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STUDY OF CORROSION INHIBITION FOR MILD STEEL IN HYDROCHLORIC ACID SOLUTION BY NEW POLYESTER DERIVATIVE (GLYPTAL)

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ABSTRACT

The inhibitive impact of eco-friendly Polyester (Glyptal) on the corrosion behavior of mild steel was examined. The inhibitory impacts were considered on mild steel in 1 M hydrochloric corrosive solutions, utilizing weight loss, electrochemical estimations, and Scanning Electron Microscopy (SEM) systems. The inhibitory impact was considered by adding different concentrations of inhibitors (100, 200, 400, 500, and 1000 ppm) by weight of the solution. The corrosion of steel was inhibited ceaselessly with the amount of inhibitor added. It came to a high state of inhibition with 500 and 1000 ppm of inhibitor concentration. SEM investigation uncovered that the expansion of inhibitor impedes the consumption forms, where the inhibitor is covering the outside of the metal, so it forestalls the metal surface to be in contact with the corrosive medium.

Keywords : Corrosion, mild steel, polyester; glycerol

1. INTRODUCTION

Corrosion is a continuous decimation of material on account of its response with nature. It is a noteworthy modern issue that has pulled in many agents in later a long time [1,2]. In the fields of oil and oil industry, consumption speaks to a tremendous level of the yearly monetary misfortunes. The most critical consumption types in the oil industry are neighborhood and general consumption. Another issue in the task of pipelines is interior consumption. The consumption issues are constantly connected with the gear upkeep and task. This led to halting the procedure incompletely or even totally, bringing about monetary misfortunes running somewhere in the range of 10% and 30% of the entirety upkeep spending plan. To be sure, consumption control is a fundamental issue from the application purpose of view, and it has been accounted for that inhibitors are should have been utilized which go about as an obstruction to decrease the forcefulness of the situations against the corrosion attack [3-5]. Most a typical sort of corrosion inhibitors are natural mixes. Their hindrance property is subordinate upon their practical gathering, which adsorbs on the metal surface. The greater part of the effective natural mixes goes about as inhibitors have oxygen, sulfur, nitrogen molecules, and various bonds through which they adsorb on the metal surface [6-8]. The hindrance proficiency of inhibitors increments in the request of O < N < S < P [9-11]. The utilization of polymers as corrosion inhibitors has pulled in significant consideration as of late [12]. Polymers are utilized as corrosion inhibitors since through their practical gatherings they structure edifices with metal particles and on the metal surface, these edifices involve a huge surface territory [13,14], in this way covering the surface and shielding the metal from destructive operators present in the arrangement [15]. The inhibitive intensity of these polymers is connected fundamentally to the cyclic rings, heteroatom (oxygen and nitrogen) that is the real dynamic focuses of adsorption [16]. In view of the novel attributes of polymers which have turned out to be generally utilized, they have pulled in more consideration particularly in logical research and modern fields, for example, the oil business, consumption inhibitor, and covering of pipelines [17-19]. The polymers have numerous points of interest, the most noteworthy of which is that it simple to get ready, high dissolvability furthermore low thickness [20].

Polyester derivative (Glyptal) has been produced in this article by response between glycerol and phthalic anhydride. This polymer was then explored for its capacity in the aggressive aqueous medium to avoid corrosion of the mild steel.

2. EXPERIMENTAL

2.1. Materials

2.1.1. Synthetic substances

phthalic anhydride, anhydrous sodium acetate, and glycerol

2.1.2 Solutions

a- Hydrochloric corrosive acid

1 M HCl was utilized as a destructive acid and was set up by weakening concentrated HCl (37%) to a required fixation utilizing bi-refined water.

b- Inhibitor

100 ml stock of polyester derivative (Glyptal) was set up by dissolving an ideal load of each compound in 100 ml of outright ethanol, and after that, the five unique focuses 100, 200, 400, 500 and 1000 ppm were set up by weakening with known convergence of hydrochloric corrosive.

2.1.3. Steel composition

All tests were performed on a mild steel terminal having the accompanying substance arrangement (wt.%): 0.09% C, 0.09% Si, 0.46% Mn, 0.03% P and the rest Fe.

