PROPANOYL(1Z)-N-(2,6-DIMETHYLPHENYL)-2-OXOPROPANEHYDRAZONOATE AS INHIBITOR FOR CORROSION OF 6061 AL ALLOY15 % (V) SIC_(P) COMPOSITE IN HYDROCHLORIC ACID MEDIA

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ABSTRACT: The corrosion inhibition effect of Propanoyl(1Z)-N-(2,6-dimethylphenyl)-2-oxopropanehydrazonoate (PDOH) in the corrosion of 6061 Aluminium alloy-15%(v) $SiC_{(p)}$ composite in 0.5 and 1M hydrochloric acid medium at four different temperatures (30, 40, 50 and 60 °C) was investigated using potentio-static polarization (Tafel extrapolation and Linear polarization) and weight loss methods. The results obtained reveal that PDOH is an efficient corrosion inhibitor with around 96% inhibition efficiency within the range of temperature studied. Leftward and downward shifts in Tafel plots were observed with the addition of the inhibitor, indicating that PDOH inhibits the corrosion process effectively, and that it is a cathodic inhibitor. Corrosion rate increases and inhibition efficiency decreases with increase in temperature. Results obtained by Tafel extrapolation, linear polarization, and weight loss methods are in agreement. The adsorption of the inhibitor onto the surface of the 6061 Al alloy 15 % (v) SiC_(p) composite is found to obey Temkins' adsorption isotherm that verifies the assumption of mono-layer adsorption on a uniform homogeneous composite surface with an interaction in the adsorption layer. The inhibition is therefore governed by the physisorption mechanism.

ABSTRAK: Kesan perencatan kakisan Propanoyl(1Z)-N-(2,6-dimethylphenyl)-2oxopropanehydrazonoate (PDOH) ke atas kakisan komposit aloi Al 6061-15%(v) SiC_(p) dalam media asid hidroklorik 0.5 dan 1M pada suhu-suhu yang berbeza (30, 40, 50 dan 60° C) telah dikaji menggunakan polarisasi statik-upaya (extrapolarisasi Tafel dan polarisasi Linear) dan kaedah kehilangan berat. Keputusan diperolehi menunjukkan PDOH adalah perencat yang efisien dengan 96 % keupayaan perencatan bagi julat suhu yag dikaji. Anjakan ke kiri dan ke bawah plot Tafel dapat dilihat dengan penambahan perencat, menunjukkan PDOH merencatkan proses kakisan dengan berkesan, dan ia adalah perencat katodik. Dengan peningkatan suhu, kadar kakisan meningkat dan keberkesanan perencatan menurun. Keputusan dari ekstrapolasi Tafel, polarisasi linear dan kehilangan berat.adalah saling bersetuju antara satu sama lain. Penjerapan perencat ke atas permukaan komposit aloi 6061 Al alloy 15 % (v) SiC_(p) memenuhi penjerapan Temkins' isoterma yang mengesahkan andaian penjerapan lapisan-mono ke atas permukaan komposit homogenus yang seragam melalui interaksi pada lapisan penjerapan. Perencatan dikawal oleh mekanisma fizijerapan.

KEYWORDS: potentiostatic polarization; aluminium alloy composite; adsorption isotherm; corrosion inhibition; physisorption

1. INTRODUCTION

Aluminium and its alloys and composites represent an important category of materials due to their high technological value and wide range of applications, especially in aerospace industry and military applications. The use of these materials in light weight applications because of high strength to weight ratio is widespread and these usages expose them to environments that could be acidic or alkaline [1]. Generally, aluminium alloys and composites are highly resistant to corrosion owing to the formation of a protective oxide layer on their surface [2]. Corrosion does take place when this protective Al₂O₃-3H₂O layer is either unstable or defective. Corrosion in Al alloys and its composites is either pitting or inter-granular corrosion. Pitting takes place in environments where the protective Al₂O₃-3H₂O film is partially stable. In these cases, corrosion usually originates adjacent to the flaws in the microstructure of the film [3]. Inter-granular corrosion results in selective corrosion at the grain boundaries or any precipitate free zones that might be found adjacent to them, with the remainder of the matrix undergoing very little corrosion. Inter-granular corrosion occurs because of the formation of precipitates along the grain boundaries of Al and its alloys which are more anodic with respect to the interior of the grains. As a result, preferential dissolution occurs at these sites where these precipitates or precipitate free zones undergo anodic reactions [4].

