

This work aims to the identify level of hybrid nanocomposite coatings of a stainless steel alloy that is used in the manufacture of mineral reservoirs for the storage of oil products in the oil products distribution company (Opdc). Corrosion is one of modern society's most serious engineering problems where losses incurred due to it each year are estimated at billions of dollars. Technological options have to be exercised to protect against corrosion and an effort to combat these losses. To overcome this severe problem, several successful efforts have been made using corrosion inhibitors. Corrosion inhibitors are compounds used in low concentrations to prevent or slow down the corrosion process. The used metal (low carbon steel St-37) was coated with zinc phosphate as an initial layer, cellulose nitrate reinforced with MgO nanopowder by weight percentage (3 wt. %) as an intermediate layer, and epoxy resin reinforced with weight reinforcement percentage (2 wt. %) of particles (MgO+coke coal (1:1)) as a final layer. In addition, a cognitive scale was prepared from (hardness, adhesion strength, chemical corrosion test as well as electrochemical corrosion test. It was found the hardness increased with coated by an initial layer and the value of adhesion strength of triple coating layers was (232 Psi). Chemical and electrochemical corrosion tests have shown the efficiency of prepared coating layers in corrosion inhibiting and metal protection. The used inhibitors in the work are inexpensive materials that allow solving the problem of rational nature management by reducing corrosion and providing the transition to the use of environmentally safe efficient technologies

Keywords: corrosion, zinc phosphate, cellulose nitrate, coke coal, chemical and electrochemical corrosion

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USING THE HYBRID COMPOSITES AS COATING LAYERS TO INHIBIT THE CHEMICAL CORROSION IN OIL MINERAL RESERVOIRS

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1. Introduction

Metals remain the main structural material that is indispensable in a series of industrial synthetic substances production. There is an enhanced need to protect them against corrosion given the increase in the volume of metal production [1]. The corroded metal loses all of its mineral properties due to its degradation and returns to the form in which it originally existed as an ore by chemical combination with a non-metal such as oxygen, sulfur, etc. [2, 3]. Corrosion occurs in all types of metals. The effect of solid particles on the liquid moving medium on the metal is significant, and the continuous movement of these particles removes the protective interstitial layer of the corrosion products between the liquid and the metal [2, 3]. Corrosion is a rusting layer on the surface of the metal that is porous and often leads to the weakening of the metal, reducing its durability and thickness, and creating holes that lead to damage [4]. The most effective method of eliminating corrosion influence is the use of corrosion inhibitors to ensure the safe operation of reservoirs and increase their durability, which is considered an important element of the environmental safety of production [5, 6]. Due to technological progress and rapid growth in the forms of equipment and machinery that put them in contact with chemicals under different operating conditions, there have been many forms of corrosion [7, 8]. Economics

and safety are the two main reasons for the importance of corrosion [9, 10]. The economic factor is a very important motivation for much of the research on corrosion where it is divided into (1) direct losses (include the costs of replacing corroded structures) and (2) indirect losses (include loss of efficiency, loss of product, contamination of the environment, and stop the work) [11–16]. Therefore, research is a relevant area of research for the synthesis of corrosion inhibitors to reduce corrosion aggressiveness of water-oil mixtures depending on defining the optimal parameters.

2. Literature review and problem statement

Up to this date, many approaches have been proposed and used to inhibit corrosion. The paper [17] presents the results of research on prepared epoxy coatings containing different volume fractions of zinc phosphate and studied their inhibitive properties by electrochemical impedance spectroscopy (EIS) and immersion tests showing that zinc phosphate has a corrosion inhibitive effect, the best concentration of zinc phosphate is 30 vol. %, and the epoxy coating with zinc phosphate has a self-healing function on the steel surface. The paper [18] presents the results of research on the development of nanocrystalline zinc phosphate coatings on mild steel surfaces using nano zinc oxide particles, the