2.2. preparation of the polyester derivative (Glyptal)

The engineered methodology was portrayed in the writing detailed by Gabriela V et al [21]. Polyester was readied utilizing phthalic anhydride (10.00 g) with glycerol (4.0 mL) and 0.50g of sodium acetic acid derivation were brought into a three-necked round base cup 250 ml fitted with a Dean-Stark cylinder, reflux condenser, mechanical stirrer, thermometer, and nitrogen bay cylinder. The temperature was expanded up to 160 °C and was kept at this temperature for 1 hour with persistent mixing, to guarantee that water was dispensed with amid this period, at that point the delivering compound was recrystallized from methanol. The orchestrated inhibitor was shown in Scheme 1, and the substance structure was affirmed by FT-IR spectroscopic examination utilizing Nicolet iS10 FT-IR spectrometer, Thermo Fisher Scientific (USA).

2.3. A Technique utilized for Corrosion Measurements

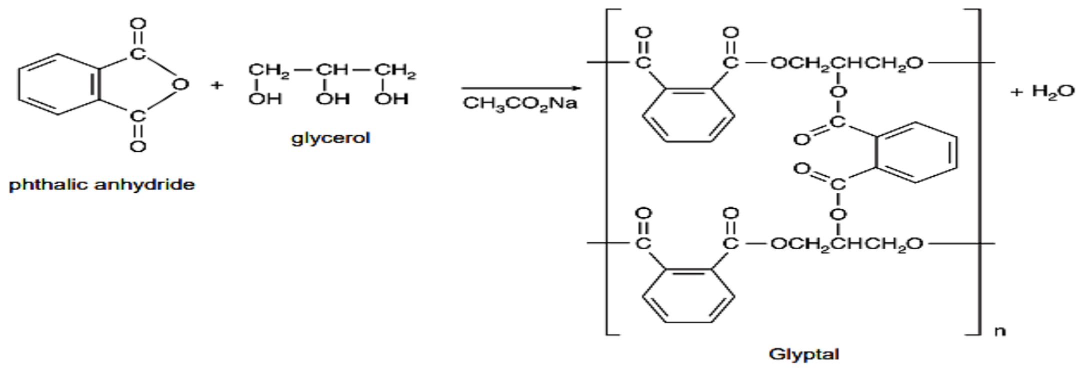
2.3.1. Chemical estimations

The pre-gauged test examples were drenched in 1 M HCl acid with and without different concentrations of polyester (Glyptal). Following 12 hours, the test examples were recovered, washed with refined water, flushed with ethanol, dried with $(CH3)_2CO$ and reweighed utilizing an electronic gauging balance, the distinction in weight was taken as the corrosion mass misfortune, a similar technique was rehashed after 24, 36, 48,60-and 72-hours presentation. The restraint productivity IE% and consumption rater (CR) from mass misfortune are determined by:

$$\%IE = (W_2 - W_1 / W_2) \text{ X}100 \quad (1)$$

Where W_1 and W_2 are the weight reduction of the mild steel in the presence and absence of inhibitor, separately.

$$\text{The level of surface coverage } (\theta) = IE/100 \quad (2)$$



Scheme 1 Synthesis of the polyester derivative (Glyptal)

The corrosion rate (CR) was determined from the accompanying condition

$$CR=(m_1-m_2)/ (S.t) \quad (3)$$

where m_1 is the mass of the example before corrosion, m_2 the mass of the example after consumption, S the all-out region of the example, t the drenching time and CR the corrosion rate [22].

2.3.2. Electrochemical strategies

Electrochemical estimations were performed with a conventional three-anodes cell utilizing Volta lab 40 (Tacussel Radiometer PGZ301) potentiostat and constrained by the Tacussel consumption examination programming model (Voltamaster 4) at under static condition. All examinations were led in a traditional three-terminals glass cell get together with a platinum wire as helper anode, immersed calomel cathode (SCE) as reference terminal and mild steel as working terminal.

A- Potentiodynamic polarization bends were acquired by fluctuating the potential naturally from - 800 to - 300 mV in connection to an unfaltering state open circuit potential (EOCP) with the sweep rate 2 mV s^{-1}. The polarization bends were gotten after 1h in the open circuit potential.

B- Electrochemical impedance spectroscopy (EIS) estimations were done utilizing a potentiostat (VoltaLab PGZ-301) appended to the Zsimpwin programming program. The estimations were completed utilizing AC signal (10 mV) top to crest at OCP in the recurrence scope of 100 kHz–50 MHz. In all trials, the mild steel anode was likewise permitted to achieve its steady open-circuit potential (OCP), which happened after 1h. EIS outlines are assumed in the Nyquist portrayal.

