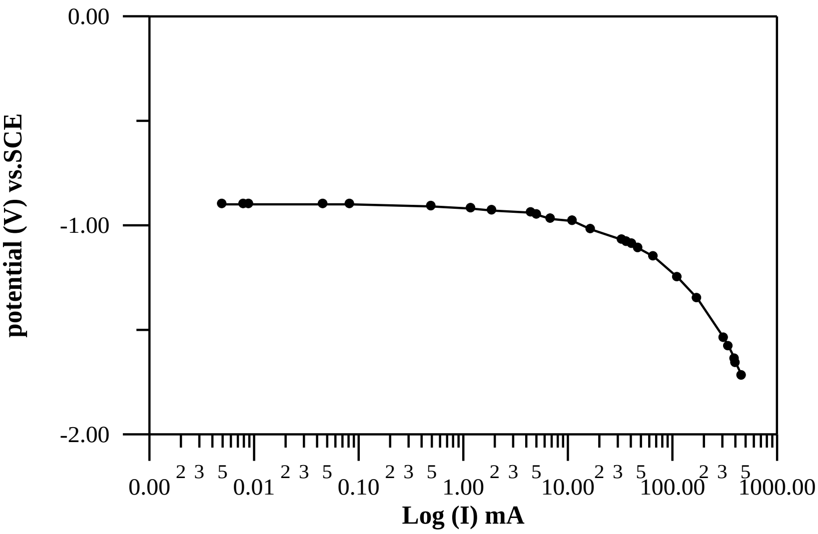


Fig.(8) Cathodic polarization curve of low carbon steel specimen in 35% DAP solution at T= 50 C °

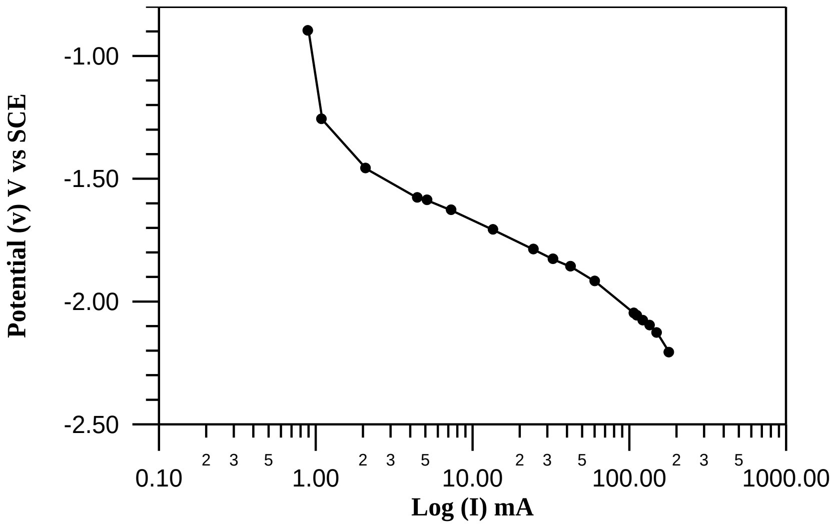


Fig.(9) Cathodic polarization curve of low carbon steel specimen in 5% DAP solution and 20 ppm theourea at room temperature

