

Study of Coating Effect on Electrochemical Behavior for Oil Storage Tank

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Abstract

Cathodic protection is employed intensively on the pipe steel in oil and gas industry. It is a technique of prevention against the corrosion. This paper will discuss the using of sacrificial anodes and effectiveness of coating (with paint and Electrochemical Precipitation Coating) on the low carbon steels storage tank. To understand corrosion behavior, the extrapolation theory by polarization curves were used. Experimental tests were carried out on coated (with paint and Electrochemical Precipitation Coating) and bare low carbon steels storage tank with and without sacrificial anode (magnesium anode) by immersing in 3.5%NaCl solution. The results revealed that, the values of corrosion rate and corrosion potential were decreased with using the Electrochemical Precipitation Coating more than the same values with using paint coating of steel storage tank in 3.5 NaCl wt. %.

Keywords: Electroplating, Coating, Polarization Curve, Electrochemical Precipitation Coating, Paint .

1-Introduction

Protected surface the material from environmental attack, by application of an organic, inorganic or metallic coating [9]. Combination of protective coating and cathodic protection is the most effective and the most economical method of protection. The selection of the type and specifications of coating should be carried out by

considering the life cycle management of the construction. However, it should also be noted that, protection effect will be obtained only if the cathodic protection system is compatible with the chosen coating[7,2]. Chemical Precipitation coating (electroplating) has been a very widely employed technique to impart corrosion resistance to steel structures. When the underlying steel

substrate e.g. sheet metal is required to be deformed for applications such as automobiles, the coating needs to exhibit good formability. When the coating begins to crack its corrosion resistance starts to deteriorate due to the exposure of base steel to the atmosphere [10]. the chromium coating acting as solid lubricant at the interface during the deformation of several electroplating coatings of thickness up to 30 mm (3). In the evaluation of painted galvanized steels, various laboratory techniques have proven most useful with electrochemical impedance spectroscopy (EIS) as a sensitive quantitative technique for measuring coating degradation and corrosion protection. Sacrificial anode systems depend upon the differences in corrosion potential that are established by the corrosion reactions that occur on different metals or alloys. The more active metal (anode) is sacrificed to protect the less active metal (cathode). The amount of corrosion is dependent on the metal being used as an anode and is directly proportional to the amount of current supplied.

Another factor is the anode efficiency, which accounts for the anode's self-corrosion rate and the corrosion rate for the amount of cathodic protection current [6]. The effects of corrosion often require costly repairs and continued maintenance during a structure's life. When steel is exposed to an aggressive environment, or if the

design details or workmanship are inadequate, corrosion of the reinforcement may become excessive, and the concrete may exhibit signs of distress [10]. Sacrificial anode cathodic protection systems provide cathodic current by galvanic corrosion. The current is generated by metallicly connecting the structure to be protected to a metal/alloy that is electrochemically more active than the material to be protected. (Both the structure and the anode must be in contact with the electrolyte) Current discharges from the expendable anode to the electrolyte and onto the structure to be protected [3]. If however, a much less inert object (that is with much more negative potential, such as a magnesium anode) is placed adjacent to the structure to be protected, such as a pipeline, and a metallic connection (insulated wire) is installed between the object and the structure, the object will become the anode and the entire structure will become the cathode. The galvanic cathode protection system is called a sacrificial anode cathodic protection system because the anode corrodes sacrificially to protect the structure. Galvanic anodes are usually made of either magnesium or zinc because of these metals' higher potential compared to steel structures [6,7]. There are three materials that are commonly used as galvanic anodes: magnesium, aluminum alloy, and zinc, such as shown **Figure 1**.

