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Study the effect of Ni-P coating and 4,5-dimethyl- 1,2-dithiol-3-thione inhibitor on the corrosion of carbon steel

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Abstract

The carbon steel is widely used in the petroleum industry because of its excellent mechanical properties, but it is exposed to different environments, Such as hydrochloric acid who are commonly used for pickling and also for the removal of rust and scales in petroleum industries. In this work, we have studied the protection against corrosion of carbon steel by applying the Ni-P alloy coating deposited on a steel substrate compared to another method of protection by adding the 4,5-dimethyl- 1,2-dithiol-3-thione inhibitor in an aggressive medium (1M HCL) using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The results obtained are shown that This organic compound inhibits the acidic corrosion even at low concentration, is good inhibitors and are in good agreement. The efficiency of the inhibition Is increase with the increase of inhibitor concentration to reach the optimal values of 8×10^{-5} mM and the best coating of nickel-phosphorus at current density 5 A dm^{-2}. The obtained results showed that the Ni-P alloy coating Decreases the corrosion rate of carbon steel better than the inhibitor 4, 5-dimethyl- 1, 2-dithiol-3-thione.

Keywords: Ni-P coating, corrosion inhibitor, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS).

Introduction

Iron and its alloys used by industrial engineers in the construction of gas and oil pipelines and storage because of its excellent mechanical properties and low cost.[1] Corrosion is one of the most important factors in the chemical industry. It is usually the main cause of many of the problems encountered in operating in the production lines of these industries, which is often responsible for faults and production stops. This serious scourge has puzzled many researchers and become their main concern. There are several ways to protect metals, including the coating method and the use of corrosion inhibitors. The latter are widely used to mitigate metal erosion exposed to various media, because of their cost, effectiveness and ease of application. The most common are organic compounds due to their useful adsorption.[2] These organic particles protect the surface of the metal by forming a protective coating layer, preventing direct contact of metals with the aggressive medium, or reducing reaction rates, oxidation rate and / or reduction or both, by preventing active anodic and / or cathodic sites. The nature of the inhibition process depends mainly on the molecular structure and CI reaction mode with the metal, with the properties of the metal Surface, environment, absorption of solvent or ionic species.[3] The most effective inhibitors containing heterogeneous ring compounds contain heterogeneous atoms N, S, O or P.[4] On the other hand, the second way to protect metals from corrosion is the coating method. The most commonly used coatings are Ni-P based alloys because of its important properties such as corrosion resistance, good weldability, high electrical conductivity, smooth surface formation and symmetry, low coefficient of friction, electrical activity and paramagnetic properties.

[5-7] and which are produced by electrolytic reduction of nickel cations from an aqueous solution using various reducing agents. for example, sodium hypophosphite. Recently, much attention has been paid to the corrosion behavior of nickel and phosphorus coatings and their

properties, including the content and distribution of phosphorus. A passive layer on Ni-P coatings has been found to be easier than pure nickel plating in acidic environments because of the presence of nickel-plated phosphorus. [8]. In [9] was determined that the corrosion potential and charge transfer resistance of the Ni-P coating increase with increasing phosphorus content. According to Mimani and Mayanna [10]many factors affect the corrosion resistance of Ni-P coatings: the proportion of phosphorus in an alloy studied by many researchers. [6,8,11] The degree of crystallization, the size and direction of the granules, the phase, the structural change ,The highest corrosion resistance is associated with the amorphous coatings demonstrated by Raicheff and Zaprianova [12]; Lu and Zangari **[**11**]** have shown that the difference in corrosion resistance between electrodeposition Ni-low P and Ni-High P is partly due to structural variations. It is an amorphous and heterogeneous structure with a low P content, homogeneous and amorphous with a high phosphorus content, the porosity, is due to the preferential disintegration of nickel even in the open circuit potential, which enriches phosphorus on the surface layer and then oxidizes phosphorus in the coating surface to form a homogeneous layer of the hypophosphate. This latter prevents water molecules from interacting with nickel Thus inhibiting nickel oxidation**,** [13]which is the first step to form either two Ni^{+2} soluble or negative nickel film.

In this paper, we studied two goals. The first goal is to deal with the preparation and characterization of electrodeposition Ni–P coating deposited on carbon steel. The second goal is to evaluation and comparison of the corrosion rates of the Ni-P coating and corrosion inhibitor on the carbon steel in 1 M HCl It was studied by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods.