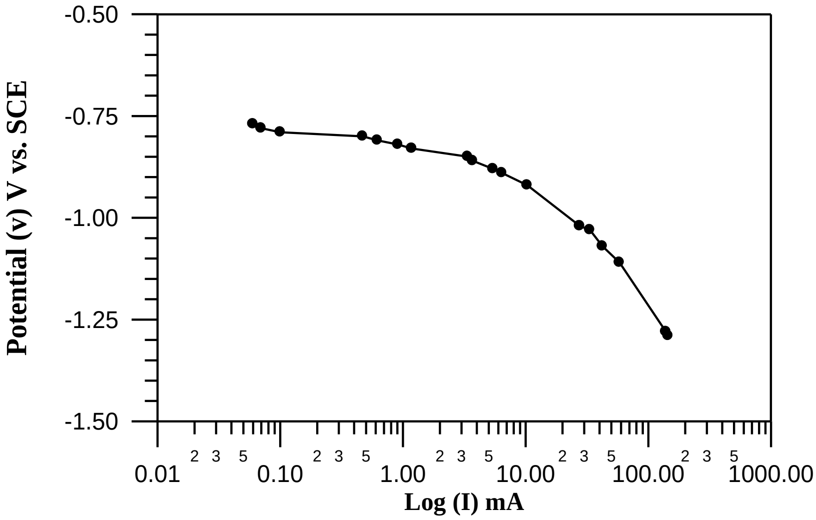


Fig.(10) Cathodic polarization curve of low carbon steel specimen in 5% DAP solution and 20 ppm theourea at T= 35 C °

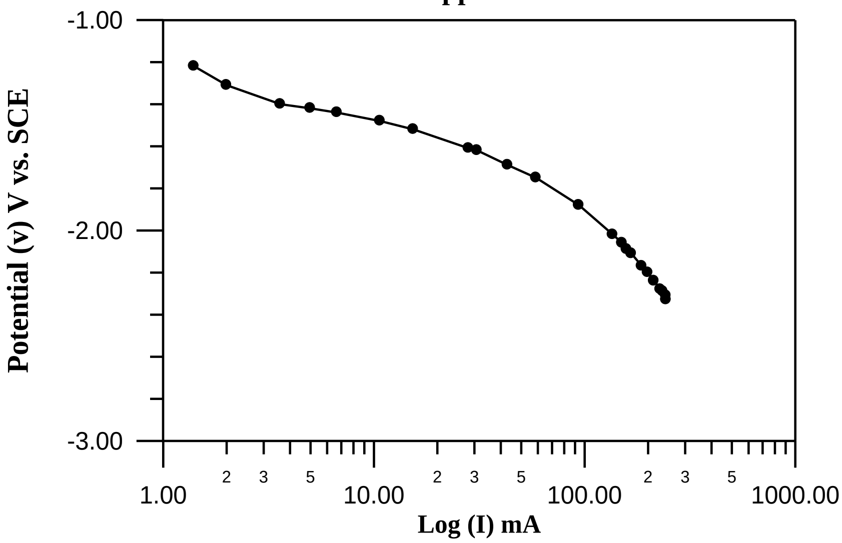


Fig.(11) Cathodic polarization curve of low carbon steel specimen in 5% DAP solution and 20 ppm theourea at T= 50 C °

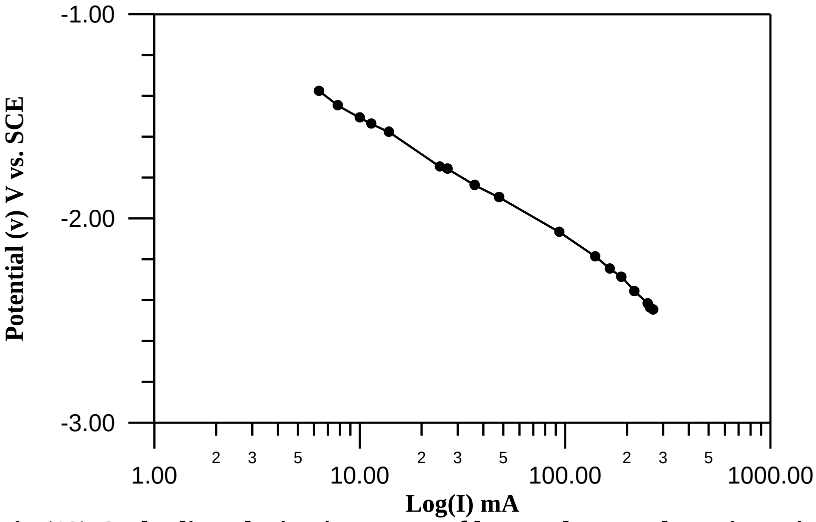


Fig.(12) Cathodic polarization curve of low carbon steel specimen in 35% DAP solution and 20 ppm theourea at room temperature