2.3.3. Scanning Electron Microscope (SEM) Analysis

The surface movies were shaped on the mild steel examples by inundating them in 1M HCl arrangement with and without various groupings of inhibitor for a timeframe of 24hrs. After the submersion time frame, the examples were taken out, dried and the idea of the film-shaped on the outside of the metal example was dissected by SEM methods to look at the surface morphology. JEOL JSM5500 examining an electron magnifying lens was utilized for this examination.

3.RESULTS AND DISCUSSION

3.1. Substance structure affirmation of the prepared Inhibitor

The basic attributes of the prepared polyester (Glyptal) were affirmed by FT-IR spectroscopy in the range 4000–500 cm^{-1}. Fig. 1 delineates the FT-IR spectra of (Glyptal) polymer. The ingestion due to the – CH_2 - and – CH groups of the esterified and un-responded glycerol are found in a wrap at 2950, 2932 and 2855 cm^{-1}, which are related to the extending of the C-H of aliphatic mixes. The C-H extending of the phenylene ring of the phthalic corrosive can be distinguished by the ingestion at 3070-3040 cm^{-1}. The nonappearance of assimilation at 1711 cm-1 (allocated to – COOH dimmers) proves that the esterification response was practically finished for all the polyester, in this manner the ingestion between 3300-3000 cm^{-1} is related to adsorbed water and un-responded –OH groups.

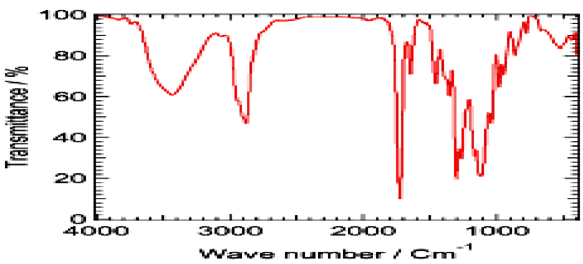


Fig. 1. FT-IR chart of the synthesized (Glyptal) polymer.

3.2 Study the Protection Efficiency of Mild Steel Electrode by the Chemical Testing Technique (weight loss).

The corrosion rates, Coverage surface, and inhibition efficiency values, of mild steel determined to utilize weight reduction information, for different focuses (100,200,400,500 and 1000ppm) of (Glyptal) polymer in 1M HCl preparation are exhibited in Table 1. It very well may be derived that there is a critical decrease in the weight reduction of test examples inundated in differing concentrations of (Glyptal) polymer in contrast with the clear arrangement. Moreover, as the concentration of polymer builds, the weight reduction lessons. The decrease in the weight reduction could be ascribed to the adsorption of

(Glyptal) polymer. The adsorption of this polymer on the metal surface makes an obstruction to the disintegration of the metal in destructive media [22]. It is evident from Fig.2 that the consumption rate of the mild steel within the sight of (Glyptal) polymer diminishes with the expansion in the concentration of the (Glyptal) polymer. The dependability of the inhibitive conduct of polymer by the pattern of hindrance productivity as a component of time. The estimations of hindrance effectiveness (IE%) for every centralization of (Glyptal) polymer was recorded in Table 1. It was seen that the hindrance proficiency increments with an expansion in inhibitor focus This show that weight reduction is very reliant on the convergence of the inhibitor.

3.3. Study the protection efficiency of the Mild Steel electrode by the electrochemical technique

3.3.1. Potentiodynamic polarization

Fig.3 demonstrates the potentiodynamic polarization bends for mild steel in 1M HCl in the nonappearance and nearness of changed concentrations of (Glyptal) polymer. It tends to be seen in Fig. 3 that both anodic and cathodic responses of the corrosion procedure of mild steel terminal were restrained in the wake of including polymer into the acidic medium. The nearness of (Glyptal) polymer in the acidic solution results in a move of current thickness to bring down one in contrast with that in clear arrangement. These outcomes show that (Glyptal) polymer goes about as a blended kind inhibitor. At the end of the day, the expansion of inhibitor to 1 M HCl reduces the anodic disintegration of steel and retards the cathodic response. The adsorbed defensive film of inhibitor on steel surface obstructs by hindering the dynamic locales of the steel. Along these lines, real surface zone accessible for anodic and cathodic responses is diminished. Electrochemical parameters, for example, anodic (B_a) and cathodic Tafel inclines (B_c), consumption potential (E_{corr}), corrosion current thickness (i_{corr}), obtained from extrapolation of polarization bends are given in Table 2. It is obvious from Table 2 that the estimations of