results showed that these coatings enhanced corrosion resistance where the nano ZnO increases the number of nucleating sites for phosphating and faster attainment of steady-state during nano zinc phosphating but it was observed that there was no significant effect between the concentrations of 0.1–0.25 g/L of nano ZnO because of the nano ZnO no acts as a nucleating agent, decreases the number of nucleation sites for deposition and increase the size of the phosphate crystal clusters formed which enabled lower coating weight. The paper [19] presents the results of research on the function of talc as a corrosion inhibitor reservoir and its ability to absorb and release corrosion inhibitors to achieve active corrosion protection in an epoxy ester coating and found the organic and inorganic corrosion inhibitors were loaded in the talc particles, the modified particles showed corrosion inhibition in solution and coating phases, and organic and inorganic species revealed synergistic corrosion inhibitive effects. The paper [20] presents the results of research on the corrosion rates of mild steel in different aqueous solutions under different operating conditions by using the weight loss technique in the absence and presence of epoxy coating and found that corrosion rates increased with temperature and salt concentration and decreased with pH values and the presence of coating reduces the corrosion rates to significant values in acidic solutions. MgO nanoparticle was used effectively with epoxy coating in saline solutions and improved the coating performance with a maximum value of 93.7 % but in saline solution the performance of coating was poor. The paper [21] presents the results of research on the accelerated formation of zinc phosphate coatings with enhanced corrosion resistance on carbon steel by introducing α -zirconium phosphate was evaluated and found that α -zirconium phosphate (α -ZrP) is used as a new eco-friendly accelerator of phosphate coatings, and α -ZrP effectively increases phosphate efficiency, reduces the phosphate grain size, and forms a denser phosphate coating. The paper [22] presents the results of research on the effect of catholyte on the kinetics of corrosion was studied and revealed the dependence of the corrosion rate of carbon steel 09G2S on the concentration of the reagent alkali and catholyte at different pH values where a comparative assessment of the use of the most effective concentration of catholyte to increase the corrosion resistance of the material has been carried out. The paper [23] presents the results of research on the preparation of metal matrix nanocomposites using Fe as base material reinforced with Al_2O_3 and doped with CeO_2 using the powder metallurgy technique. It was observed that corrosion rate and corrosion current density was highest for pure Fe samples whereas 1.0 % CeO_2 doped Fe- Al_2O_3 metal matrix nanocomposite system showed the formation of nano amorphous layer on the specimen surface. Analysis of variance shows that the different compositions of samples have changed the outcome of corrosion behavior.

3. The aim and objectives of the study

This study aims to find inhibitors that would effectively protect the steel of oil reservoirs against corrosion in water-oil mixtures at high concentrations of mineral salts in water.

To achieve this aim, the following objectives are accomplished:

- to examine of the used metal using an OE thermo spectrometer;

- to determine the effectiveness of the synthesized hybrid nanocomposite use the following tests: Hardness, Adhesion force, and Atomic Force Microscope (AFM);

- to calculate the rate of chemical and electrochemical corrosion of St-37 steel and to establish the optimum dose of the synthesized inhibitor in a water-oil mixture using the Tafel extrapolation and immersing methods.

4. Materials and methods

Corrosion treatment in mineral reservoirs is used for the storage of oil products in the oil products distribution company (OPDC) by manufacturing a three-layer coating. The coating mechanism is as follows: the used metal was coated with zinc phosphate as an initial layer, cellulose nitrate reinforced with MgO nanopowder by weight percentage (3 wt. %) as an intermediate layer, and epoxy resin reinforced with weight reinforcement percentage (2 wt. %) of particles (MgO+coke coal (1:1)) as a final layer.

Take a corrosive piece (50×50 cm) from one of the out-of-service reservoirs in the oil products distribution company with 6 mm thickness; the thickness of it was reduced from 6mm to 3 mm. The piece was cut into two groups of coupon samples (1.5×1.5 cm and 3×3 cm) as shown in Fig. 1.



Fig. 1. Coupon samples after cutting

The used metal was analyzed by using spectrometer OE Thermo ARL 3460. The coupon samples shall be placed in diluted zinc phosphate solution with water 1:10 at 90 °C for 10 minutes as shown in Fig. 2, 3.



Fig. 2. Coupon sample during phosphate process



Fig. 3. Coupon samples after phosphate process

Coupon samples were coated by cellulose nitrate reinforced by MgO nanopowder with weight reinforcement percentage (3 wt. %) as an intermediate layer and epoxy resin reinforced with weight reinforcement percentage (2 wt. %) of (MgO+coke coal (1:1)) as the final layer as shown in Fig. 4, 5, respectively.



Fig. 4. Coupon samples coated by an intermediate layer



Fig. 5. Coupon samples coated by a final layer

The hardness of the used metal before and after the phosphates process was measured. Atomic Force Microscope (AFM) was used to find the extent of homogeneity of the prepared coating layers. The adhesion force test is used to find the less tensile stress needed to rupture or detach the prepared coating layers. The corrosion rate of the prepared coating layers was studied by using the Tafel extrapolation method. The chemical corrosion test was carried out by immersing the coupon samples in the water accompaniment with three oil products (gasoline, gas oil, and kerosene) for (1, 3, 24, 48, 72, and 96) hours.

5. Results of the studying using the hybrid composites as coating layers for inhibiting the chemical corrosion in oil mineral reservoirs

5. 1. Analysis of the Used Metal

Based on the spectrometer (OE Thermo ARL 3460), the weight percentage of alloying elements was shown in Table 1.

Table 1

The alloying elements and weight percentage of low carbon steel (St-37)

Alloying elements	Weight percentage
Fe	98.899
C	0.16
Si	0.07
S	0.02
P	0.01
Mn	0.71
Ni	0.001
Cr	0.04
Mo	0.08
Cu	0.01

From the results shown in Table 1 has been found that the classification of used metal is (St-37) a low carbon steel (C=0.16) according to ASTM.