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Materials and Methods.

Electrodeposition of Ni–P alloy Coating.

The electroplating Ni-P coating was deposited on the carbon steel substrate, from a solution containing ($NiSO_4.7H_2O$), sodium hypophosphite ($NaH_2PO_2.\ 2H_2O$) (Table 1), distilled water was used for electrolyte preparation. The electroplating cell contains a nickel sheet (30×10×2 mm^3) of commercial purity (99.99%) as anode and an carbon steel substrate were used as a cathode, the chemical composition of carbon steel presented in Table 2 with of (20 ×10 ×5 mm^3). The substrates were mechanically polished with SiC abrasive paper (120 - 1200). They were rinsed with distilled water, were degreased in (50 g l^{-1} Na2CO3 and 15 g l^{-1} NaOH) for two minutes at a temperature of 35°C. The solution, then pickled in 10% HCl solution to remove oxide traces, and finally washed with bi-distilled water. The pH value of the bath was adjusted by adding hydrochloric acid or sodium hydroxide solution. The surface morphology of the Ni-P coatings was examined by scanning electron microscopy (SEM) FEI QUANTA 200. The compositions of the Ni–P coating were determined with energy-dispersive x-ray spectroscopy (EDS) analysis tool attached to SEM. Finally, a Bruker x-ray diffractometer (XRD) (D8 Advance model) with Cu Kα radiation (1.5406 A^0) was used to analyze the structure and the coating phase's composition.

Table1. Bath composition and deposition conditions used for Ni–P coatings

Electrolytes	Concentrations	Deposition conditions	
$NiSO_4{\cdot}7H_2O$	52 *g l*$^{-1}$	Temperature	75 -80^{0}C
$NaH_2PO_2.2\ H_2O$	26 *g l*$^{-1}$	Current density	5 A.dm^{-2}
H_3BO_3	24 *g l*$^{-1}$	Time	30 min
NaCl	40 *g l*$^{-1}$	pH	3
$C_7H_5NO_3S$	0.1 *g l*$^{-1}$		

Table2. Chemical composition of carbon steel

Element	*C*	*Mn*	*Cu*	*Al*	*S*	*Si*	*P*	*Nb*	*Ti*	*Mo*	*V*
Wt(%)	0.16	1.17	0.19	0 .04	0 .07	0.2 3	0.007	0.01	0.01	0.06	0.01

In order to test the adhesion of the Ni-P coatings, the samples were heated for 30 minutes at 250 °C and then submerged in water at room temperature. [14] Hardness measurements were performed on the Wilson 402UD Wolpert instrument, according to the Vickers method, with an applied load of 100 N for 10 seconds. Mean values were taken for at least five measurements performed at different locations in each sample. The tight adhesion of the Ni-P coating is due to the roughness of the carbon steel surface.

Corrosion tests

The corrosion phenomenon has been investigated, using two methods: Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Potentiodynamic polarization measurements were conducted at ambient temperature using an electrochemical measurement system controlled with a voltalab PGP 201 corrosion analysis. Have been conducted by using a standard three-electrode cell with the Ni-P electrodes ($1cm^2$), as a working electrode, Pt as an auxiliary electrode and saturated calomel electrode as a reference electrode, all have immersed in a glass cell with a capacity of 500 mL contains 1M HCl solution. All potentials are reported vs. SCE.

For Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), the working electrode is the disc cut from carbon steel and coated specimens with an exposed area of 1.0 cm^2. The potentiodynamic polarization tests were conducted with a scan rate of 20 mV min^{-1}. and in a potential range from - 600 to -200 mV. Corrosion rate (µm y^{-1}), corrosion potential E_{corr} (mV) and corrosion current density I_{corr} (µA cm^{-2}) have been calculated by using Tafel extrapolation technique provided by Volta Master 4 software. The i_{corr} values were used to calculate the inhibition efficiency. The inhibition efficiency, E (%) is calculated by the following expression. [15]

$$E\,(\%) = (1 - \frac{\text{icorr}}{i^0\text{corr}})X100 \qquad (1)$$

Where i_{corr} and i^{o}_{corr} are the corrosion currents densities in the presence and absence of the inhibitor in the solutions, respectively.

