



Study the Preparation of Polymeric Coatings Supported by Nanomaterials to Inhibit Corrosion in the Oil Tanks

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Abstract:

In order to determine the most suitable composite coatings to inhibit corrosion in the oil tanks, the protection method was studied by the method of multiple layers of protection. Where there were three layers of protection, the base layer is a phosphate process using zinc phosphate, the second layer is a base painting (Hydrazine Hydrate with an epoxy zinc coating), while the top layer was a composite coating matrix of unsaturated polyester and epoxy supported by different fraction weight of nanomaterials. The top layer was supported by nano kaolin with 1% weight fraction, nano magnesium oxide with 3% weight fraction and nano zinc oxide with 5% weight fraction. The three layers were painted on metal pieces (1.5cm*1.5cm) of corroded tanks used to store diesel fuel. The hardness of the metal parts was studied before and after the phosphate process, where the results showed that the sample surface hardness was 123 HB and after the phosphate process was 131 HB.

The chemical corrosion and electrochemical corrosion test were carried out for a group of samples that were painted only once with a topcoat and again with three layers of paint. The results showed that the best protection against corrosion is the sample that painted with three layers of coating, and the top coating supported by a nano magnesium oxide, it has lowest corrosion current value (162.59 nA/cm²). Furthermore, the adhesion test showed that the coating supported by nanomaterials have higher

adhesion strength than those that are not supported by nanomaterials. Where the highest adhesion strength was (776 Psi) for magnesium oxide nanoparticle coating.

Introduction:

Corrosion is a degradation of a material, usually metallic, because of the reaction with its environment, mostly corrosion is electrochemical in nature.[1, 2] The oil industry uses various materials, including metals. The low Carbon steel is the main element and skeleton of oil industries, its used because of Carbon steels are usually Featuring by their high levels of hardness like Hardness (penetration resistance), ductility (resistance to fracture), and toughness (resistance to impact loading).[1] Oil tanks occupy a special niche among carbon steel structures at petrochemical plants and oil refineries[3]. But the Carbon steel is manmade materials produced by apply an energy to convert raw iron materials to steel metal. Because, the steel metal is not stable and undergo to corrosion by the oxidation, this lead to corrosion occur in various segments of the gas and oil industry by different mechanisms.[3,4] the presence of water associated with petroleum products is a major cause of corrosion, and is a general problem in the oil industry costing billions of dollars in a year.[5,6] there is a protection methods to inhibit corrosion in the oil industry like cathodic protection, coatings, addition of inhibitors to carbon steel, or a combination of these methods. The inhibitor of Corrosion defines as inorganic or organic, either chemicals, which, when added in small quantities to a system, reduce the corrosion rate of the metal/alloy. An inhibitor coating system consists of multiple layers of coatings with different properties and purposes. Depending on the desired characteristics of the coating system. A typical inhibitor coating usually consists of a top coat, one or several intermediate coats, and a primer.[7] This study aims to establish a corrosion inhibiting system consisting of several layers of coats to protect oil tanks.

Finally, this study aims to reach the best corrosion protection system in the oil tanks used to store diesel fuel especially from the corrosion resulting from the water associated with the fuel.

Material and methods:

This research was done in three stages: -

First stage: metal specimen Preparation.

A metal piece with size (30cm*30cm) was taken from a corrosive oil tank belonging to (the Iraqi Ministry of Oil – Oil Products Distribution Company) as shown in the Figure (1). The metal used in oil tanks was a low Carbon steel alloys (St-37) after analyzed by using spectrometer OE thermo ARL 3460. In the (Iraqi Ministry of Industry and Minerals – State Company for Steel Industries), Table (1) chemical composition for st-37 alloy. The corroded metal piece was polished and smoothed to remove the corroded part, and then cut into specimens with size (1.5cm*1.5cm) and thickness (3m.m) as shown in Figure (2). Finally, the hardness of the samples was checked by using (hardness INNOVA test - Holland Origin) and found it was equal to 123HB.