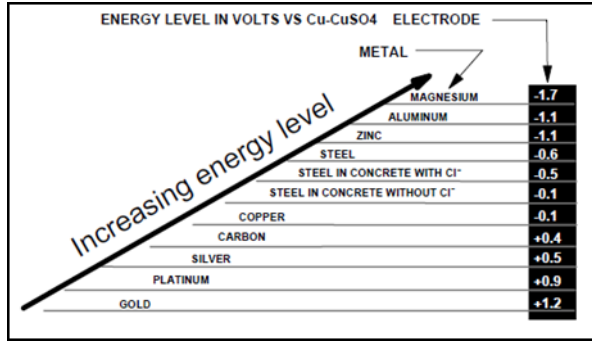


Fig. (1) Galvanic Energy Series (3).

The protection offered by organic coatings is mainly determined through isolation from the aggressive environment, by adhesion opposing corrosion initiation at the coating interface, and through structural changes taking place during curing of the coatings. An organic coating system often consists of a conversion coating, primer and a top coating. Therefore, many times, coatings that have good barrier properties would be better choices for isolating the corrosive environment from the protected structure, although sometimes it is necessary to have a porous coating so that the penetrated electrolyte can trigger the inhibitive action of the pigment in the coating [6]. In Chemical Precipitation, Surface appearance and coating thickness are the result of many process parameters, including steel chemistry, variations in immersion

time and/or bath temperature, rate of withdrawal from the galvanizing bath, and control of the cooling rate by water quenching or air cooling [10]. Electroplated chromium coatings are notable for their high resistance to tarnish, their high hardness and wear resistance as well as their low coefficient of friction resistance to cold welding. With a thickness of 0.2-0.6 μm and bright silver to matt appearance, they are widely used as decorative finishes. Thus, special design effects can be achieved [4,1]. Chromium plating is performed with a chromium salt solution and a passive anode made of lead. Trivalent chromium solutions are limited to low deposition rates and are mainly used for the 15 deposition of thin decorative coatings.

2- Experimental work

2.1 Materials

The material that has been studied in present work was made of steel (low carbon steels grade AISI 1012), are widely used in chemical and petroleum storage tank. The analyze by the Specialized Institution of Engineering Industries-Baghdad. The chemical composition of material is shown in **Table 1**.

Table (1) Chemical Composition of Low Carbon Steel.

Comp. Wt %	C	Si	Mn	P	S	Cr	Mo	Cu	Ni	Fe
Measured	0.12	0.160	0.664	0.036	0.043	0.029	0.016	0.05	0.058	Balance

2.2 Preparation of Specimens

Surface preparation is the most important step in the application of any coating. In this work, the specimens cut from storage tank, the cutting achieved by cutting machine. The specimens for electrochemical measurements and coating (Electrochemical Precipitation Coating and painting) were prepared by cutting the specimen with dimensions (1.5x1.5x0.5)cm, then Grinding process was carried out by using disk rotary instrument with different grades of emery papers (SiC) in sequence of (320, 500, 800, 1000, and 1200) grit to get facing free surface. The specimens were washed with water and alcohol and dried in the air, polished process was carried out by using special polishing cloth and alumina (Al₂O₃) solution of grain size of (0.3µm), Etching process was done by immersing the each sample in etching solution which consists of (3-5% HNO₃ and 95-97% alcohol) for (30) seconds, and Examination process by using optical microscope (Type, Nikon.120, Japan) with digital camera and computer.

Microscopic examination and surface preparation was executed in the Production Engineering and Metallurgy Department /University of Technology.

2.3 Electrochemical Measurements of Oil Storage Tank

Corrosion is the deterioration of a material through reaction with its environment, this deterioration occurs mainly through an electrochemical

process (electrochemical test was conducted according to the ASTM G5). The electrochemical process consists of four distinct parts: Anode, Cathode, Electrolyte, and Glass Path as shown as **Figure 3**.