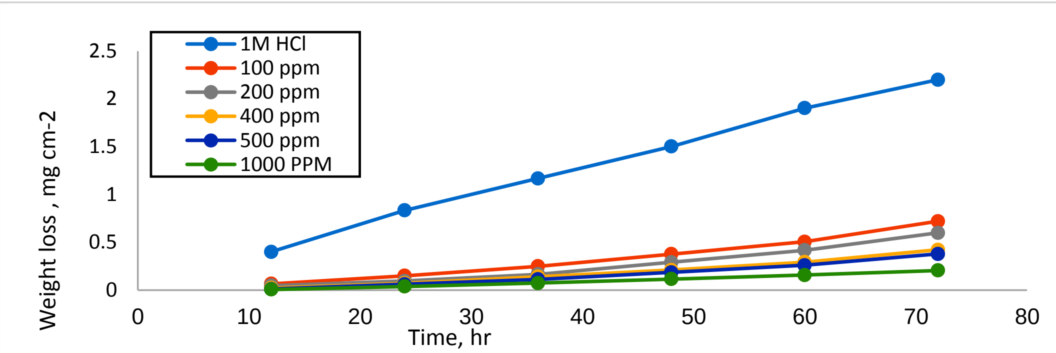


Fig. 2. weight loss-Time curve for the corrosion of mild steel in 1M HCl solution in the absence and presence of different concentrations of (Glyptal) polymer inhibitor at 298K.

Table 1. Corrosion rate (CR), Coverage surface(θ) and the inhibition efficiency (IE%) of mild steel in 1M HCl solutions in the absence and presence of different concentrations of (Glyptal) polymer inhibitor obtained by weight loss method at 25°C.

Inhibitor	Concentration (ppm)	Rate of corrosion (CR) (mg cm^{-2} hr^{-1})	Coverage surface (θ)	Efficiency (IE %)
(Glyptal) polymer	Blank	15.28	-	-
	100	4.99	0.6732	67.32
	200	4.15	0.7279	72.79
	400	2.92	0.8086	80.86
	500	2.62	0.8285	82.85
	1000	1.41	0.9072	90.72

corrosion current thickness (i_{corr}) observably diminish in the nearness of inhibitor, which proposes that rate of electrochemical response was hindered because of the arrangement of a defensive film of inhibitor on the steel surface and this defensive film made an obstruction between the metal and destructive medium. The hindrance proficiency was determined to utilize the accompanying condition [20]:

$$IE\% = 1 - i_{corr(1)} / i_{corr(2)} \times 100 \quad (4)$$

where $i_{corr(1)}$ and $i_{corr(2)}$ are the consumption current densities of steel in the nearness and nonappearance of inhibitor, separately. It very well may be seen from the determined outcomes (Table 2) that (Glyptal) polymer hinders the corrosion of steel to a considerable degree and that the degree of restraint is subject to the inhibitor focus. These outcomes uncovered that the corrosion current thickness (i_{corr}) diminished astoundingly with the expanding inhibitor fixations, prompting an expansion of hindrance productivity. In this manner, it could be reasoned that the anodic disintegration of steel and the cathodic responses were both repressed by the inhibitor by only hindering the response destinations superficially.

3.3.2. Electrochemical impedance spectroscopic measurements (EIS)

Fig. 4 demonstrates the Nyquist plots of mild steel in the nonappearance and nearness of (Glyptal) polymer. The plot is made from a half circle, which expanded outstandingly with inhibitor fixation. This outcome shows that the charge-move process prevalently controls the corrosion restraint of steel. The width of the impedance plot fundamentally increments, proposing that the consumption security increments with the expansion of inhibitor. The impedance parameters got from these figures are given in Table 2. The fitting outcomes demonstrated that the R_{ct} values expanded and the C_{dl} values diminished with inhibitor focus. It very well may be inferred that the bigger the distance across of the half circle is the more thickly the framed film. An enormous R_{ct} is related to a slower consuming framework, because of diminishing in the dynamic surface important for the corrosion response. The abatement in C_{dl} values within the sight of (Glyptal) polymer inhibitors has been credited to a reduction in the dielectric consistent and