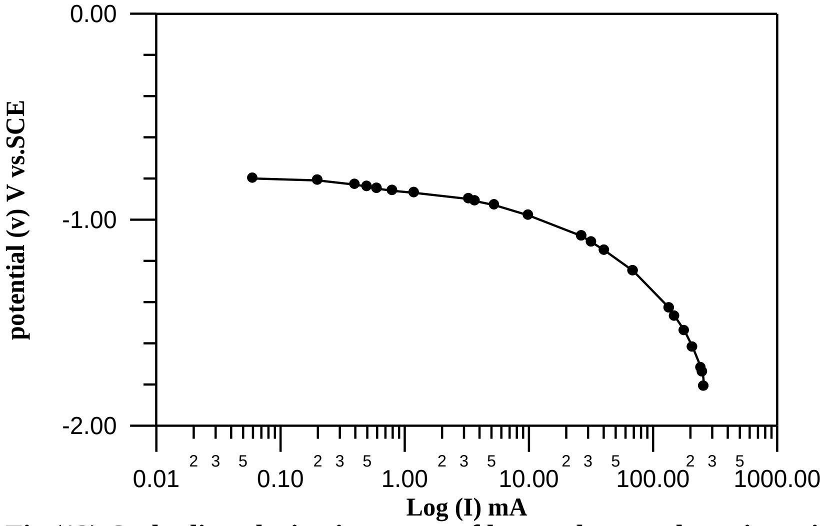


Fig.(13) Cathodic polarization curve of low carbon steel specimen in 35% DAP solution and 20 ppm theourea at T= 35 C °

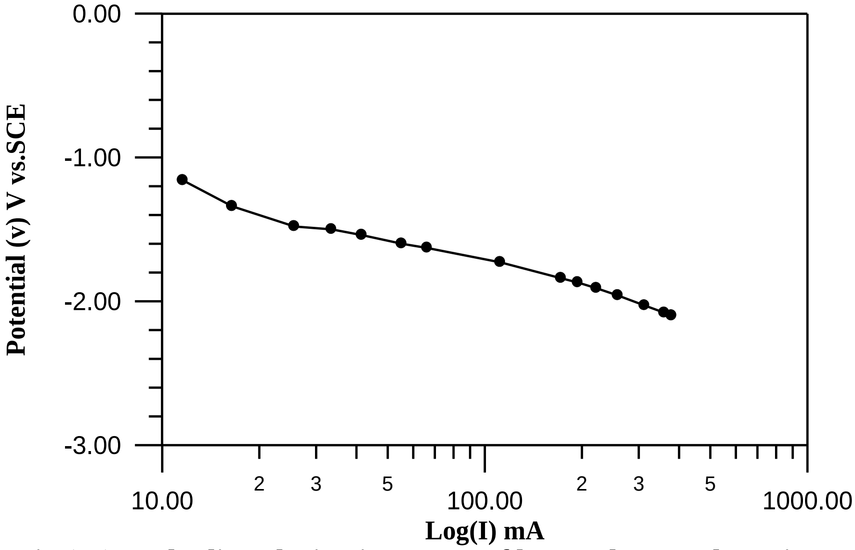


Fig.(14) Cathodic polarization curve of low carbon steel specimen in 35% DAP solution and 20 ppm theourea at T= 50 C °

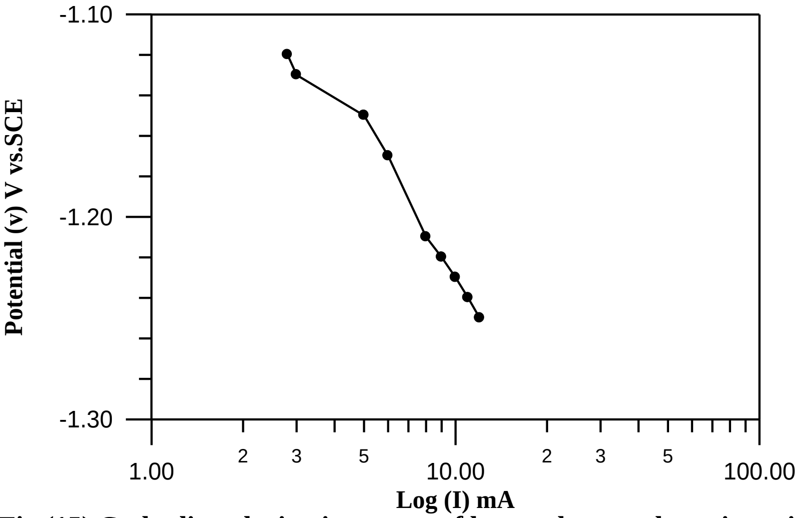


Fig.(15) Cathodic polarization curve of low carbon steel specimen in 5% DAP solution and (20 ppm theourea + 20 ppm hexamine) at room temperature