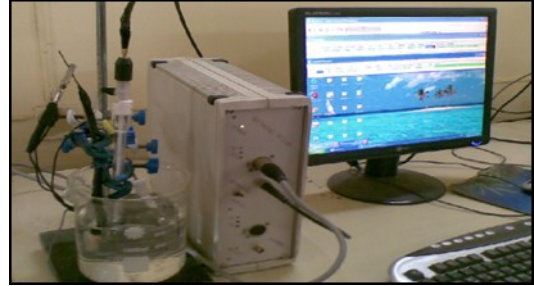


Fig. (3) Potentiostat (Wenking LT87-Germany). These four parts constitute what is called the “corrosion cell”. An electrochemical test cell used for the study consisted of a glass vessel with separate inlets for working electrode, reference electrode and counter electrode. Platinum electrode was used as a counter electrode and a saturated calomel electrode (SCE) was used as a reference electrode. The working electrode consist from simple storage tank and simple magnesium (as sacrificial electrode). A luggin probe-salt bridge was used to minimize the ohmic resistance. Potentiodynamic polarization studies were carried out in 3.5% NaCl solution (prepared using analytical grade sodium chloride dissolved in distilled water). The measurements were carried out at 25-27°C in stagnant electrolyte exposed to the atmosphere. In this paper, to understand the operation of a Sacrificial (Galvanic) cathodic protection system for storage tank, it is extremely important to understand the corrosion behavior by tafel

extrapolation diagram for simples with and without coating (Electrochemical Precipitation Coating and panting), existence and not existence Sacrificial (Galvanic) cathodic protection, that achieved by Potentiostat device (Wenking LT87-Germany). Before starting the experiment the working electrode was allowed to stabilize in the electrolyte in order to obtain a stable open circuit potential (OCP). In all the cases, the polarization curves were obtained by starting the potential scan from a cathodic potential. The corrosion rate was calculated by using the following equation [10,6]:

$$\text{Corrosion rate (mpy) (mpy)} = 0.13 \times I_{\text{corr.}} \cdot e/D$$

Where:

I_{corr} : Corrosion current density $\mu\text{A}/\text{cm}^2$.

e:Equivalent weight (for steel =25.5).

D: Density of metal (for steel 7.9 gm/cm³).

e:Equivalent weight (for Cr =17.332).

D : Density of metal (for Cr =7.1 gm/ cm³).

2.4 Electrochemical Precipitation Coating

The electrochemical precipitation process consists of three basic steps, surface preparation, precipitation, and inspection. Each of these steps is important to obtain a quality precipitation coating. Before

The immersion time in the Chemical bath will vary depending upon the

commencement of the electrochemical precipitation test, the specimens were cleaned with acetone followed by an ultrasonic cleaning in distilled water. Surface preparation is usually performed in sequence by caustic (alkaline) cleaning and water Cleaning, also the Hydrochloric acid HCL and Sodium hydroxide NaOH for removes organic contaminants including dirt, water-based paint markings, grease and oil. In Electrochemical Precipitation preparation, the first step is cleaning it by immersing in solution contain (NaOH 100 g/L), wash it with water, immersing it in solution (50%HCL), then followed by good washing of water, immersing in solution (8% H₂SO₄), wash with water and material to be coated is immersed in a bath of Chemical solution (that consist Chromic acid CrO₃ + Sulphuric acid H₂SO₄) at temperatures over (40-50°C) [11], the **Table2** shown Electrochemical Precipitation parameter .

Table 2 Electrochemical Precipitation Parameter.

Chromium Electroplating	Parameter s
Chromic acid CrO ₃	250 g/L
Sulphuric acid H ₂ SO ₄	1:100
Temperature	55 ° C
Time (minutes)	15
Current	3.36 A (30-80 A/dm ²)

dimensions and chemistry of the material being coated. The coating

device is found in University of Technology, this device is constant of: Power Supply, Controller, Coating Val, Electrodes (working-low carbon steels, reference).

2.5 The Metallurgical Bond

Correlation between the coating and the metal base was measured by Tensile Testing Machine device named (Tinus Olsen) made in England maximum operating capacity is 50KN, 220 / V, 50HZ available in the Ministry of Science and Technology Department of Materials Research.

