

Short Communication

Performance of Stainless Steel AISI 317L in Hydrochloric Acid with the Addition of Propargyl Alcohol

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AISI 317L stainless steel is a material that is used in many industries, including the manufacturing of equipment and components applied in the oil & gas industry, which are subject to acidification or acid stimulation. Acid stimulation consists, essentially, of hydrochloric acid injection of 5 to 28% (% volume) in oil and gas wells to stimulate or restore the permeability of the reservoir rock, which increases the production of oil and gas. To avoid or to reduce the attack of hydrochloric acid on stainless steel AISI 317L, the corrosion inhibitor, propargyl alcohol base, is added. Thus, the present paper aims to analyze AISI 317L stainless steel's corrosion resistance using gravimetric (mass loss) and electrochemical (polarization) laboratory tests with and without the addition of 1% (volume) propargyl alcohol in hydrochloric acid solutions at concentrations of 5 and 10% (% volume) at temperatures of 25°C, 40°C and 55°C. The laboratory results are very promising in protecting the AISI 317L stainless steel in hydrochloric acid solutions.

Keywords: AISI 317L, Corrosion, Corrosion Inhibitors, Propargyl Alcohol, Hydrochloric acid.

1. INTRODUCTION

One of the techniques used in the process of stimulating oil wells is the acid stimulation or acidification, which consists, essentially, of an acid solution injection in reservoir rock to solubilize part of the minerals present in the mineralogical composition, which increases or recovers the permeability of a rock formation, and consequently, increasing the productivity of the well [1,2]. On the other hand, it is also common for calcareous incrustations to occur in pipes and to reduce oil production as they are tough, rugged adherents to the metallic surface. The formation calcium carbonate scale inside the tubes cause operational problems and compromise the integrity of the oil production. As the materials are normally made of carbon steel, the removal of these deposits is made

through the pressurized injection of hydrochloric acid (HCl) with the addition of a corrosion inhibitor whose anti-corrosion protection is quite promising according to the literature [1-4].

In the production of oil and gas during recent years, due to the development of the technological sector, there was a significant increase in the use of new alloys, special valves, rod pump and other components (electrically insulated of carbon steel) that have replaced traditional carbon steel.

AISI 317L austenitic stainless steel is used in various components of oil production, and is characterized by a high molybdenum content that is about 3.0% (by weight), while traditional AISI 316L austenitic stainless steel has 2% molybdenum. The increased molybdenum content results in an increased resistance to a chemical attack in welded joints and, in particular, resist corrosion at the pitting and crevices. The best features, namely fluency and mechanical strength at high temperatures, have not yet been optimized when compared to conventional stainless steels. The designation "L" (<0.035 carbon) in AISI 317L stainless steel ensures the resistance to sensitization during welding or when thermic processes are applied due to low carbon content in the chemical composition [5-7].

Normally, passivation is the process by which stainless steel will spontaneously form a chemically inactive surface upon exposure to air or to other oxygen-containing environments. This oxide layer, which is present on the stainless steel's surface, is called the passive layer or the passive film. The chromium present in the stainless steel allows a chromium-oxide layer to form, whose function is to protect the steel from attacks. This layer has the ability to self-repair, but if it is damaged, corrosion may occur [8].

Although it is stainless, AISI 317L steel, depending on the conditions and the environment to which it is exposed, may be corrosive. Some acids, such as hydrochloric (HCl), sulfuric (H₂SO₄), phosphoric (H₃PO₄) and hydrofluoric (HF) acids, when in contact with stainless steel, remove the passive oxide layer that gives it corrosion resistance; thus, the steel becomes susceptible to corrosion. In this way, it is not recommended to use AISI 317L stainless steel in environments containing those acids.

The breakdown of passivity on various metals and their pitting or passive alloys occurs in the presence of aggressive ions. Austenitic stainless steels, when immersed in aqueous solutions containing halide ions, such as chloride (Cl⁻) and fluoride (F⁻), are susceptible to localized and punctate attacks. The Cl⁻ or F⁻ ions penetrate into the oxide layer through pores and defects more easily than other ions, which leads to pitting. Pits provide locations to start and then propagate cracks and, thus, reduces the materials life span [9].