Table (1) Chemical composition for st-37 alloy

Sample description	Fe%	C%	Si%	Mn%	P%	S%	Cr%	Ni%	Mo%	Cu%
St-37	98.99	0.11	0.03	0.45	0.02	0.01	0.11	0.09	0.01	0.18

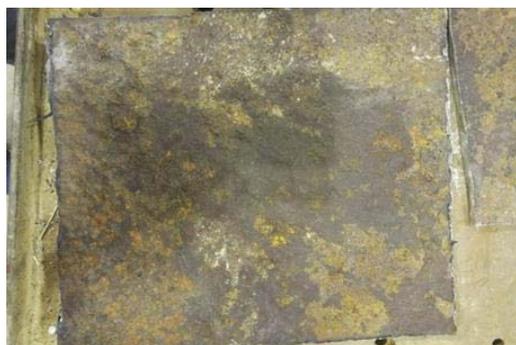


Fig. (1) The corroded metal piece (30*30cm)



Fig. (2) Corroded piece after polishing.

Second stage: corrosive medium Preparation.

Corrosive medium was simulated for use in electrochemical and chemical corrosion testing. It was prepared by mixing 20% water with 80% diesel fuel using a separation funnel as shown in Figure (3), then left for 24 hours until the water was separated from the diesel fuel and considered as a water-associated fuel and used as a corrosive environment for the oil tanks.



Fig. (3) Separation funnel

Third stage: Inhibitory layers Preparation.

The polymers (G-5533A) and (D-5542A) were supplied from Iraqi Modern Paint Industries Company, unsaturated polyester resins (UPR) was supplied from Saudi Industrial Resins Limited. Table (2) shows the physical properties of polymers material used in this study. A Zinc Oxide Nanoparticles (Zno) and Magnesium Oxide Nanoparticles (Mgo) that were supplied from Skyspring Nanomaterials, Inc, Kaolin Nano clay that was supplied form NANOSHAL LLC., USA as shown in Table (3)

Table (2) Physical specifications of polymer materials.

	(G-5533A)	(D-5542A)	UPE
Base	Epoxy resin	Epoxy resin	polyester
Physical State	Dense liquid	Dense liquid.	Liquid. [Clear.]
Odor	Pungent	Pungent	Pungent
Color	Grey	white	red
Density	1.4 – 1.5 kg/l	(1.3 – 1.4) kg/liter	1 To 1.3 G/Cm3 [25°C (77°F)]
Spreading rate	(3-4)m ² /l	(3.5 – 6) m ² /l	-
Solid by volume	62±2%	-	
Gloss level	matt (0 – 35)	gloss (90 – 100)	-
Flash Point	26 °c	38°c	Closed Cup: 30 To 33°C
Vapor Density		-	3.6 [Air = 1]

Table (3) Physical specifications of reinforcement materials

	Zinc Oxide Nanoparticles	Magnesium Oxide Nanoparticles	Kaolin
Formula	ZnO	MgO	Al ₂ Si ₂ O ₅ (OH) ₄
Form	powder	powder	powder
Color	white	white	white
Purity	+99%	99.9%	+99%
True density	5.606 g/cm ³	-	258.2 g/mol
APS	10-30 nm	10-30 nm	< 80nm
SSA	-60 m ² /g	> 50 m ² /g	-

A layer of zinc phosphate (primary layer) (P) has been applied and considered as a last line of defense to inhibitive the corrosion. Phosphate process was performed using zinc phosphate solution and diluted with distilled water by (10 ml per 100 ml), and then heat the solution to a temperature range between (85-90)C°. The metal specimen was immersed in

Zinc phosphate solution for a period of 15 min. Figure (4) shows the different between specimen covered by zinc phosphate and another specimen.