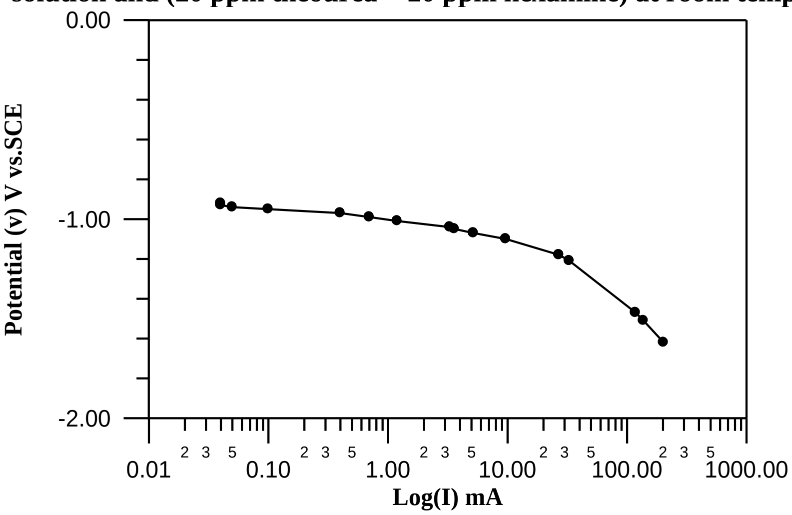


Fig.(16) Cathodic polarization curve of low carbon steel specimen in 5% DAP solution and (20 ppm theourea + 20ppm hexamine) at T= 35 C °

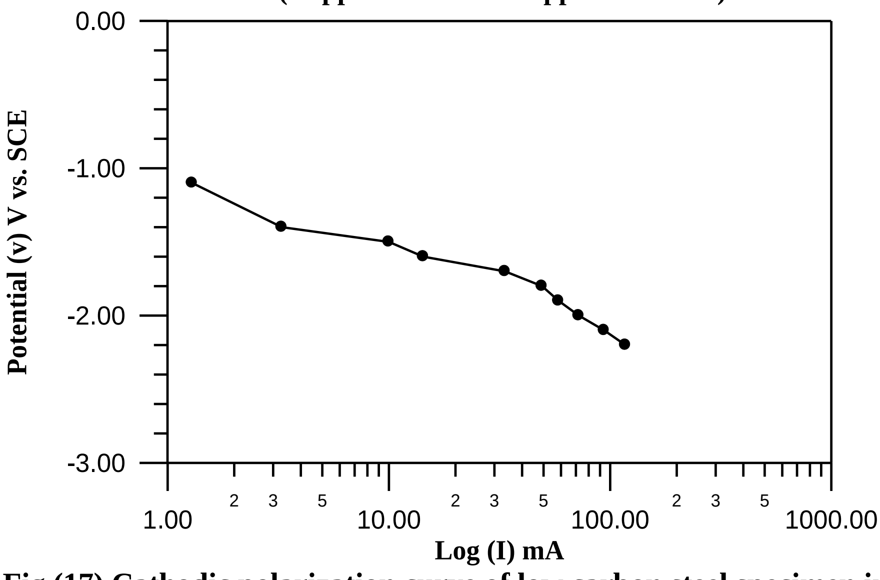


Fig.(17) Cathodic polarization curve of low carbon steel specimen in 5% DAP solution and (20 ppm theourea + 20ppm hexamine) at T= 50 C °