5. 2. Determining the effectiveness of the synthesized hybrid nanocomposite

5. 2. 1. Hardness test

Table 2 shows the hardness values of the steel alloy (St-37) before and after the phosphates process.

Table 2

The hardness of coupon samples

Coupon samples	Hardness (HB)
Without	130
Phosphates	148

Let's note that the hardness of the alloy after the phosphates process is increased because of the increase in phosphate ratio in the stable austenite, which leads to an increase in the values of hardness thus eliminating internal cracks or micro corrosion (residual effects of corrosion). This is consistent with the findings of the researcher [24].

5. 2. 2. Adhesion force test

The adhesion force test was carried out for prepared coating layers, it result was shown in Table 3.

Table 3

Values of adhesion force

Coupon samples (Intermediate layer)+ (Final layer)	Adhesion force (Psi)
(Cellulose Nitrate+3 wt. % MgO)+ (2 wt. % hybrid)	232

From Table 3 let's observe the value of adhesion force of the cellulose nitrate is large because the mechanical bonding of the cellulose nitrate with the steel surface is good. The adhesion force increases with increased sliding contact between the metal surface and the coating material.

5. 2. 3. Atomic force microscope test

The AFM image for the prepared coating layers of the sample is illustrated in Fig. 6.

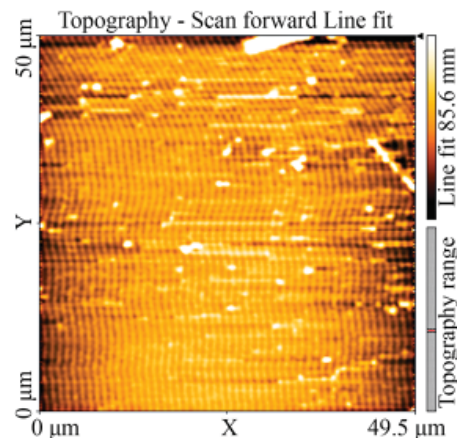


Fig. 6. The topographic surface of prepared coating layers

Through the AFM image, let's note that the sample has higher homogeneity of the surface and this is evident from the value of the root mean square ($Sa=27.694$ nm) thus obtaining better mechanical properties.

5.3. Determining the rate of chemical and electrochemical corrosion

5.3.1. Chemical corrosion test

The change of weight of prepared coating layers immersed in the water accompaniment with three oil products (gasoline, gas oil, and kerosene) for (1, 3, 24, 48, 72, and 96) hours shows in Table 4.

Table 4

Chemical corrosion for prepared coating layers

Time of Im-mersion (hour)	Oil Product		
	Gasoline	Gas Oil	Kerosene
1	20.78	19.95	20.32
3	20.78	19.95	20.32
24	20.78	19.95	20.32
48	20.78	19.95	20.32
72	20.78	19.95	20.32
96	20.78	19.95	20.32

Table 4 shows that the prepared coating layers have high homogeneity and there are no cracks which are weak areas that allow the passage of the oil product thus inhibiting corrosion because MgO is an anti-cracking and corrosion-resistant material and coke coal is a sweeping material of H_2S that is considered an anticorrosive catalyst [25].

5.3.2. Electrochemical Corrosion Test

Fig. 7 shows the polarization curves of the prepared coating layers sample, which was drawn using the Tafel extrapolation method [26].

Fig. 7 shows the value of corrosion current density is ($i_{corr}=17.34$ nA/cm²) and corrosion potential is ($E_{corr}=-274.4$ mV), this value consider the least corrosion rate where the inhibitor coat acts as a dielectric material and oxidizes with the surface of the steel and its union with oxygen prevents corrosion of the metal and this reduces the reaction or stops it [27].

6. Discussion results of the studying using the hybrid composites as coating layers for inhibiting the chemical corrosion in oil mineral reservoirs

The results in (Table 1) show the classification of the used metal as low carbon steel ($C=0.16$). It is a type of steel alloy that is characterized by strength and hardness also called High-strength low alloy (HSLA) steels or micro-alloyed steels. They have better mechanical properties (yield strengths greater than 275 MPa) and greater resistance to atmospheric corrosion than conventional carbon steels. In (Table 2) the hardness of zinc phosphates gave higher mechanical protection than those without a coat because the increase in the hardness can be explained due to the combined effects of better densification and reduced grain size. However, with increasing ZnO content, hardness values increased for samples from 130 HB to 148 HB.