Electrochemical impedance spectroscopy (EIS) was conducted in an electrochemical measurement system (Voltalab40) which comprises a PGZ301 potentiostat and carried out in the frequency range of 10 khz to 1 Mhz. The applied sinusoidal signal amplitude is 10 mV. Impedance spectroscopy (EIS) was used to investigate the electrode/electrolyte interface and processes that occur on the carbon steel with and without DMDTT, and Ni-P coating in 1M HCl solution. Impedance measurement was recorded after the stabilization of electrode at open circuit potential (OCP) for 30 min. In Nyquist plots that were obtained, the imaginary component of impedance (Z_i) according to the real component of impedance (Zr) for each excitation frequency. The EIS plots are fitted through the EC-Lab software program. The double-layer capacitance (C_{dl}) was calculated from the following equations. [16]

$$f\,(-Z_{max}) = \frac{1}{2\pi R_{ct} C_{dl}} \qquad (2)$$

where $f(-Z_{max})$ is the frequency at maximum imaginary component of the impedance and R_{ct} are the charge transfer resistances.

Results and Discussion

Ni–P Coating Morphology structural and Chemical Analysis

The surface morphology of the Ni-P alloy was studied using SEM which is shown in Fig.1 the morphological image shows the similar spherical nodular structure made up of typical broccoli-like forms and one big nodule including many fine small nodules.

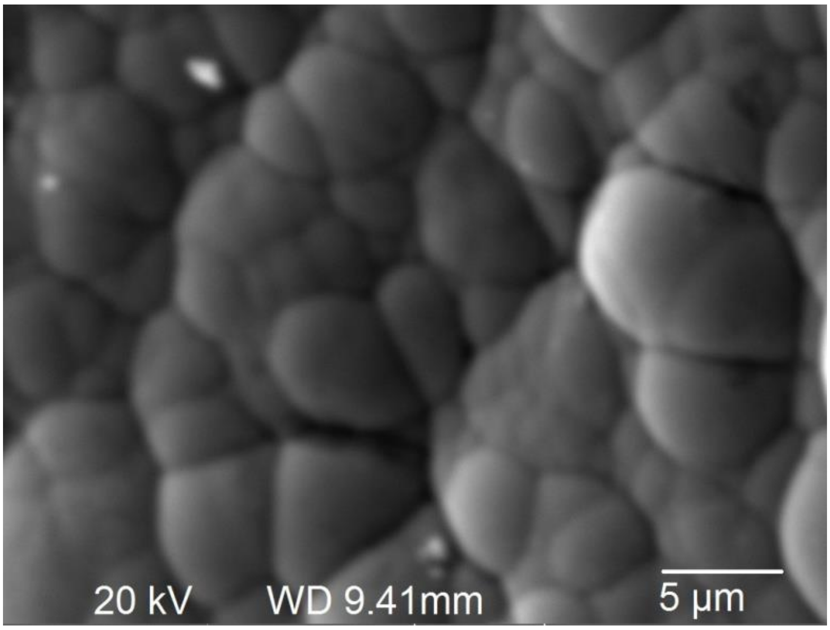

Fig. 1 SEM morphologies of Ni–P alloy deposits at plating current density, 5 A dm^{-2}.

The Ni-P deposition was selected for EDX analysis. Using the EDS mapping analysis, it was determined that Ni and P distribution in the deposited Ni-P coating was homogeneous, as shown in Fig. 2. The EDX analysis determined that the Ni content in the deposited Ni-P layer was 88.77 wt % by weight and P content was 11.23wt% by weight. It is high phosphorus.

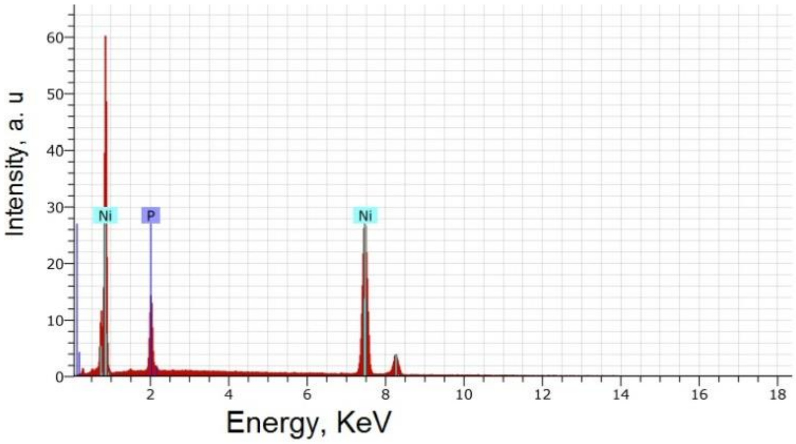

Fig. 2 EDX analysis of Ni–P alloy deposits at plating current density 5 A dm^{-2}.