AISI 317L stainless steel forms a passive film under oxidizing conditions; however, in the presence of non-oxidizing acids, such as hydrochloric, hydrofluoric, sulfuric and phosphoric acids, that film is destroyed and, consequently, there is an increased probability of pitting, crevices and even uniform corrosion.

To avoid or to minimize the aggressive action of hydrochloric acid on the metallic surface of AISI 317L stainless steel, specific corrosion inhibitors are added to form a film on the metal surface that inhibits or reduces corrosion reactions. Corrosion inhibitors are widely used to provide protection against corrosion in different environments and temperatures.

The main objective of the laboratory tests is to evaluate the action of hydrochloric acid (with and without corrosion inhibitor) on equipment manufactured with AISI 317 L aiming your application in the petroleum industry.

2. MATERIALS AND METHODS

2.1 Mass loss measurement

The material evaluated in this work was an AISI 317L austenitic stainless steel plate used for manufacturing the coupons whose chemical analysis is presented in Table 1. The coupons used in the gravimetric tests (mass loss) had the following dimensions: 2.70 cm x 1.0 cm x 0.65 cm. The metal surface was prepared with grade 100 sandpaper. The coupons were cleaned with acetone and ethanol and then dried in a kiln at 60°C. The test coupons were weighed using a digital electronic balance.

Table 1. The chemical composition of AISI 317L austenitic stainless steel.

C (%)	Mn(%)	Si(%)	S(%)	P(%)	Cr(%)	Ni(%)	Mo(%)	Fe(%)
0.024	1.34	0.47	0.003	0.031	18.13	11.41	3.02	balance

The corrosive medium used was a 5% and 10% (% volume) hydrochloric acid (HCl) solution of high purity, while the concentrations of the corrosion inhibitor, based on propargyl alcohol (2-Propyn-ol-1), was fixed at 1% (% volume). The choice of corrosion inhibitor in concentration of 1% was based on the experience of the authors in acidification processes in carbon steel. It is important to inform that this acidification process in oil production has duration of 3 to 8 hours. Therefore, it is essential that the corrosion inhibitor protects the valves and other equipment manufactured in stainless steel AISI 317L in order to guarantee the integrity and no need to replace this equipment, resulting in the reduction of operational costs.

Gravimetric assays (weight loss) were performed in glass containers with a capacity of 100 mL. The coupons were completely immersed in 80 mL of acid solution, which left the remaining capacity of the container free for the evolution of hydrogen that resulted from the acid attack. The jars were maintained at temperatures of 25°C, 40°C and 55°C in a thermostatically controlled bath. The testing times were fixed at 1, 2 and 3 hours of exposure.

Immediately after completion of the test, the coupons were removed from the corrosive medium; every deposit was first rinsed in water, next in alcohol and then quickly dried with hot air, then they were re-weighed with the same accuracy so that the weight loss could be determined according to ASTM G 31-72 [10].

The corrosion rate (CR) of each solution analyses was defined by the following expression:

$$\text{Corrosion rate} = \text{CR} = (W_o - W_i) / S.t,$$

where W_o and W_i are the loss weight in the absence and in the presence of corrosion inhibitor respectively, S is the area (cm^2) and t is exposure time (h).

2.2 Potentiodynamic polarization measurements

The electrode was used as a form of the sample analysis. After the electrodes were prepared, the samples were sanded in a polishing machine with grade 100 to 1200 sandpapers. After this procedure, the samples were washed and passed through ultrasonic cleaning equipment for 3 minutes, in order to remove possible residues that may have been aggregated during sanding.

After cleaning, the samples were polished, also in a polishing machine, with 1 μ m alumina solution. Thereafter, they were washed and totally dried with a dryer, leaving no marks on the sample surface. After drying, the sides and vertices of the sample were covered with colorless enamel to waterproof the edges. The sample exposure area used in the tests is 0.25 cm² [11].

Next, the samples were inserted into a conventional polarization cell with a volume of 200 mL. The electrochemical cell used consists of a working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE). The polarization curves were recorded using a Type III Autolab potentiostat by varying the potentials in steps of 60 mV/min over a potential range of -300 mV to +300 mV with respect to open circuit potential [11].