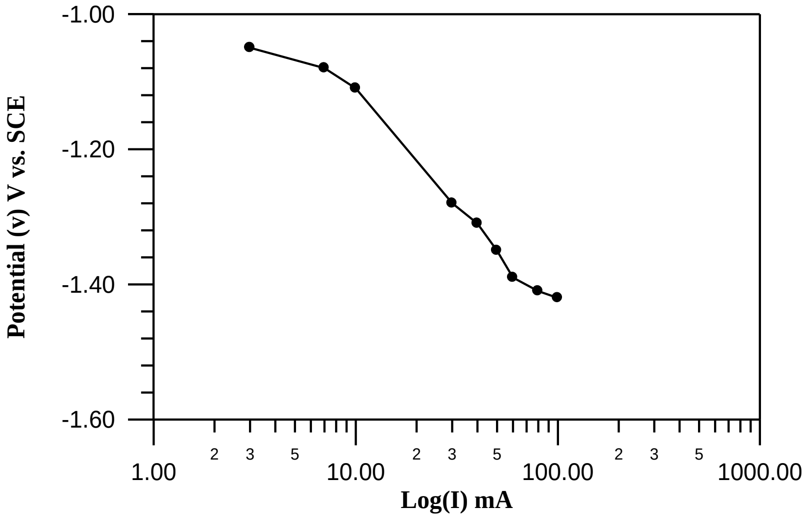


Fig.(18) Cathodic polarization curve of low carbon steel specimen in 35% DAP solution and (20 ppm theourea + 20 ppm hexamine) at room temperature

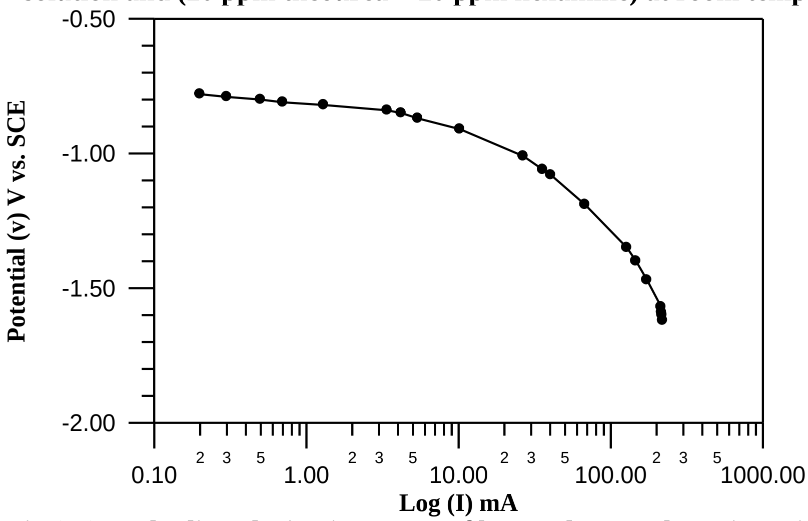


Fig.(19) Cathodic polarization curve of low carbon steel specimen in 35% DAP solution and (20 ppm theourea + 20ppm hexamine) at T= 35 C °