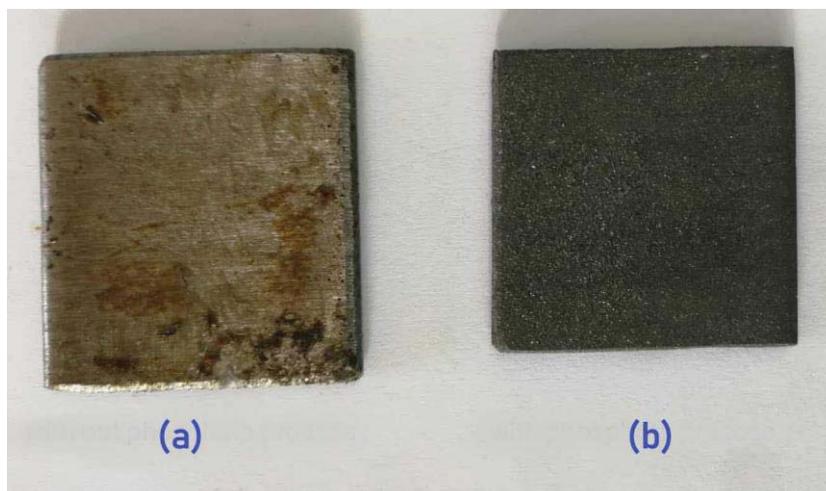


Figure 4: Two specimen before and after treatment with phosphate zinc oxide

a) Without phosphate process

b) With phosphate process

A Basic primer coating (G-5533A) from Iraqi Modern Paint Industries Company was adopted as an intermediate layer (B). The basic primer coating is consists of a two component, a polyamide epoxy zinc primer and its hardener (H-5530) with mixing ratio (by weight) (60:40) % (epoxy zinc primer: hardener). The basic primer coating has high resistance to water, acids, alkalis, salt, petroleum products and crude oil, bridge structures, external and submersible iron beams. Then we add a Hydrazine Hydrate ($\text{NH}_2\text{NH}_2\text{H}_2\text{O}$) (CASR NO. 7803-57-8) to basic primer with ratio (0.30 gm per 100 gm), hydrazine reduces the occurrence of oxidation processes of the metal by air molecules, because hydrazine form an adsorptive layer on the metallic surface. It leads to adsorption of air molecules. [8]

A top inhibitor coating, matrix polymers coating was prepared consists of an unsaturated polyester resin (UPE) and epoxy resin (EP) with a mixing ratio (UPE: EP) (80:20) %. Then take the previous ratio of matrix polymer and support it with a different weight fraction of nano kaolin, nano magnesium oxide, and nano zinc oxide. A hybrid top coating was mad that consists of a matrix polymer plus to mixture from kaolin, magnesium oxide, and zinc oxide. These mixing ratios were selected and supported by different

proportions of nanomaterials based on a previous study, where demonstrated that this ratio has the best mechanical characteristics like hardness test, wear test and impact test. [9]

A Paint spraying machine was used to paint the metal specimen with the above manufactured inhibitor coatings. Table (4) shows the specimen with different number of layers and inhibitor coatings.

Table (4) Number of layers for each specimen

Specimen No.	Primary layer (zinc phosphate)	intermediate layer (zinc epoxy)	Top layer
ST	No	No	NO
P	Yes	No	NO
O	No	No	(UPE:EP)(80:20) matrix polymer
K	No	No	1 gm of nano kaolin per 99 gm of (UPE:EP)(80:20) matrix polymer
M	No	No	3 gm of nano Mgo per 97gm of (UPE:EP)(80:20) matrix polymer
Z	No	No	5 gm of Zno per 95 gm of (UPE:EP)(80:20) matrix polymer
H	No	No	Mixture of (1 Kaolin + 3 Mgo + 5 Zno) gm per 291 gm(UPE:EP)(80:20) matrix polymer
PB	yes	Yes	NO
PBO	yes	yes	(UPE:EP)(80:20) matrix polymer
PBK	yes	yes	1 gm of nano kaolin per 99 gm of (UPE:EP)(80:20) matrix polymer
PBM	yes	yes	3 gm of nano Mgo per 97gm of (UPE:EP)(80:20) matrix polymer
PMZ	yes	yes	5 gm of Zno per 95 gm of (UPE:EP)(80:20) matrix polymer
PMH	yes	yes	Mixture of (1 Kaolin + 3 Mgo + 5 Zno) gm per 291 gm(UPE:EP)(80:20) matrix polymer

Result and Descusion:

Electrochemical corrosion test (Extrapolation Tafel Method), tafel curves gives information of corrosion process kineticss by measuring the potential $E_{(corr)}$ and the current density $I_{(corr)}$ of specimen. The specimen has the less value of current density shell be the lowest in corrosion rate. Figure (5) shwos that the specimen with three layer coatings have minimum current density of corrosion. Also Figures (6 – 8) show the relation between $E_{(corr)}$ versus $I_{(corr)}$ And their effect on the rate of corrosion for every specimen. Electrochemical corrosion test was done in Iraqi Ministry of Science and Technology – Coroption of Research and Industerail Development.