The corrosive medium used was a solution of 5% and 10% (% volume) hydrochloric acid (HCl) that was of high purity, while the concentration of the corrosion inhibitor, based on propargyl alcohol (2-Propyn-ol-1), was fixed to 1% (% volume). The temperature maintained in the cell was 25°C, 40°C and 55°C by using a thermostatically controlled bath. For each temperature was done a test with and another without corrosion inhibitor. After each test was conducted an analysis with an optical microscope was performed to identify pitting on the metallic surfaces.

Based on the polarization curves obtained from the electrochemical cell under the laboratory conditions mentioned above, the polarization resistance (R_p), the corrosion current density (i_{corr}) and the inhibition efficiency (IE %) were determined.

Those parameters values were obtained by extrapolating the Tafel lines of the polarization curves for 5 % and 10% HCl solutions using the Stern-Geary constant, which results from a combination of the anodic and cathodic Tafel slopes.

The polarization resistance and the corrosion current density show the corrosion level. For higher current density and lower polarization resistance, higher corrosion rates values are obtained.

2.3 Identification of pitting on the sample surfaces after the end of the assays for determining the polarization curve.

To identify the occurrence of pitting on the metallic surface, the following laboratory operations were followed. Soon after the electrochemical assays were performed, the samples represented by the electrodes were placed on the ultrasound equipment so that possible deposits could be removed.

Later, the samples were dried with hot air. Then, they underwent metallographic polishing with a 0.3 μ m alumina (Al₂O₃) solution, were washed with distilled water and ethyl alcohol before being dried with hot air again. Each sample underwent metallographic etching for 20 s in a modified Behara reagent that was composed of 20 mL of hydrochloric acid (37 % HCl), 80 mL of distilled water and

0.6 g of potassium metabisulfite ($K_2S_2O_5$) [12,13]. Finally, the samples were analyzed using an optical microscope.

3. RESULTS AND DISCUSSION

3.1 Mass loss measurement

The results indicate that the use of 1% (% volume) propargyl alcohol in the hydrochloric acid solutions reduced the corrosion rate on AISI 317L stainless steel as shown in Figure 1. The essays showed that the mass loss rate growth as the hydrochloric acid concentration and the test temperature were increased in the absence of the corrosion inhibitor. Based on the results presented, considering the greater immersion time (3 hours), it was possible to verify the efficiency of the corrosion inhibitor. It was observed that the propargyl alcohol had protection efficiency in all the experimental conditions studied.

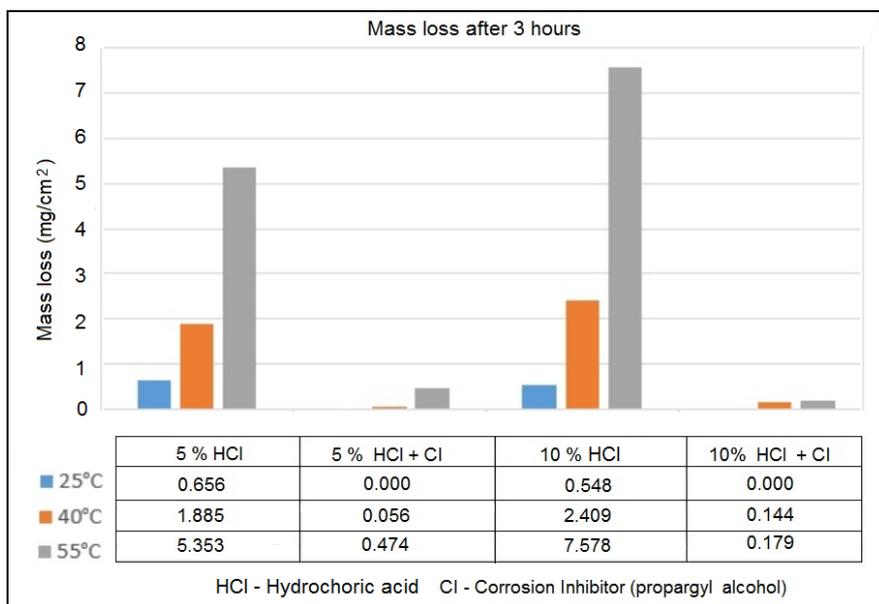


Figure 1. Mass loss test results for 5% and 10% HCl at 25°C, 40°C and 55°C, with and without inhibitor.