Fig. 3. Clearly show the XRD pattern of the Ni-P alloy coating. There is only one peak amplitude shown in the spectrum, and this coating is considered to have an amorphous structure. Similar results have been reported in the literature [17, 18] indicating that deposits with phosphorous contents more than approximately 8 wt % are essentially amorphous.

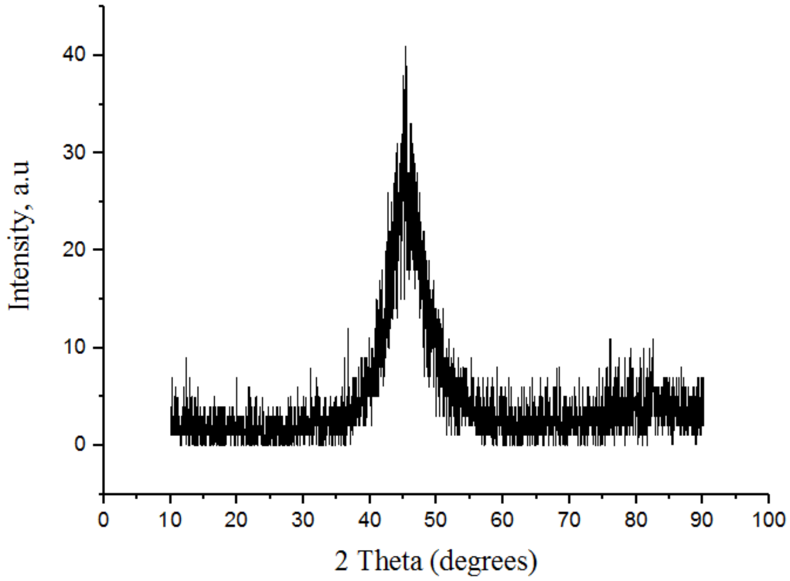

Fig.3. XRD pattern of Ni–P alloy deposit at plating current density 5 A dm^{-2}

Based on the measured value of hardness, it was determined from the five measurements to mean at different locations of the Ni-P coating. That the average value of the microhardness of the Ni–P coating was (365 H_VN_{100}). The microhardness of the deposited low-phosphorus Ni–P coating became higher in comparison with the values received for the high-phosphorus Ni–P coatings. As the content of phosphorus in Ni–P coatings increases, the microhardness of the coating decreased due to the microstructural changes (a decrease in crystallinity). [19] The microhardness of Ni–P coating (low-phosphorus) was higher compared with the values obtained for the high-phosphorus. The hardness of high-phosphorus (8-10 wt % P) Ni–P coatings ranges from 410 to 600 HVN_{100}.[20]

Corrosion tests.

Potentiodynamic polarization of the deposited Ni-P coatings.

Fig.4. Shows the polarization curves of an carbon steel substrate with and without Ni–P coatings electrodeposited at different current densities in (1M HCl) solutions. Based on the Tafel extrapolation analysis the values of the corrosion potential, E_{corr}, and the corrosion current density, i_{corr} for samples with the optimal Ni–P coating and the carbon steel were

determined. The values of the E_{corr} for the carbon steel and the optimal Ni–P coating were -497 and -267.4 mV, respectively, and the values of the i_{corr}, for the carbon steel and the optimal Ni–P coating, were 50.85 and 2.6 µm cm^{-2}, respectively (Table. 3). As can be observed the Ni-P coating shows a better corrosion resistance than the carbon steel substrate alone indicating thus the beneficial effect due to the presence of the coating. The corrosion potential (E_{corr}) value was shifted towards a more positive potential and the corrosion current density (i_{corr}) value decreased when the coating was present. In general, an amorphous Ni- P alloy coating has a better corrosion resistance than carbon steel. The increased corrosion resistance of the Ni-P coating is due to the interaction of phosphorus with the acidic medium to form the hypophosphite anions (H_2PO^{-2}). The latter act to form a barrier between the alloys and electrolytes to wetting the cooling of nickel atoms on the surface of the coating by inhibiting the mass transport of water. [13]

Table 3. Corrosion properties of Ni–P alloy coatings electrodeposited at different current densities.