Hydrochloric acid solutions are used for pickling, chemical and electrochemical etching and in various chemical process industries wherein Al alloy composites are used. In such cases it becomes very important to use corrosion inhibitors so as to protect the material against excessive corrosion [5]. The effect of any particular organic compound on the corrosion behaviour of metals in acid system depends on the type of metal, environment contamination and its interaction with the surface of the metal. The inhibiting action of organic compounds has been mainly attributed to adsorption of the inhibiting molecule on the surface of the material. This adsorption affects the electrochemical behaviour involved in the corrosion process of metals/alloys/composites [6]. Organic compounds are widely used in various industries as corrosion inhibitors in acidic environments. The effective organic inhibitors contain nitrogen, sulphur and oxygen atoms. These heteroatoms are capable of forming coordinate covalent bond with metal owing to their free electron pairs and thus act as inhibitor. Compounds with π -bonds also generally exhibit good inhibitive properties due to interaction of π orbital with metal surface. The organic inhibitors function through adsorption on the metal surface blocking the active sites by displacing water molecules and forming a compact barrier film to decrease the corrosion rate.

The inhibition effect of 3-methyl-4-amino-5-mercapto-1,2,4-triazole on the corrosion behaviour of 6061 Al alloy 15 % (v) SiCp composite has been reported [7]. This triazole compound was found to act as an anodic inhibitor with a maximum efficiency of 58 % at 30 °C. Allyl thiourea was used as an inhibitor for the corrosion of 6061 Al alloy 15 % (v) SiCp composite in HCl medium and showed a maximum efficiency of 70% in the temperature range of 30 - 50 °C [8].

In the present work, inhibitive action of Propanoyl(1Z)-N-(2,6-dimethylphenyl)-2-oxopropanehydrazonoate (PDOH) on the corrosion behavior of 6061 Al alloy 15 % (v) SiC_(p) composite in 0.5 and 1 M hydrochloric acid medium at four different temperatures (30 - 60 °C) has been investigated using Tafel extrapolation technique. The results obtained are cross checked by Linear polarization and weight loss methods.

2. EXPERIMENTAL METHOD

2.1 Specimen

6061 Al alloy 15 % (v) SiC_(p) composite having aluminum alloy 6061 as the matrix and 15 vol. % of silicon carbide particles of mean diameter 25 μ m are manufactured in the form of cylindrical bars of length 120 mm and diameter 40 mm at Vikram Sarabhai Space Centre (VSSC), Trivandrum by stir casting process. Specimen of required length is cut from the extruded bar and machined to the required diameter. The specimen with an exposed bottom surface area of 0.95 cm² is polished with emery papers of different grades degreased with acetone and then rinsed with distilled water and finally dried in air. Then the specimen surface is covered with Teflon tape, to enable the required surface getting exposed to the media. Specimen acts as the working electrode in the three electrode cell system and is connected to the potentiostat along with the reference and counter electrodes. This composite material has the chemical composition (% wt): 0.25 Cu; 1.0 Mg; 0.60 Si; 0.20 Cr and balance Al.

2.2 Inhibitor

Propanoyl(1Z)-N-(2,6-dimethylphenyl)-2-oxopropanehydrazonoate (PDOH) is prepared by dissolving 2,6-dimethylaniline (2.26g, 0.01 mol) in dilute hydrochloric acid (22.0 ml i.e 9.0 ml 12 M HCl dissolved in 13.0 ml water) and cooled to 0°C in an ice bath. To this, a cold solution of sodium nitrite (3.2 g, 0.0462 mol in 10.0 ml of water) is added, as the temperature of the reaction mixture maintained below 5 °C. The resulting diazonium salt solution is filtered into a cooled solution of ethylacetoacetate (3.4 ml) and sodium acetate (7.0 g) in ethanol (100 ml). The resulting yellow-orange solid is filtered, washed with ice cold water, dried in air and recrystallized from methanol. [Yield 3.65 g, 86.5 %; Mol.wt. 278.30]. Purity of the compound is checked by its melting point (346 – 348 $^{\circ}$ C) and elemental analysis [9].



Fig. 1: Structural formula of PDOH.

2.3 Medium

Analytical reagent grade HCl (Merck) and double distilled water are used for preparing test solutions of 0.5 and 1 M HCl.

2.4 Tafel Extrapolation Studies

The polarization studies are performed using a Wenking Potentiostat (LB 95L) and a three electrode cell system. The steady state Tafel extrapolation studies are made from - 250 mV versus OCP to +250 mV versus OCP in steps of 20 mV from the cathodic side and the corrosion currents are noted. The Tafel plots of potential versus logI are drawn and the corrosion current density (I_{corr}) and the corrosion potential (E_{corr}) are determined. The corrosion rate, the degree of surface coverage (θ) and the percentage inhibition efficiency (% *IE*) are calculated. The experiments are performed with 1 M HCl at four different temperatures (30-60 °C). Temperature is maintained within ±1 °C.