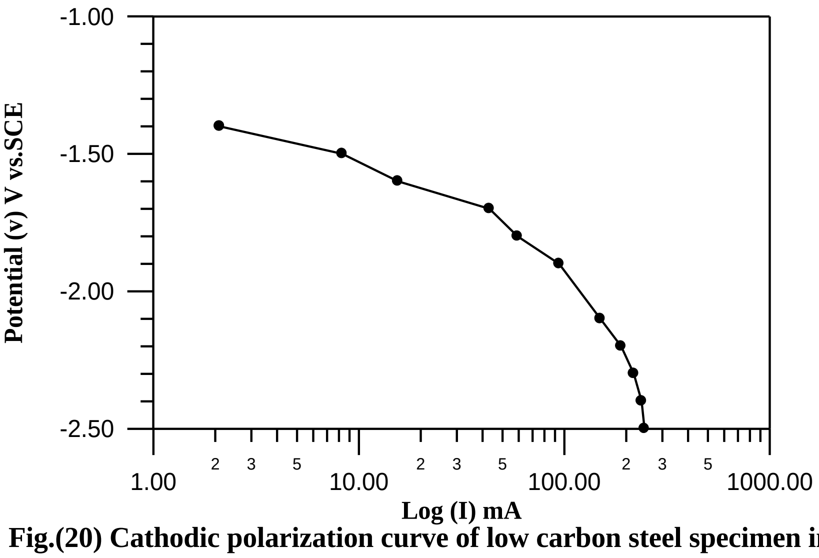


Fig.(20) Cathodic polarization curve of low carbon steel specimen in 35% DAP solution and (20 ppm theourea + 20ppm hexamine) at T= 50 C °

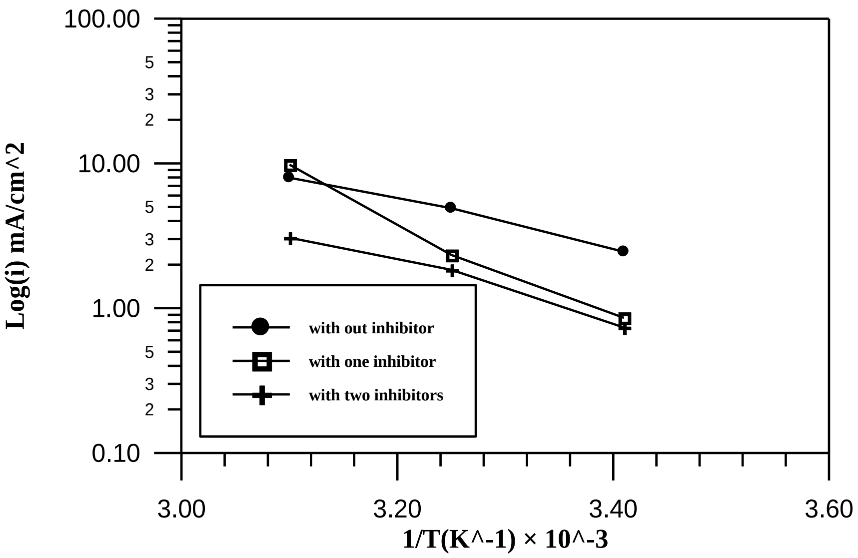


Fig.(21) Variation of corrosion current density with temperature (293 K, 308 K, 323 K) at different inhibitors for low carbon steel specimen in 5% DAP solution