J (A dm^{-2})	E(i=0) (mV)	R_p Ω cm^2	I_{corr} (µA cm^{-2})	Corrosion rate (µm y^{-1})
Blank	-497.0	264.67	50.8594	594.8
1	-436.5	934.98	20.1053	235.1
3	-416.5	668.83	26.2974	307.5
5	-267.4	9.71×10^3	2.0636	24.13
7	-272.5	4.06×10^3	3.8793	45.37
9	-353	1.03×10^3	14.0098	163.8

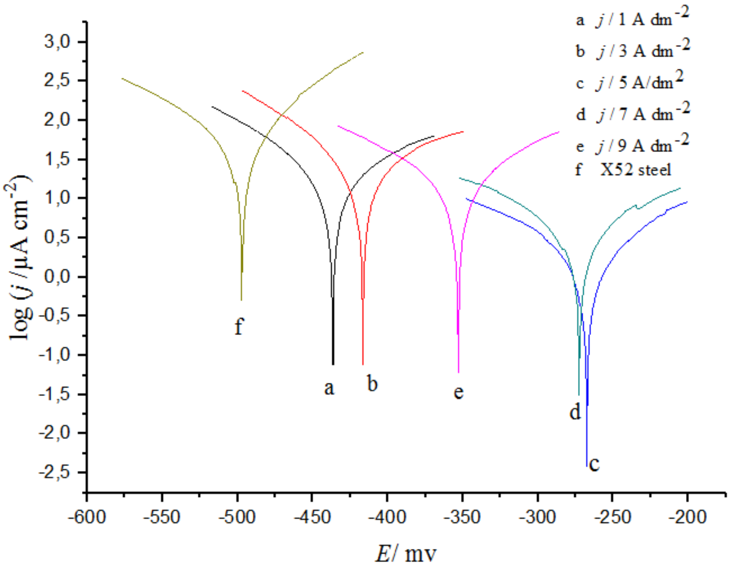

Fig 4. Polarization curves of Ni-P alloy coatings electrodeposited at different current densities

Potentiodynamic polarization of carbon steel with different concentration of DMDTT.

The potentiodynamic polarization curves of the carbon steel in 1M HCl solutions with and without the addition of different concentrations of DMDTT are shown in Fig. 5. The electrochemical corrosion parameters that are obtained from the polarization curves are shown in Table. 4.

Table. 4 Corrosion properties of carbon steel in 1M HCl with different concentrations of DMDTT

DMDTT (mM)	E(i=0) (mV)	R_p Ω cm^2	I_{corr} (µA cm^{-2})	Corrosion rate (µm y-1)	E (%)
00	-497.0	264.67	50.8594	594.8	00
2×10^{-5}	-502.3	1.6×10^{3}	9.1122	106.5	82.08
4×10^{-5}	-491.5	3.16×10^{3}	4.3395	50.75	91.46
6×10^{-5}	-503.2	1.65×10^{3}	7.5959	88.84	85.06
8×10^{-5}	-504.0	2.99×10^{3}	4.0053	46.84	92.12
10×10^{-5}	-495.1	578.32	15.7650	184.3	69.00

This result suggests that the addition of the inhibitors leads to a decrease of anodic dissolution and also retards the hydrogen evolution reaction; the best inhibition efficiency was about 92.12 % at concentration 8×10^{-5} mM. It can be seen that the corrosion current density (i_{corr}) decreased and inhibition efficiency (E %) increased by increasing inhibitor concentration. This is due to that the sulfur atom contains an electronic pair that helps it to stick to the metal and thus form a barrier between the steel and the HCl. The displacement of E_{corr} indicates that the corrosion inhibitor is a cathodic inhibitor.