3- Results and Discussion

3.1. Results of Corrosion Rate

Microscopic examinations of storage tank surface (depending on ASTM B 487), show that corrosion types depend on types of coatings, thickness of coatings, and corrosion environments. Some of these types are Uniform corrosion and Pitting corrosion, the pitting type of corrosion is major importance in storage tank or other structures designed to liquids or gas. These types of corrosion were observed in all the experimental specimens and used as function to measured corrosion rate with used the polarization curve (6).

The typical appearance of a pit as shown in **Figure (4)**.

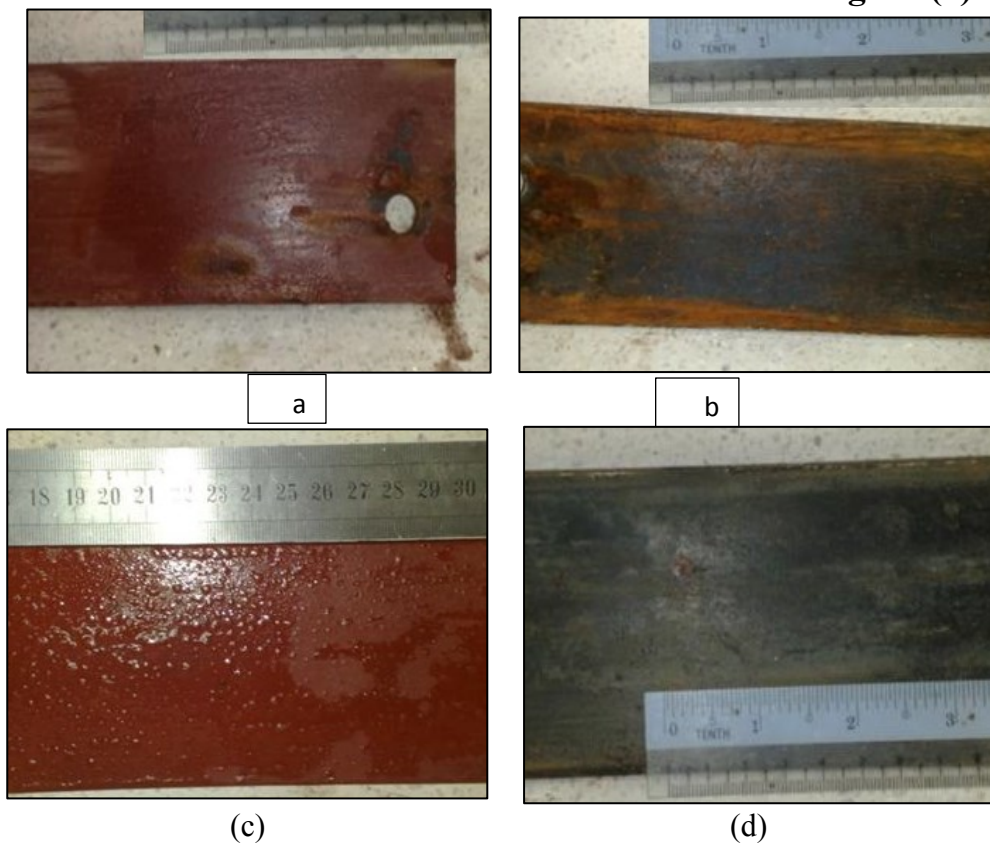


Fig.(4) Samples storage tank with paint coating at 3.5%NaCl , Samples without (SACP), (a) Coated Sample (b) Bare Sample, with (SACP) (c) Coated Sample (d) Bare Sample

Under certain conditions the bottom of the pits may exhibit crystallographic facets whereas in other cases round electro polished bottoms are observed, generally covered with precipitated corrosion products [6])

The paint film has been damaged as a result of the steel rusts. Rust creeps under the paint film, which is lifted up from the steel surface. Corrosion continues until the damage has been repaired.