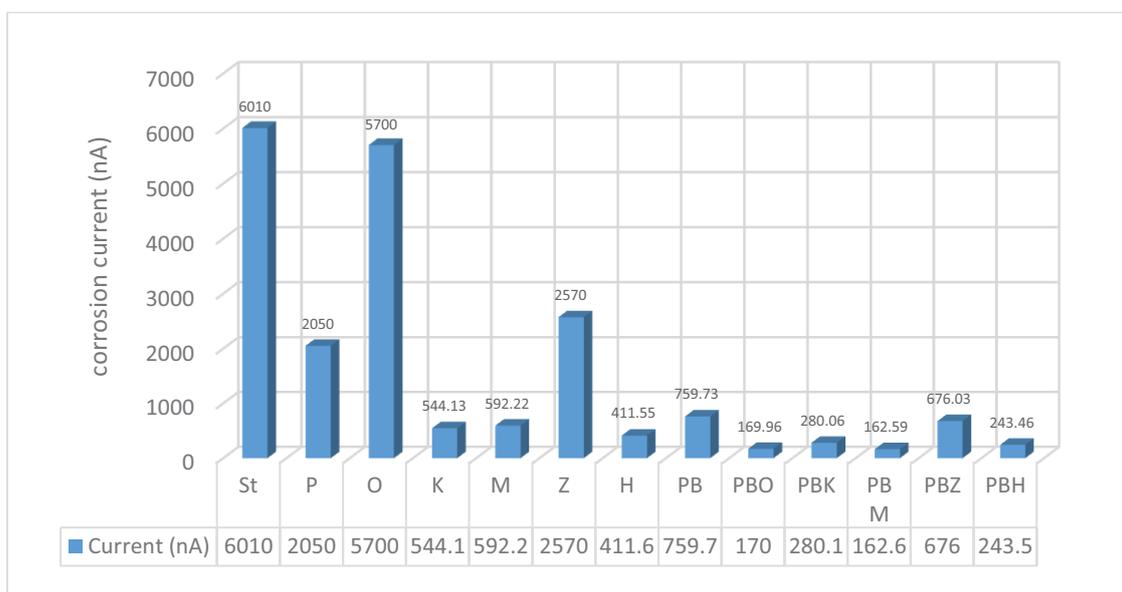


Fig. (5) The current density of corrosion for each specimen

It was found that processing the sample with two layers (phosphate layer P and intermediate layer B) led to a low rate of corrosion of the metal specimens because of the presence of Hydrazine Hydrate, which interact with the atoms of oxygen, which in turn prevent the occurrence of oxidation currency of the metal. In addition to the presence of zinc and phosphate, it was found that both ZN and Po form passive layers on the metal surface. These layers protect the metal from corrosion [10] As shown in Figure (6).