The immersion process of iron shown in Fig. 2, 3, indicates that phosphates gave chemical protection to the surface of the metal because zinc phosphate is an inert or stable compound that does not convert into oxides and is soluble in water or acids, it has a high packing factor on the surface of the metal and zinc is a waste element because it has a reduction potential less than iron as it limits the arrival of humidity on the surface of steel thus prevent corrosion and is a good base for the cohesion of the layers paint so there are no cracks allow entry to water or acids.

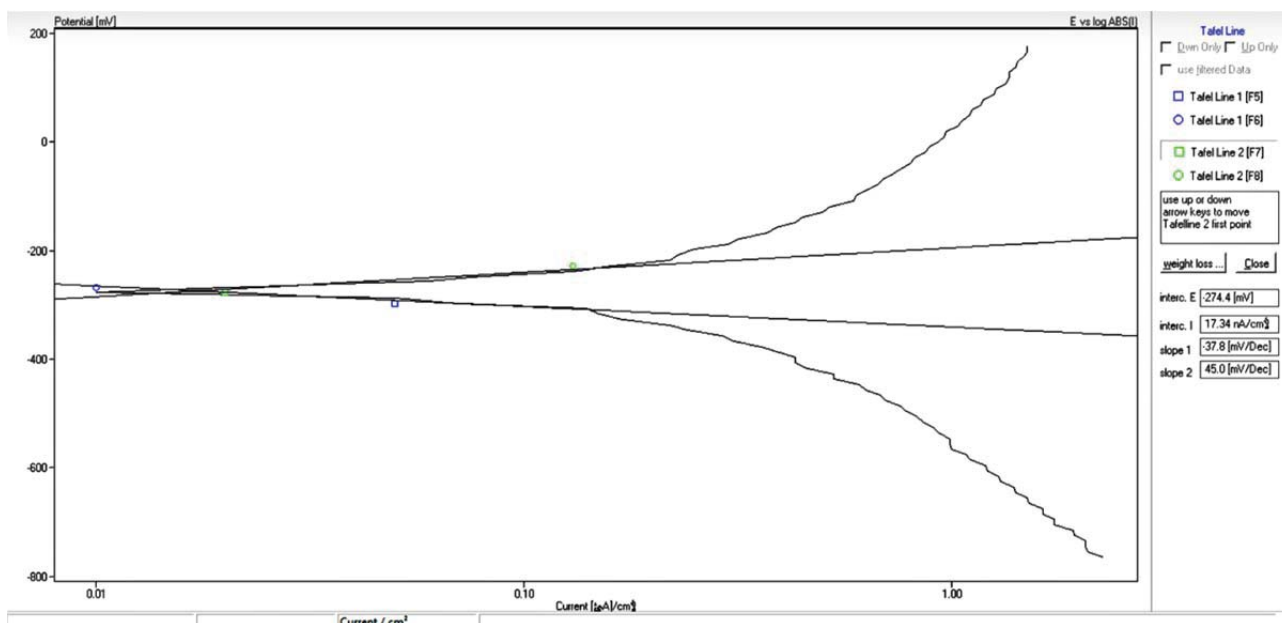


Fig. 7. Electrochemical corrosion of prepared coating layers

The corrosion rate of the used metal determines by the Tafel extrapolation method shown in Fig. 7, with applied potentials of about 300 mV vs. SCE to get the polarization curves for the cathodic and anodic reactions well away from the corrosion potential and recording the current. The relationship between the current density (current of the corrosion) and the potential is linear, this means that the increase of the current shall be with constant potential and any change in the potential proof is that the corrosion occurred. The tangents represent the cathode and anodic behavior and the intersection point of these tangents represents the corrosion current.

The multidisciplinary nature of corrosion possesses large limitations some of which are: corrosion mechanisms, corrosion-resistant alloy development, alloy processing, and fabrication corrosion, surface treatment and coating, computational materials science, data analytics, etc.

In the proposed method, inhibitors were used to treat corrosion in oil tanks and could not be used in pipelines designated for transporting petroleum products. This defect in the method could be overcome by converting the corrosion inhibitor into a liquid substance and mixing it with the oil product, and this would help to discourage corrosion in the pipelines carrying petroleum products. The oil tanks are in good condition, and this in turn will lead to an increase in the service life of these containers so that it is possible to benefit from them in the work for a longer period.

Let's convert the inhibitor from a solid state to a liquid state, this conversion requires a lot of time and special equipment that is not available everywhere and is difficult to obtain at present.

7. Conclusions

1. Based on the result of the OE spectrometer has been found that the classification of used metal is (St-37) a low carbon steel ($C=0.16$).

2. According to the value of hardness (130 HB), the used metal (St-37) is considered mild mineral hardness. Mechanical properties increase with coated zinc phosphate coating and increase with the increase in the reinforcement ratio of nanomaterials.

3. It has been shown that the used inhibitors are quite effective in water-oil mixtures based on the results obtained from chemical and electrochemical corrosion tests.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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