2.5 Linear Polarization Method

Linear polarization studies are carried out in the potential (*E*) range of -20 mV versus OCP to +20 mV vs OCP in steps of 5 mV from the cathodic side and the steady state corrosion currents (*I*) are noted. The slope of E vs I are used to determine the corrosion current density (I_{corr}) and the corrosion rate (CR).

2.6 Weight Loss Method

Specimen surface of 1 cm^2 is exposed to 100 ml of HCl solution for 6 hours. Prior to exposure, the surface is polished with different grades of emery paper and rinsed with distilled water and acetone, then dried and finally accurately weighed. After exposure, again the specimen is gently polished, rinsed with distilled water and acetone, then dried and accurately weighed. The difference in weight gives the weight loss. Experiments are conducted with 0.5 and 1 M HCl in the presence and absence of inhibitor at 30 °C.

3. RESULTS AND DISCUSSION

The electrochemical parameters for the inhibiting action of PDOH on the corrosion of 6061 Al alloy 15 % (v) $SiC_{(p)}$ composite in 0.5 and 1 M HCl solution are studied by potentiostatic polarization technique at four temperatures. The results are presented in Table 1 and 2.

The corrosion rate, and the percentage inhibitor efficiency (% *IE*) are calculated by using the following relations [10].

$$CR_{(mpy)} = \frac{0.1288 \times Eq.wt \times I_{corr}}{D}$$
(1)

where, I_{corr} is the corrosion current density in μ A/cm², Eq. wt is the specimen equivalent weight in g, D is the specimen density in g/cc and 0.1288 is the metric and time conversion factor.

$$\% IE = \left(\frac{I_{corr} - I_{corr(inh)}}{I_{corr}}\right) \times 100$$
⁽²⁾

where, I_{corr} and $I_{\text{corr(inh)}}$ are the corrosion current densities in μ A/cm² in the absence and presence of the inhibitor respectively.

The inhibiton efficiency by weight loss method is calculated by using the following expression [11].

$$\% IE = \left(\frac{W - W_{inh}}{W}\right) \times 100 \tag{3}$$

where, W and W_{inh} are the values of weight loss of the specimen after immersion in test solution without and with inhibitor, respectively.

It is observed from the polarization results (Tables 1 & 2) and the polarization curve (Fig. 2) that there is a large negative shift in the corrosion potential (E_{corr}) and a drastic reduction in the corrosion current density (I_{corr}) and corrosion rate (CR) values. The shift in corrosion potential in the negative direction indicates that PDOH is an efficient cathodic inhibitor.



Fig. 2: Tafel extrapolation plot for PDOH in 1 M HCl at 30 °C.

Table 1: Electrochemical parameters for the
corrosion inhibition of 6061 Al alloy 15 %
(v) $SiC_{(p)}$ in 0.5 M HCl medium.

Table 2: Electrochemical parameters for the corrosion inhibition of 6061 Al alloy 15 % (v) SiC_(p) in 1 M HCl medium.

Temperature (°C)	c (10 ⁻¹ molL ⁻¹)	E	CR (mpy)	IE (96)	Temperature (°C)	c (10 ⁻⁴ molL ⁻¹)	E	CR (mpy)	IE (%)
30	0	-690	2054	-	(-/	0	-700	4520	-
	0.9	-725	248	87.95		0.9	-750	1889	58.65
	1.8	-741	179	91.29	30	1.8	-752	1561	65.46
	3.6	-738	134	93.50		3.6	-748	1151	74.54
	4.5	-750	86	95.80		4.5	-747	945	79.09
	5.4	-719	161	92.15		5.4	-749	1027	77.28
40	0	-690	3698	-		0	-700	6573	-
	0.9	-741	382	86.67		0.9	-765	2817	57.15
	1.8	-743	368	90.06	40	1.8	-775	2306	64.92
	3.6	-742	279	92.45		3.6	-772	1699	74.16
	4.5	-723	177	95.22		4.5	-780	1430	78.25
	5.4	-715	329	91.11		5.4	-760	1557	76.31
50	0	-690	4930	-		0	-720	7806	-
	0.9	-750	740	85.00	-	0.9	-748	3492	55.27
	1.8	-749	559	88.67		1.8	-750	2794	64.21
	3.6	-746	452	90.83	50	3.6	-751	2087	73.52
	4.5	-745	263	94.67		4.5	-753	1738	77.74
	5.4	-740	477	90.33		5.4	-751	1882	75.89
60	0	-710	5546	-		0	-700	11608	-
	0.9	-737	1231	77.81	60	0.9	-740	5681	51.06
	1.8	-741	1027	81.48		1.8	-745	4572	60.61
	3.6	-736	822	85.18		3.6	-750	3369	70.98
	4.5	-731	575	89.63		4.5	-752	2876	75.22
	5.4	-725	904	83.71		5.4	-743	3118	73.14