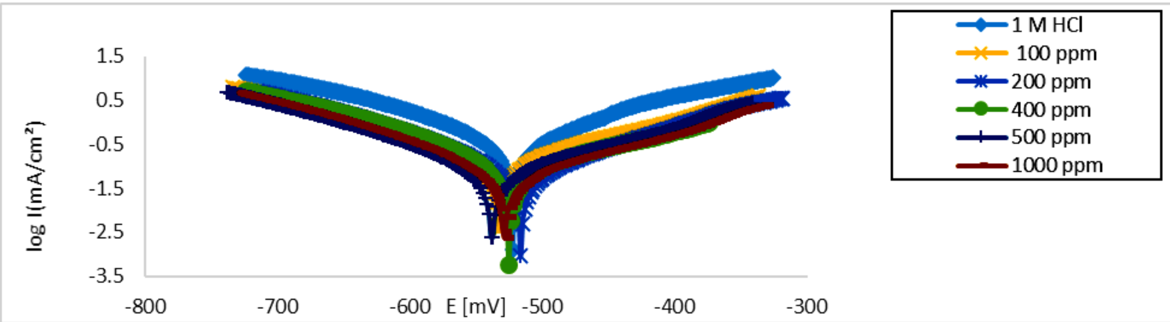


Fig. 3. Potentiodynamic polarization curves for mild steel electrode in 1M HCl in the absence and presence of different concentrations of compound (Glyptal) polymer.

Table 2. Inhibition efficiency values for steel in 1M HCl with different concentrations of inhibitor calculated by Polarization and EIS methods.

Polarization Method							EIS Method		
Conc. (ppm)	R_p (Ωcm^2)	$E_{corr.}$ (mV)	I_{corr} ($mAcm^{-2}$)	β_a ($mV\ dec^{-1}$)	β_c ($mV\ dec^{-1}$)	IE (%)	Rct Ohm	Cdl ($\mu F/cm^2$)	IE%
Blank	69.09	-522.6	1.0405	199.9	-188.4	-	60.92	653.0	-
100	180.31	-520.1	0.3511	190.1	-149.3	66.25	171.7	174.9	64.51
200	220.89	-536.0	0.2333	184.1	-156.6	77.75	248.2	114.1	75.45
400	250.49	-539.1	0.2054	175.9	-144.5	80.25	278.3	114.3	78.10
500	278.42	-543.6	0.1711	158.0	-144.3	83.55	328.6	112.2	81.46
1000	298.75	550.4	0.1375	151.8	-139.9	86.78	390.7	64.34	84.40

additionally an expansion in the twofold electric layer thickness, because of inhibitor adsorption on the steel/electrolyte interface. The restraint proficiency determined by the accompanying condition [20]:

$$IE\% = 1- R_{ct\,(1)} / R_{ct(2)} \times 100 \qquad (5)$$

where R_{ct} (1) and R_{ct} (2) are the charge move protections in the HCl solutions in the nonappearance and within the sight of the inhibitors, separately. The estimations of IE% expansion with inhibitor fixations as appeared in Table 2. This is credited to the expansion of surface inclusion of inhibitive film on a steel surface with the convergence of the inhibitors. This outcome demonstrated a similar pattern as those got from potentiodynamic polarization estimations.

3.4 Scanning Electron Microscope (SEM) Analysis

Examining electron micrographs of the mild steel surface when of the submersion in 1 M HCl with and without expansion of (Glyptal) polymer was taken to build up whether a restraint is because of the development of a natural film on the metal surface. The got micrographs are exhibited in Fig. 5. Parallel highlights on the cleaned mild steel surface before introduction to the destructive media were seen in Fig. 5a, which are related to cleaning scratches. Fig. 5(b and c) demonstrate the mild steel surface after 24 hr of inundation in 1 M HCl without and with (Glyptal) polymer. The subsequent of the high-goals SEM micrograph (Fig. 5b) demonstrates that the mild steel surface was emphatically harmed without the (Glyptal) polymer with the expanded number and profundity of the pits. In any case, there are fewer pits and splits seen in the micrographs within the sight of (Glyptal) polymer (Fig. 5c) which recommends a development of defensive film on mild steel surface which was in charge of the consumption restraint. To be sure, (Glyptal) polymer has a solid propensity to stick to the metallic surface and can be viewed as a great inhibitor for mild steel consumption in a typical hydrochloric medium. The high inhibitive exhibition of this polymer subordinate recommends a solid holding of the (Glyptal) polymer on the metal surface because of the essence of solitary sets from (oxygen) and π-orbitals, hindering the dynamic destinations and subsequently diminishing the corrosion rate.