3.2 Potentiodynamic polarization measurements

Polarization curves for the AISI 317L stainless steel in 5% and 10% (volume) hydrochloric acid solutions in the absence and presence of propargyl alcohol (1% volume) at 25°C, 40°C and 55°C are shown in Figures 2 and 3. As a first vision, these polarization curves (anodic and cathodic branches) demonstrate that the addition of propargyl alcohol in the HCl solution causes these branches on the curves to shift towards lower currents and, to a similar extent, may be the consequence of a barrier effect or the absorption of a formed film of propargyl alcohol molecules on the metal surface. The polarization curves show that there is an acceptable reduction in both the anodic and cathodic

currents in the presence of propargyl alcohol compared to the values for the HCl solution without corrosion inhibitor.

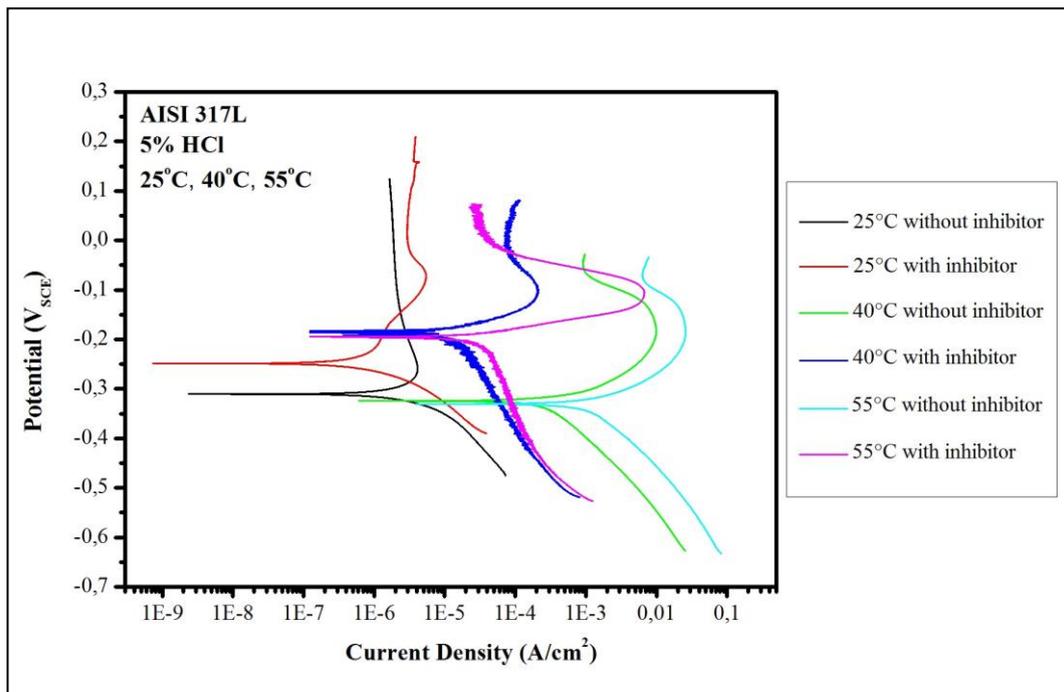


Figure 2. Polarization test results for 5% HCl at 25°C, 40°C and 55°C, with and without inhibitor.