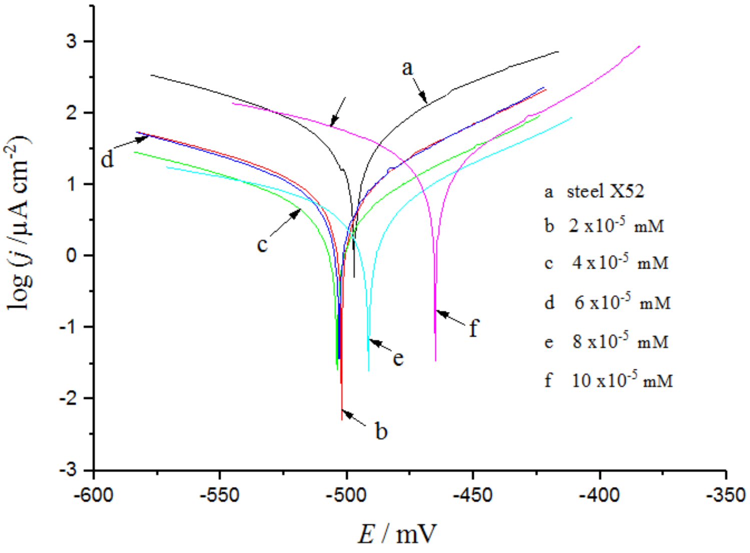

Fig5. Polarization curves of carbon steel in 1M HCl with different concentrations of DMDTT.

Fig. 6 shows the Nyquist plots of the carbon steel in 1 M HCl solutions with and without each of 8×10^{-5} mM of the (DMDTT), and Ni-P alloy coating respectively at room temperature. Table. 5 listed the impedance parameters, solution resistance Rs, charge transfer resistance Rct and double-layer capacitance (C_{dl}). It is obvious that there are just semicircle shaped plots in each diagram, Which indicates show that the (DMDTT) inhibitor and Ni-P coating are controlling only by the charge transfer process, as well as electrode surface homogeneity such that the adsorption of inhibitors is formed by compact layers. [21] Increasing Rp signifies the improvement of corrosion resistance. Among the samples, the Ni-P alloy coating shows the maximum Rp value compared with carbon steel (without and with $8x10^{-5}$ mM inhibitor) due to the interaction of phosphorus with the acidic medium to form the hypophosphite anions (H_2PO^{-2}), The latter act to form a barrier between the alloys and solution to wetting the cooling of nickel atoms on the surface of the coating . As illustrated in Fig. 7 an equivalent circuit is presented to analyze and compare the results. The represented elements shown in the circuit is a constant phase element CPE, in parallel with a resistor, Rct, which corresponds to a single capacitive loop. Rs (solution resistance), Rp (charge transfer resistance of the electrode reactions) and C (the double layer capacitance between the electrolyte and the coating).

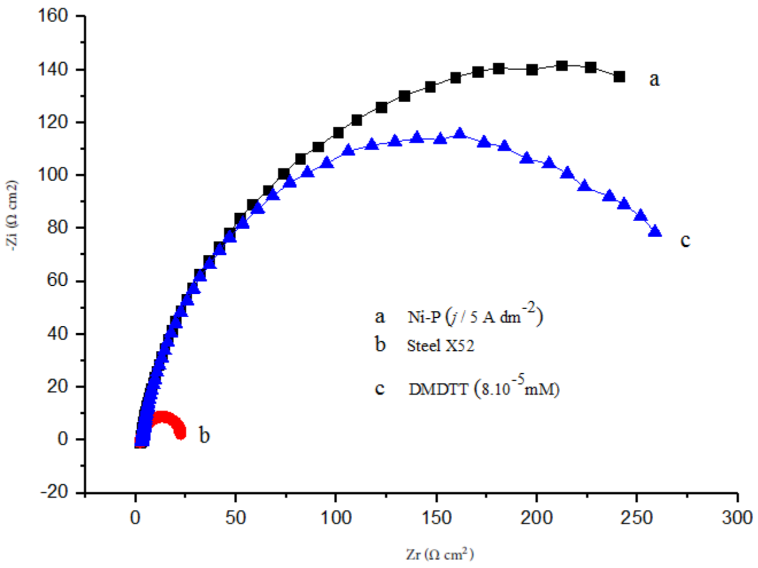

Fig. 6 Nyquist plots of carbon steel recorded in 1M HCL containing: $8x10^{-5}$ mM of DMDTT , Ni-P alloy coating .