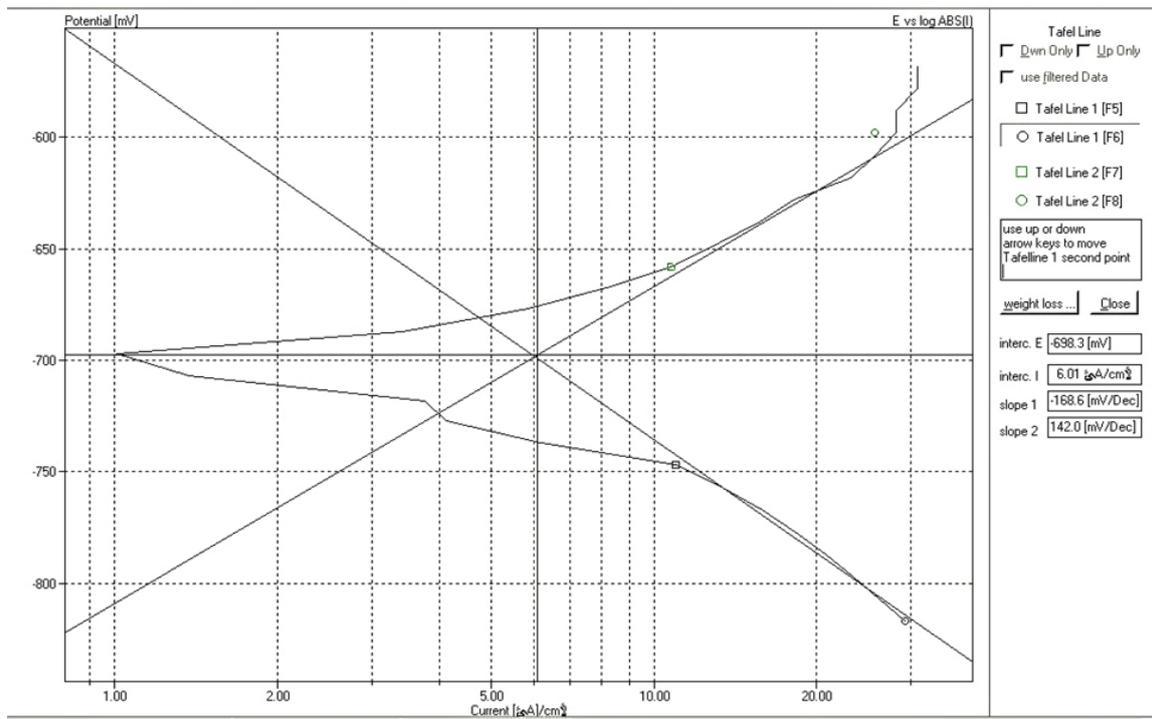


Fig. (6) $E_{(corr)}$ versus $I_{(corr)}$ for specimen with phosphate layer + basic coating (2 layers)