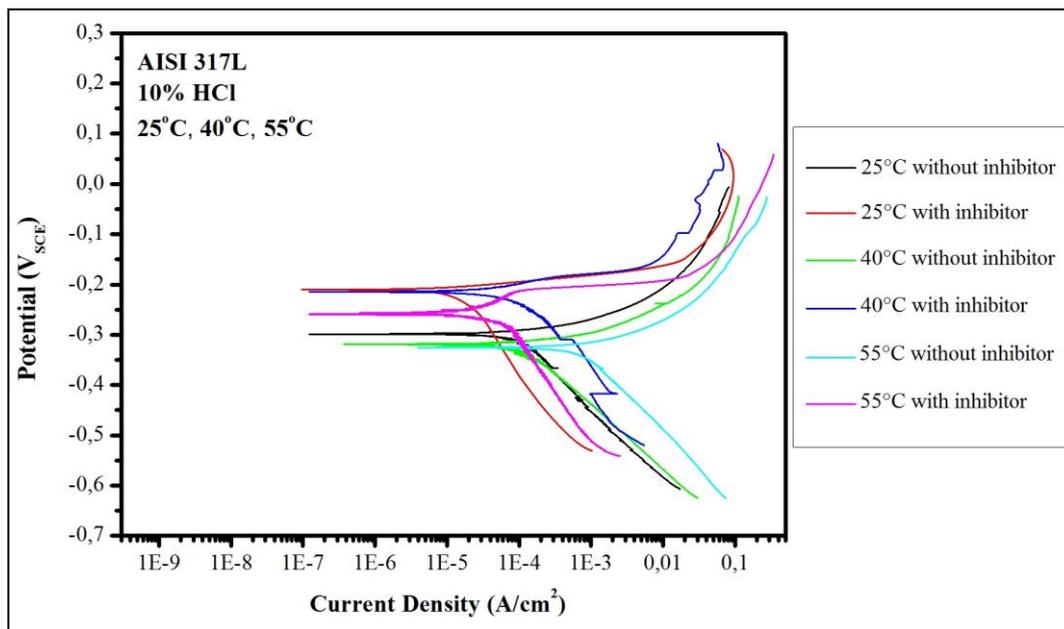


Figure 3. Polarization test results for 10% HCl at 25°C, 40°C and 55°C, with and without inhibitor.

Values for the polarization resistance (R_p), the corrosion current density (i_{corr}) and the inhibition efficiency (IE %) were obtained by extrapolating the Tafel lines of the polarization curves for 5 % and 10% HCl solutions at different temperatures and are presented in Tables 2 and 3.

Table 2. Polarization resistance and corrosion current density results for the 5% HCl solution, at 25°C, 40°C and 55°C, with and without inhibitor.

Temperature, °C	Polarization resistance, R_p , Ω		Corrosion current density, (i_{corr}), A/cm ²		Inhibition efficiency, (IE) (%)
	Without inhibitor	With inhibitor	Without inhibitor	With inhibitor	
25	5645	73671	6.57×10^{-9}	3.24×10^{-11}	99.50
40	135	4037	7.06×10^{-6}	8.37×10^{-9}	99.88
55	41	1182	7.96×10^{-5}	1.03×10^{-7}	99.87

Table 3. Polarization resistance and corrosion current density results for the 10 % HCl solution at 25°C, 40°C and 55°C, with and without inhibitor.

Temperature, °C	Polarization resistance, R_p , Ω		Corrosion current density, (i_{corr}), A/cm ²		Inhibition efficiency, (IE) (%)
	Without inhibitor	With inhibitor	Without inhibitor	With inhibitor	
25	389	1899	1.78×10^{-6}	2.67×10^{-8}	99.50
40	294	800	3.86×10^{-6}	4.99×10^{-8}	98.73
55	53	1555	1.36×10^{-4}	8.34×10^{-8}	99.93

It can be seen from Tables 2 and 3 that the addition of propargyl alcohol in the HCl solution yielded a superior IE% of 98%. The high values of IE% indicated higher surface coverage from good adsorption on metal surface. There was a reduction in current density upon addition of the corrosion inhibitor and, consequently, there was an increase in the polarization resistance. The current density increased as the temperature and the hydrochloric acid concentration increased.

Researchers have presented good results regarding the use of propargyl alcohol (2-Propyn-ol-1), in protecting carbon steel in hydrochloric acid solutions [14-17]. However, considering the same conditions, the experiment shows a good performance for AISI 317L stainless steel. Considering these facts, it can be suggested that the adsorption capacity of propargyl alcohol molecules on metallic surfaces is due to the π -electrons that interact with the metallic surfaces and, consequently, are associated with the properties of the triple bond in each propargyl alcohol molecule ($\text{HC}\equiv\text{C}-\text{CH}_2-\text{OH}$) [14-17].

3.3 Identification of the occurrence of pitting on the sample surface after the end of the assays for determining the polarization curves

Figures 4 and 5 show the metallographic analysis of pitting found in the AISI 317L stainless steel samples after conducting the polarization assays in solution of 5% and 10% (% volume)

hydrochloric acid solutions in the absence and presence of propargyl alcohol (% volume) at 25°C, 40°C and 55°C.