Well Electrochemical Precipitation Coating (chromium) give rise to more rapid corrosion at the point of damage than if the steel was uncoated. The corrosion often takes the form of pitting, which can even go through the steel [5].The pits were generated but

they do not grow to become stable pits and rapidly die. Only at potentials above the critical potential do metastable pits become stable. It should be noted, however, that pit generation is a stochastic process and therefore a distribution of potentials exist above a minimum value that can be considered the 'true' pitting potential. This lower potential usually coincides with the protection potential or repassivation potential, which is the potential at which pit growth is arrested [6].

Table (3) shows the potentiodynamic anodic polarization data obtained when the test was carried out in 3.5%NaCl at room temperature. The value of I_{corr} is shown graphically in **Figure 5**.

Table (3) The results for storage tank with paint coating at 3.5%NaCl (by tafel extrapolation method).

No.	State SACP	state Coating	Corrosion potential E_{corr} , Mv	Corrosion current density I_{corr} , $\mu A/cm^2$	Corrosion rate (C.R, mpy)
1	absence of cathodic protection SACP	Uncoated	-313	9.136×10^{-1}	38.34×10^{-2}
2		Paint coating	-324	8.005×10^{-1}	33.59×10^{-2}
3	presence cathodic protection SACP	Uncoated	-410	7.157×10^{-1}	30.03×10^{-2}
4		Paint coating	-400	4.060×10^{-2}	1.703×10^{-2}

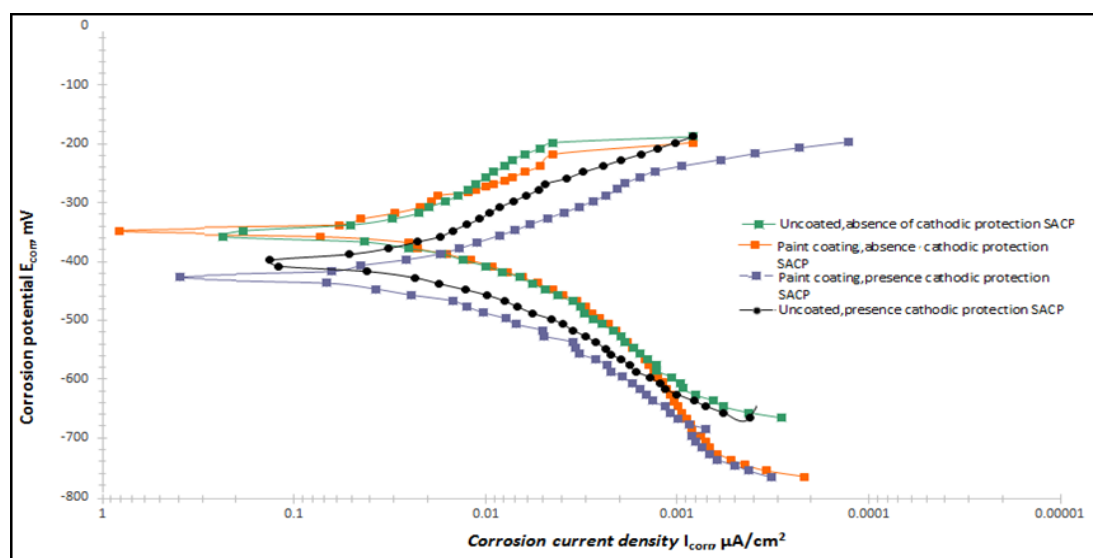


Fig.(5) polarization diagram for a storage tank with paint coating in 3.5(wt %) NaCl.