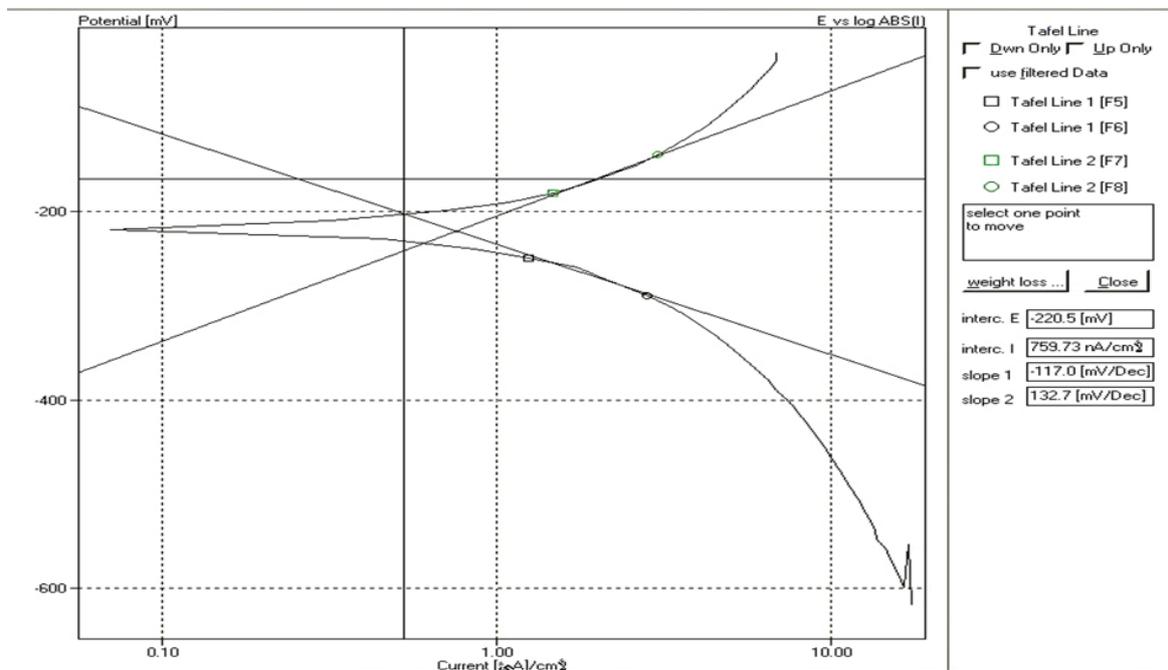


Fig. (7) $E_{(corr)}$ versus $I_{(corr)}$ for specimen without coating

It was noted that the best results were obtained when using three layers to inhibit the corrosion. Also, found that the specimen containing three inhibitor layers and top layer coating supported with nano magnesium oxide (PBM) had the lowest rate of corrosion. Where the density of corrosion current was reduced to (162.59 nA/cm^2) after (6010 nA/cm^2) for low carbon steel (st) as shown in Figures (7 and 8) because the magnesium oxide is an idle layer that protects the metal from corrosion and this agrees with a study [11].

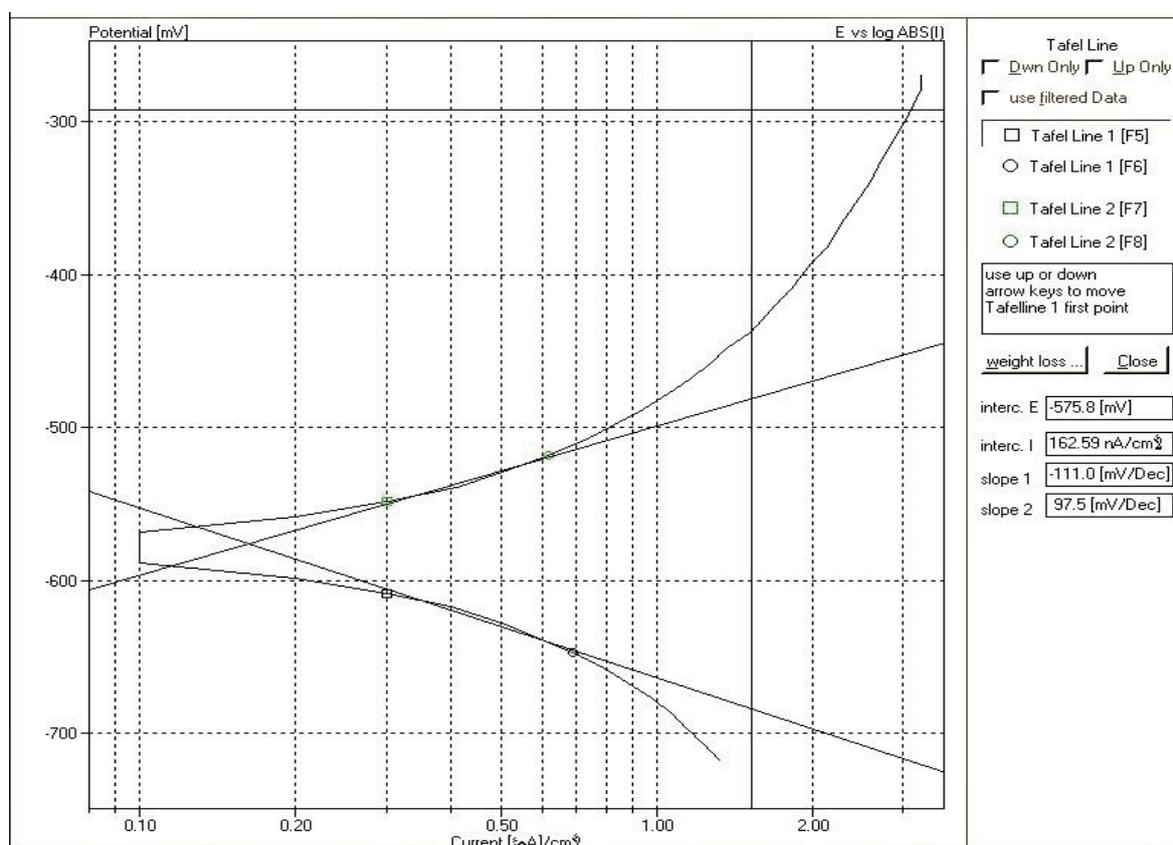


Fig. (8) $E_{(corr)}$ versus $I_{(corr)}$ for specimen with phosphate layer + baissc primer coating + matrix polymer coating supported with 3% Mgo (3 layers)

Chemical corrosion test:

Chemical corrosion testing was performed by immersing (PBO, PBK, PBM, PBZ, and PBH) specimens in corrosive medium (water associated with the diesel fuel) for multiple time periods (24, 72 and 168 hours). The above results obtained the lowest values in the corrosion rates in the electrochemical corrosion test; therefore, these specimens were selected for chemical corrosion testing.