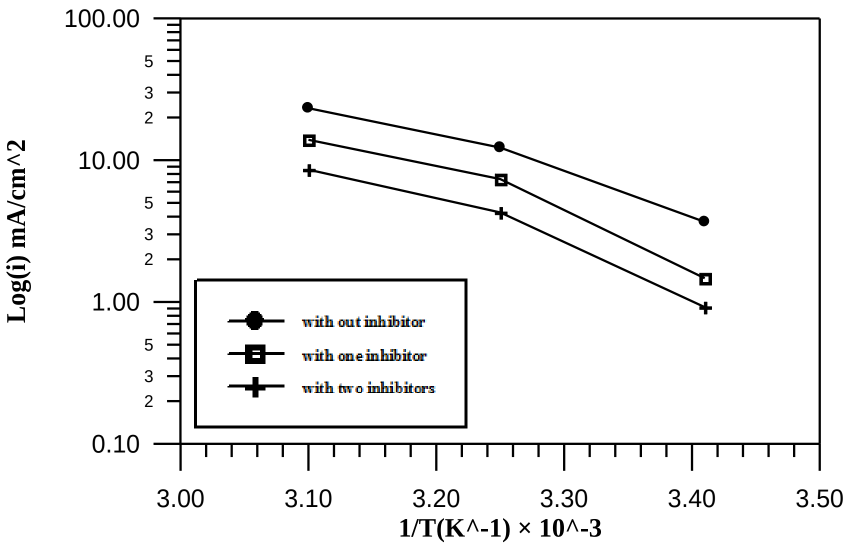
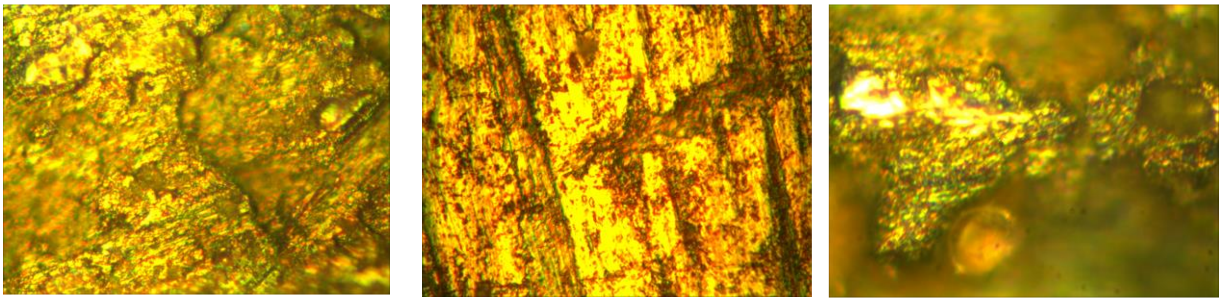
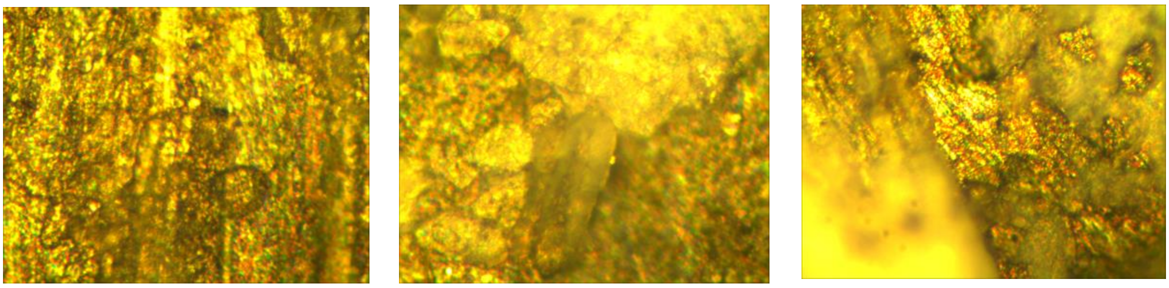


Fig.(22) Variation of corrosion current density with temperature (293 K, 308 K, 323 K) at different inhibitors for low carbon steel specimen in 35% DAP solution



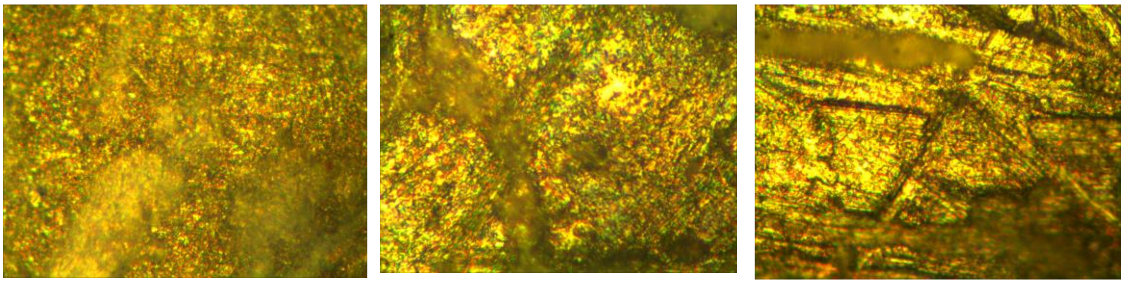
(a) At room temperature **(b) at 35 ºC** **(c) at 50 °C**

Fig.(23) microscopic test of samples after corrosion test in 5% DAP solution without inhibitor at different temperature