In this work, the chromium from type of Hexavalent chromium (Cr^{6+}) baths for hard chromium deposition was used in Electrochemical Precipitation coating. The main component of all hard chromium plating solutions is chromium trioxide (CrO_3) referred also as chromic acid. Corrosion rate determination at constant condition of 3.5(wt %) NaCl was carried out by conventional immersion test, the initial Corrosion current density for the bare samples in

stagnant 3.5 % NaCl solution for storage tank without Electrochemical Precipitation coating (absence and presence with sacrificial anode) were $7.157 \times 10^{-1} \mu\text{A}/\text{cm}^2$ and $9.136 \times 10^{-1} \mu\text{A}/\text{cm}^2$ respectively and the Corrosion current density for the coated with and without sacrificial anode sample in stagnant 3.5(wt %) NaCl solution $6.055 \times 10^{-2} \mu\text{A}/\text{cm}^2$ and 7.461×10^{-4} the corrosion rate results are in **Table4** and **Figure6**.

Table (4) The results for storage tank with Electrochemical Precipitation coating at 3.5%NaCl (by tafel extrapolation method).

No.	State SACP	state Coating	Corrosion potential E_{corr} , mV	Corrosion current density I_{corr} , $\mu\text{A}/\text{cm}^2$	Corrosion rate (C.R, mpy)
1	absence of cathodic protection SACP	Uncoated	-313	9.136×10^{-1}	38.34×10^{-2}
2		Electroplating (75 μm)	-354	6.055×10^{-2}	1.588×10^{-2}
3	presence cathodic protection SACP	Uncoated	-410	7.157×10^{-1}	30.03×10^{-2}
4		Electroplating (75 μm)	-470	7.461×10^{-4}	0.019×10^{-2}

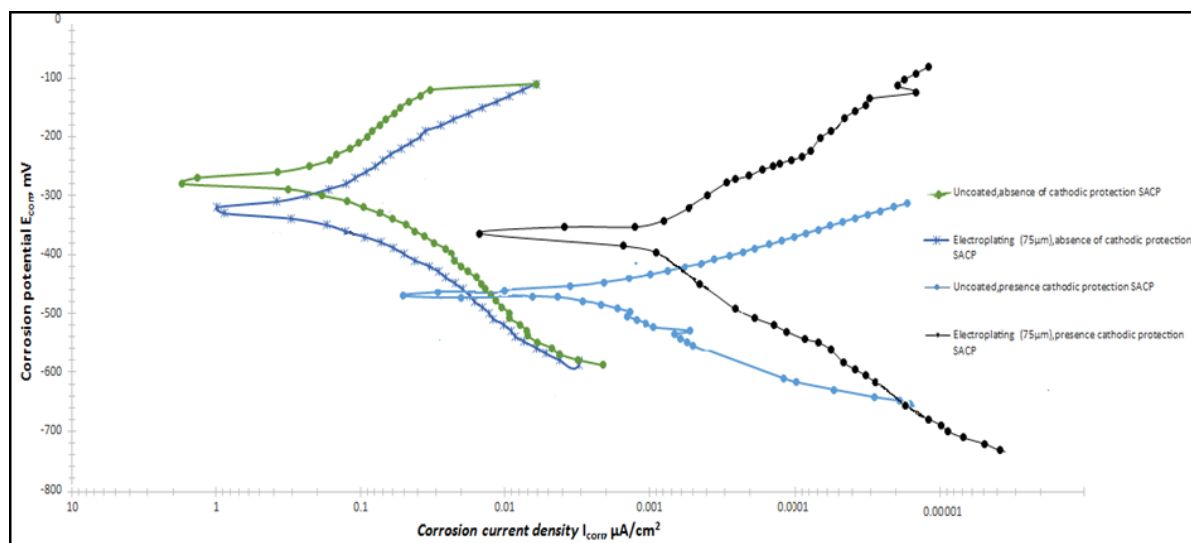
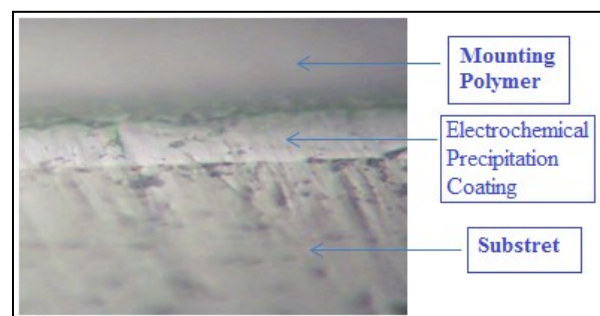