Then extracted specimen from corrosive medium and analyze the corrosive medium with (Atomic absorption device in collage of education for pure science – ibn al haithem – center laboratory) to determine the iron ratio in the corrosive medium for each specimen. The presence of iron in the corrosive medium is evidence of the occurrence of oxidation process and thus led to corrosion in metal. Figure (9) shows the iron ratio in a corrosive medium for each specimen. The iron ratio of the (PBM) specimen corrosive medium did not exceed, as shown in Figures (9 and 10). This is a sign that the corrosion process does not occur in the (PBM) specimen, this is due to the fact that the addition of nano sized MgO particles may induce significant disorder in the original polymer chain which promotes the interaction between them. Thus, confirming the complete mixing of MgO in the polymer host[12].

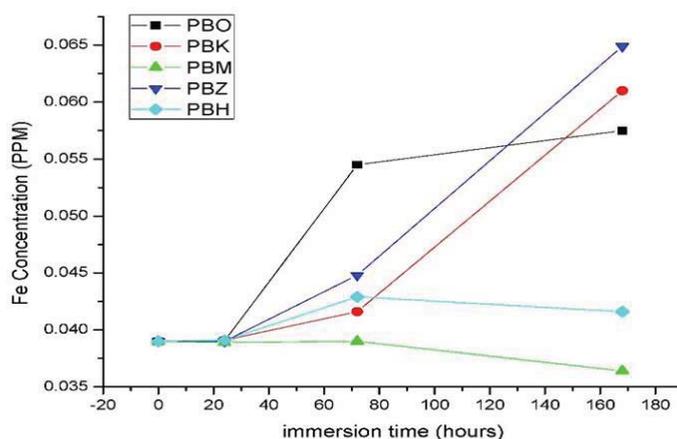


Fig. (9) Iron ratio in corrosive medium for each specimen.



Fig. (10) Immersion method of specimen in corrosive medium (chemical corrosion test).



Fig. (11) lasting adhesive tester (Posi Test AT – M model)

Adhesive force and Coating thickness test:

In Iraqi Ministry of Industry and Minerals - National Center for Packing and Packaging, the adhesion strength and thickness for (O and M) was tested as shown in Table (5).

The adhesion strength was tested by a device of American origin (Posi Test AT – M model) as shown in figure 11, a device consisting of (fastener) which Fixed on the surface of the specimen coated by a strong adhesives (adhesive epoxy device), and piston which Separates the fastener from the surface of the sample and shows on the screen of the device the force necessary for the separation process (the strength of the paste).

The thickness of the coating layer was checked using a Chinese origin device (MEGA – CHECK POCKET), which relies on the principle of magnetic induction as shown in Figure (12).

The results showed that the strength of adhesion increases after supported with nano MgO (M), where it became (776 Psi) after it was (311Psi) for the specimen (O). This is because when magnesium oxide is reinforced, surface roughness decreases as the relationship between surface roughness and adhesion strength is inverse.



Fig. (12) Layer thickness test device

Table (5) Adhesive force and coating thickness for O and M specimens

Specimen No.	Adhesive force	Coating thickness
O	776 Psi	105 μm
M	311Psi	118 μm

Conclusion:

- The specimens with three layers of coating (PBO, OBK, PBM, PBZ and PBH) are the best from other specimens in terms of their ability to inhibit the corrosion, where it got the lowest values in corrosion current density.
- The specimen (PBM) in which the three inhibitor coating layers system was used, obtained the lowest value in the corrosion rate (162.59 nA/cm^2). That is, the possibility of corrosion is a non-existent approach.
- In the immersion test, the specimen (PBM) showed that there was no corrosion in the specimen even after immersion for 7 days in the corrosive medium.
- It was found that when the matrix polymer reinforced by Nano magnesium oxide, the adhesion strength was increased to (776 Psi) after it was (311 Psi) before the reinforcement.

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