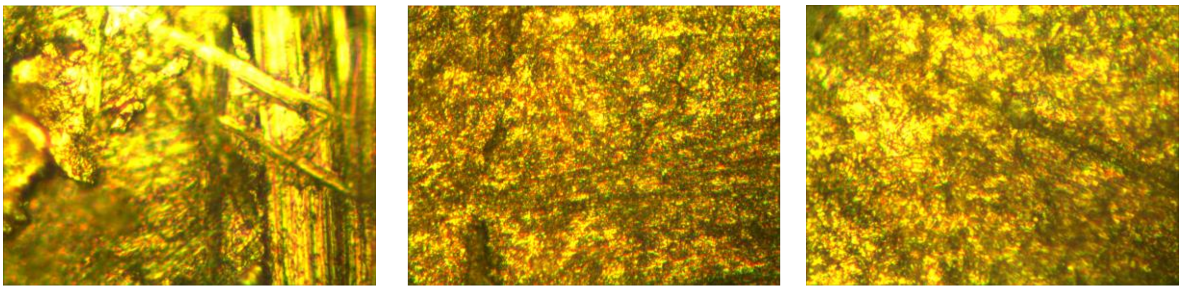
(a) At room temperature **(b) at 35 ºC** **(c) at 50 °C**

Fig.(24) microscopic test of samples after corrosion test in 35% DAP solution without inhibitor at different temperature



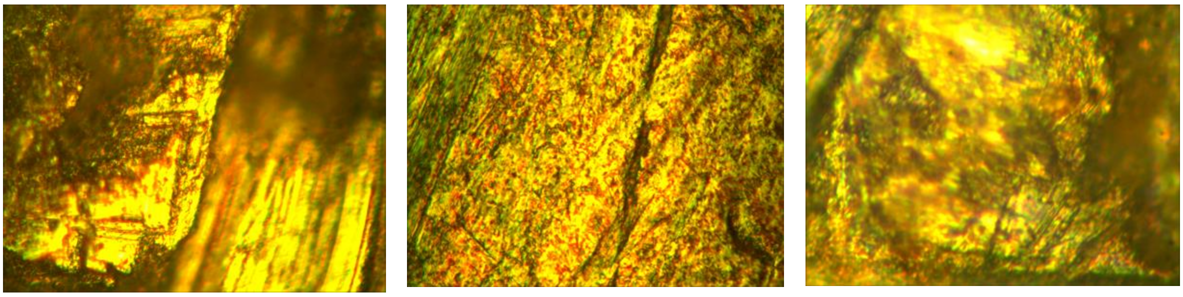
(a) At room temperature **(b) at 35 ºC** **(c) at 50 °C**

Fig.(25) microscope test of samples after corrosion test in 5% DAP solution with 20 ppm theourea at different temperature

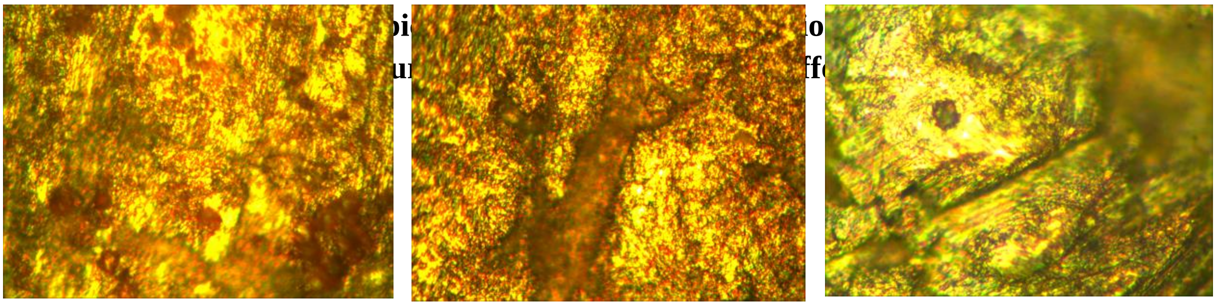


(a) At room temperature **(b) at 35 ºC** **(c) at 50 °C**

Fig.(26) microscopic test of samples after corrosion test in 35% DAP solution with 20 ppm thiourea at different temperature



(a) At room temperature **(b) at 35 ºC** **(c) at 50 °C**



(a) At room temperature **(b) at 35 ºC** **(c) at 50 °C**

Fig.(28) Optical microscopic test of samples after corrosion test in 35% DAP solution with (20 ppm thiourea +20 ppm hexamine) at different temperature