Fig. (6) The polarization diagram for storage tank with Electrochemical Precipitation coating in 3.5(wt %) NaCl.

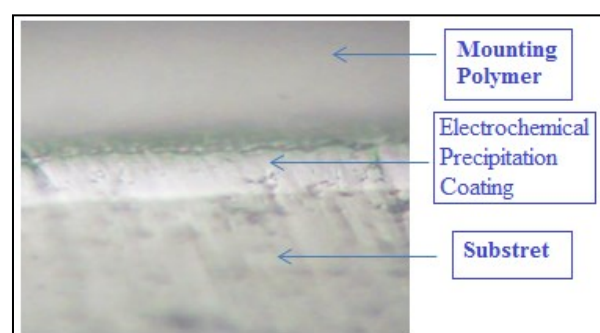
Microscopic examinations of the steel storage tank section show that coating thickness (75 μm) and substrate layers, the coating as shown in Figure (5) is observation increased corrosion rate in presence cathodic protection SACP and it decreased in stat absence of cathodic protection SACP .

The typical appearance of a pit is shown in **Figure 7**.

Under certain conditions the bottom of the pits may exhibit crystallographic facets whereas in other cases round electro polished bottoms are observed, generally covered with precipitated corrosion products (6). It has been demonstrated that stable pit growth only occurs above a certain critical potential which depends on the particular metal/anion system.



(a)



(b)

Fig. (7) Samples storage tank with Electrochemical Precipitation Coating at 3.5%NaCl , (a)Samples without (SACP), (b) Samples with (SACP)

The presence of an aggressive anion in the environment is a necessary but not a sufficient condition for the occurrence of pitting corrosion, as clearly demonstrated by experiments in which the passive film is mechanically disrupted by scratching or straining at potentials below the critical potential and repassivation occurs. The initiation of corrosion and failure of coatings usually can be identified via visual inspection because the failure of protection from organic coatings generally results in

the formation of blisters and delaminated regions (6) The Electrochemical Precipitation Coating is tightly bonded to the underlying steel, at approximately 23Mpa. In this paper the results shown that tightly bonded is approximately 21.5 Mpa, as shown in **Figure 8**, other coatings typically offer bond strengths of 2-4 Mpa, at be.

The dimensions for Specimen the Electrochemical Precipitation Coating steel storage tank is shown in **Table5**.