Extensive pitting corrosion of the steel materials is very common in solutions that contain high concentrations of chlorides (Cl⁻). Considering this fact, the objective is to show the increase in the size and shape of pitting through the polarization resistance (R_p) and the corrosion current density (i_{corr}) presented in Tables 2 and 3, where the addition of propargyl alcohol reduced the corrosive attack when experiencing high concentrations of hydrochloric acid.

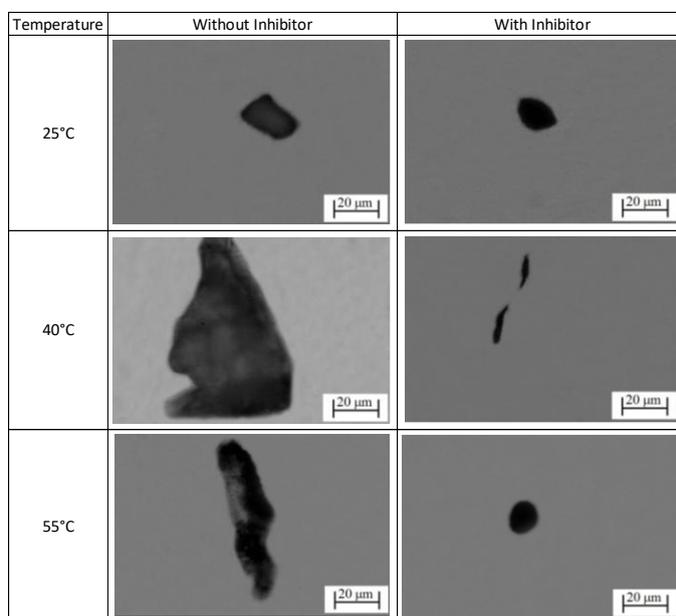


Figure 4. Microscopic analysis after the polarization test (5% HCl at 25°C, 40°C and 55°C, with and without corrosion inhibitor).

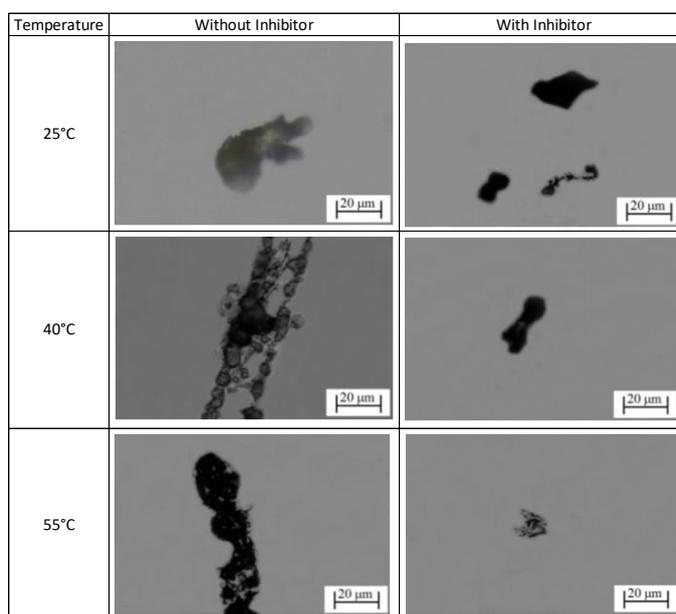


Figure 5. Microscopic analysis after the polarization test (10% HCl at 25°C, 40°C and 55°C, with and without corrosion inhibitor).

4. CONCLUSIONS

- In the gravimetric tests, it was found that the mass loss rate varied according to the hydrochloric acid concentration in the solution, the temperature at which the system was exposed and the exposure time, so that the rate increased as the HCl concentration, temperature and the exposure time increased.

- When alcohol propargyl was present in the hydrochloric acid solution, there was a mass loss rate reduction for each test situation that was analyzed. The results showed that the inhibitor's protection efficiency was above 90% in the experimental conditions studied.

- The polarization curves presented a higher current density as the temperature increased. The presence of propargyl alcohol in the assays for each analyzed temperature generated a reduction in the obtained current density results even if they were small.

- The samples analysis after the polarization tests, using the metallographic microscope, detected pitting under all the conditions, where pitting increased in assays without the corrosion inhibitor and at higher temperatures.

- AISI 317L stainless steel is susceptible to corrosion when used in environments with non-oxidizing acids. Therefore, based on the tests that were carried out, the use of propargyl alcohol effectively reduced corrosion.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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