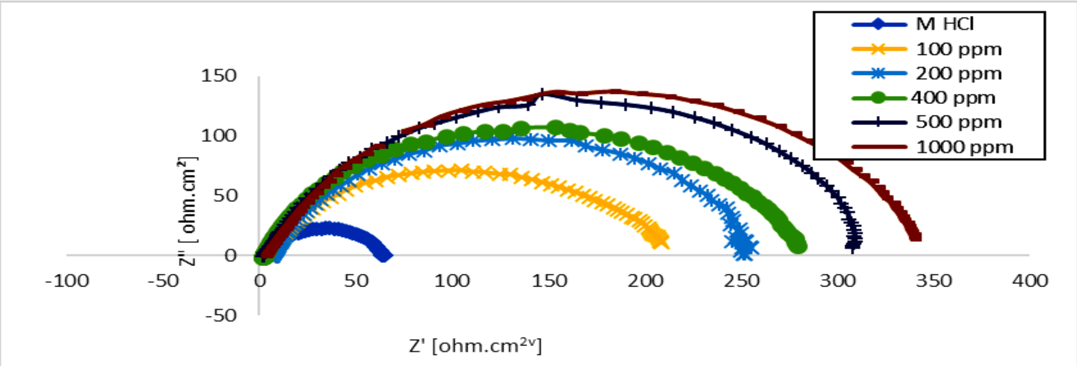


Fig. 4. Nyquist plots for mild steel in 1 M HCl without and with various concentrations of (Glyptal) polymer.

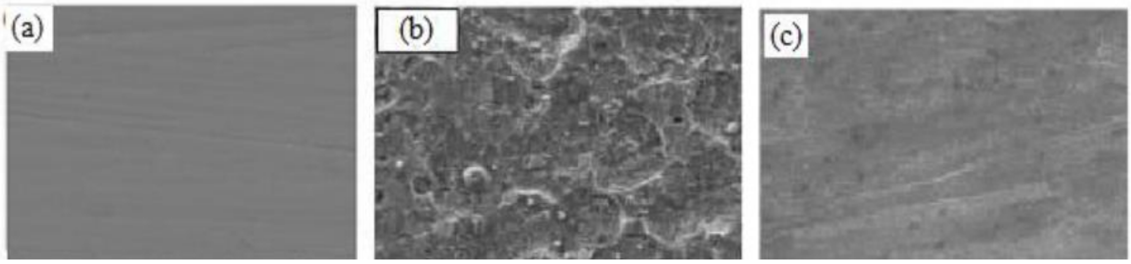


Fig. 5: SEM micrographs of mild steel: (a) unexposed, (b) exposed in 1 M HCl and (c) exposed in 1 M HCl in the presence of 1000 ppm of (Glyptal) polymer inhibitor at 25°C.

4. CONCLUSIONS

This study introduces the amalgamation and portrayal of (Glyptal) polymer for corrosion hindrance applications. The weight loss estimated inside 72 hr. demonstrates that (Glyptal) polymer go about as inhibitor in this corrosive medium. The polarization bends show that the mixes are blended sort inhibitors, influencing both anodic and cathodic consumption flows. The impedance results demonstrate that the estimation of charge exchange opposition expanded, and twofold layer capacitance diminished. The aftereffects of various procedures demonstrated a decent concurrence with one another. This understanding of the distinctive autonomous strategies demonstrates the legitimacy of these outcomes.

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الملخص العربي:

يعتبر تأكل الصلب من اخطر المشاكل التي تواجه الصناعة حيث يسبب تأكل الصلب والمعادن سنويا خسائر ضخمة.وفى مصر يسبب التآكل خسائر اقتصادية كبيرة تصل الى 4% من الدخل القومي.

يعتبر استخدام مثبطات التأكل من أهم الطرق المستخدمة لتقليل تأكل الصلب ومن أهم المثبطات المستخدمة هي المواد العضوية وخاصة البوليمرات التى تحتوى على الأكسجين والنيتروجين الذى يعمل على تقليل التآكل.

يهدف هذا البحث الى استخدام مشتقات البولى استير (جليبتال) كمثبطات لمنع تأكل الصلب المرن في وسط الهيدروكلوريك الحمضى وذلك باستخدام عدد من التحاليل والتى اثبتت فاعلية هذا المثبط حيث منع التأكل بنسبة تصل الى 90%