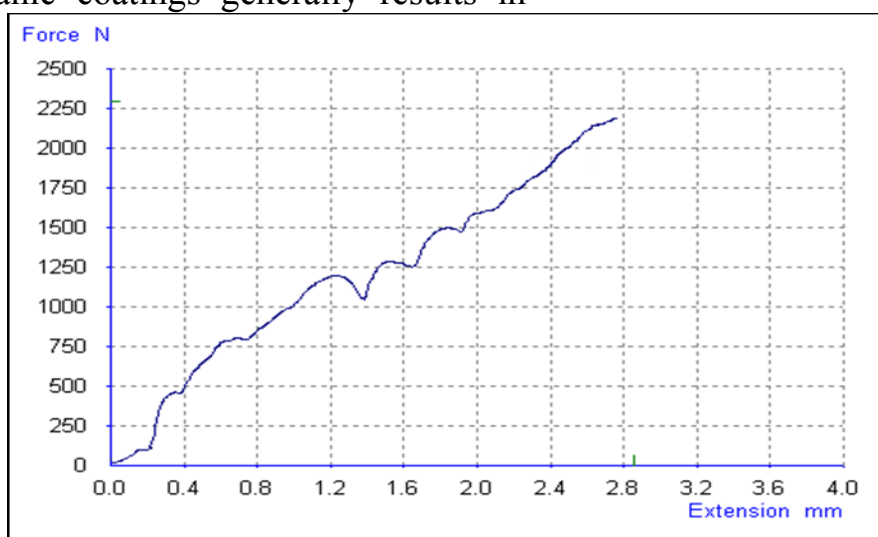


Fig.(8) Testing metallurgical bond between the Electrochemical Precipitation Coating and the underlying steel or iron

Table (5) Specimen dimensions for coating bond test.

Specimen	Thick. mm	Width mm	Tensile MPa	Max Force N
Electrochemical Precipitation Coating	10	10	21.5	2196

3.2 Efficiency of Coating

The efficiency of Electrochemical Precipitation Coating against corrosion is calculated according to the following formula:

$$\eta =$$

$$\frac{\text{Corrosion Rate without Coating} - \text{Corrosion Rate with Coating}}{\text{Corrosion Rate without Coating}} \times 100$$

The results of the efficiency of Electrochemical Precipitation Coating with thick (75 μ m) and paint coating (with absence and presence of SACP) are illustrated in **Table 6**.

Table (6) The efficiency of coating with and without CP at 3.5 % NaCl and room temperature in the present work.

Type Coating	Efficiency η (%) absence of cathodic protection SACP	Efficiency η (%) presence cathodic protection SACP
Electroplating	95	99
paint	12	94

The efficiency has proximately the same value, which is about 95% in 3.5% NaCl and the thickness layer is (75 μ m) with absence of cathodic protection SACP and to 99% with presence of cathodic protection (SACP) in 3.5 % NaCl and efficiency 94% for paint coating in presence cathodic protection (SACP).

4- .Conclusions

The result obtained from the experimental work had successfully fulfilled the objectives of the paper. The conclusions derived are listed as follows:

- Sacrificial anode cathodic protection and coating (Electrochemical Precipitation Coating (chromium) and paint), give the best protection for steel storage tank immersed in 3.5%NaCl.

- The potential of steel storage tank with (Electrochemical Precipitation Coating (chromium) less negative values from paint coating with and without applying of Sacrificial anode cathodic protection system.

- The efficiency of Electrochemical Precipitation Coating (chromium) at absence and presence of SACP with (75 μ m) thickness have values ranging from 95% to 99% in 3.5% NaCl and efficiency of paint coating at absence and presence of SACP have values ranging from 12% to 94% in 3.5% NaCl.

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دراسة تأثير الطلاء على السلوك الكهروكيميائي للخزانات الفولاذية

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الخلاصة

الحماية الكاثودية يستفاد منها بشده على الانابيب الفولاذية المستخدمه في الصناعات النفطية والغاز. وهذه التقنية تمنع او تحد من التاكل. في هذا البحث تم مناقشة ودراسة استخدام الاقطاب المضحية وفعالية الطلاءات (الطلاء بالترسيب الكيميائي والطلاء بالاصباغ) على الخزانات الفولاذية. ولفهم سلوك التاكل يتم استخدام النظرية الكهروكيميائية بواسطة منحنيات الاستقطاب حيث تم اجراء التجارب العملية على عينات من الخزانات الفولاذية المطلية واخرى غير مطلية وكذلك بوجود وعدم وجود الانودات المضحية في محلول يحتوي على 3.5% من كلوريد الصوديوم. النتائج العملية اوضحت بأن معدل التاكل وجهد التاكل يقل بأستخدام طلاءات الترسيب الكيميائي اكثر من استخدام طلاءات الاصباغ لنفس عينات الخزان الفولاذي عند 3.5% من كلوريد الصوديوم.

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