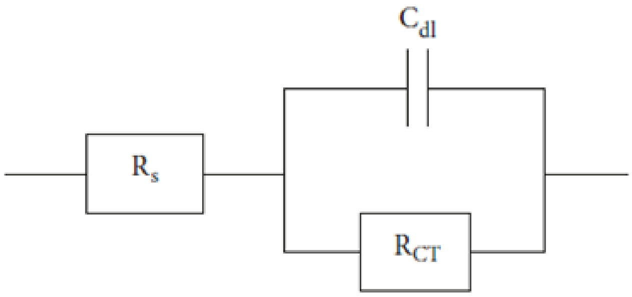

Fig. 7. Equivalent circuit for EIS

Table 5. Electrochemical impedance spectroscopy (EIS) for the corrosion of API X52 steel , Ni-P and inhibitor in 1 M HCL .

	R_s (Ω cm^2)	R_{TC} (Ω cm^2)	C_{dl} (μF cm^{-2})
Carbon steel	2.1750	15.49	0.0011
Ni-P Coating at 5A/dm^2	2.037	383.763	$2.93x10^{-6}$
DMDTT $8x10^{-5}$ mL	2.769	490.431	$2.84x10^{-6}$

Fig. 8 and Table. 6 shows the potentiodynamic polarization curves of the carbon steel with, and without each of 8×10^{-5} mM of the (DMDTT), and Ni-P coating in 1 M HCL. The polarization curve of the Ni–P coated sample is significantly shifted to more electropositive values, which means better corrosion properties of the Ni–P coated sample compared with carbon steel with, and without inhibitor (DMDTT).

Table 6. Electrochemical polarization measurements of carbon steel, Ni-P and inhibitor in 1 M HCl.

	E(i=0) (mV)	Rp Ω cm^2	Icorr (μA cm-2)	Corr rate (μm y^{-1})	E(%)
Carbon steel	-497.0	264.67	50.8594	594.8	00
DMDTT ($8*10^{-5}$)	-504.0	2.99×10^3	4.0053	46.84	92.12
Ni-P (5A/dm^2)	-267.4	9.71×10^3	2.0636	24.13	95.94

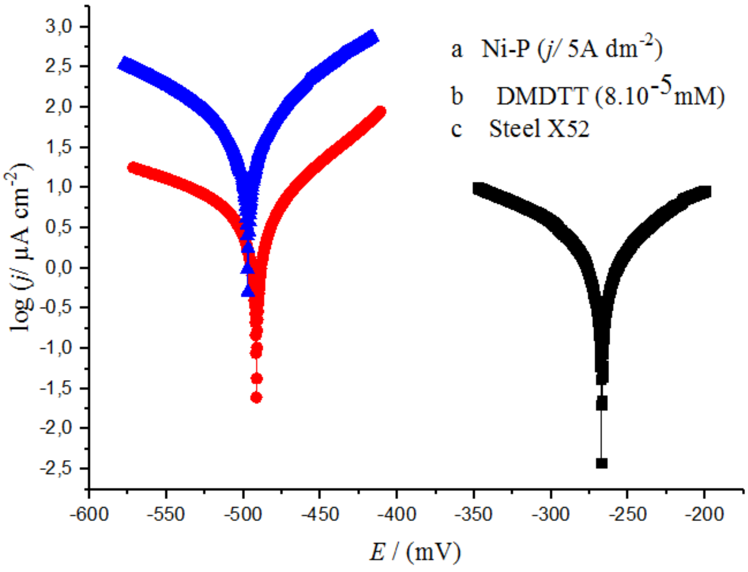

Fig8. Polarization curves of carbon steel, Ni-P (j /5A dm^{-2}) and DMDTT (8×10^{-5} mM).

Conclusion

Based on the results of the evaluation of the effect of the Ni-P alloy coating and 4, 5-dimethyl- 1,2-dithiol-3-thione inhibitor on the corrosion resistance of carbon steel. Conclusions can be made:

- Due to the proper pretreatment, deposited Ni–P coatings were successfully deposited on carbon steel. The content of Ni in the deposited coatings was 88.77 wt %, and the content of P was 11.23% wt %

- The adhesion of the deposited Ni–P coating confirmed.

- The microhardness of Ni–P coating was 365H_VN_{100}.

- The Electrochemical polarization and impedance tests have shown the Ni-P alloy coating decreases corrosion of the carbon steel better than the inhibitor 4, 5-dimethyl- 1, 2-dithiol-3-thione.

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