A comparison of the inhibition efficiency obtained from Tafel extrapolation, Linear polarization techniques and weight loss method at 30 °C is given in Table 3. The results obtained by all the three methods are in agreement.

The % *IE* increases with increase in concentration of PDOH up to $4.5 \times 10^{-4} \text{ molL}^{-1}$ (Table 1 and 2). The increase in % *IE* may be due to the blocking effect of the surface by both adsorption and film forming mechanism which decreases the effective area of attack. The results indicate that PDOH is an effective corrosion inhibitor which gives efficiency

values as high as 96 %. The inhibiting effect of PDOH may be due to its parallel adsorption at the 6061 Al alloy/SiCp composite–acid solution interface. The parallel adsorption takes place owing to the presence of one or more active centers of adsorption. PDOH might have displayed high inhibition efficiency because of the presence of hetero atoms of N in their structure as well as the presence of N rich azo group and O rich ester (carbonyl) multiple functional groups in its structure.

Table 3: Comparison of inhibition efficiencies obtained by Tafel extrapolation, Linear polarization and Weight loss methods for the corrosion inhibition of 6061 Al alloy 15 % (v) SiC_(p) in 0.5 and 1 M HCl media.

c	IE (%)							
(10° · moîL'')	Tafel Technique	Linear	Weight					
-	0.51	VI HCI	2033					
0.9	87.95	80.86	80.64					
1.8	91.29	84.77	83.44					
3.6	93.50	85.87	85.41					
4.5	95.80	92.17	90.82					
5.4	92.15	86.30	88.52					
1 M HCI								
0.9	58.65	61.26	50.49					
1.8	65.46	67.58	63.37					
3.6	74.54	72.72	72.77					
4.5	79.09	79.54	76.24					
5.4	77.28	76.24	68.32					



Fig. 3: The scanning electron micrographs of 6061 Al alloy 15 % (v) SiC_(p) composite (a) Fresh specimen (b) Specimen exposed to 1 M HCl (c) Specimen exposed to 1 M HCl containing 4.5×10^{-4} molL⁻¹ of PDOH.

The surface analysis of 6061 Al alloy 15 % (v) SiC_(p) composite is carried out using scanning electron microscope (JEOL Model 8340 LA). The scanning electron micrograph of a fresh specimen is shown in Fig. 3a. The micrographs for the specimens immersed in 1 M HCl solution at 30° C in the absence and presence of inhibitor are shown in Fig. 3b and 3c respectively. The corrosion of 6061 Al alloy 15 % (v) SiC_(p) in HCl medium is presumably due to the anodic dissolution either at the grain boundaries or at the metalmedia interface. It is seen from the Fig. 3c that the surface of the composite exposed to solution with inhibitor is smoother than of that exposed to acid solution without inhibitor (Fig. 3c). These observations suggest that the inhibitor forms a protective layer on the composite surface, which prevents the attack of acid on the surface.

To understand the mechanism of corrosion inhibition, the adsorption behaviour of the inhibitor compound on the composite surface must be known. The surface coverage values for different concentrations of PDOH from the acid solution are calculated. The surface coverage values (θ) are tested graphically by fitting a suitable adsorption isotherm. The plot of θ versus log *c* (Fig. 4) for different concentrations of PDOH shows a straight line indicating that the adsorption of the compound on the composite surface follows Temkin's adsorption isotherm. The applicability of Temkin's adsorption isotherm verifies the assumption of mono-layer adsorption on a uniform homogeneous composite surface with an interaction in the adsorption layer [12, 13].



Fig. 4: Temkin's adsorption isotherm for PDOH on 6061 Al alloy 15 % (v) SiC_(p) composite surface in 1 M HCl at different temperatures.

Table 4: Thermodynamic parameters for PDOH corrosion of 6061 Al alloy 15 % (v) SiC(p) composite in 1 M HCl solution.

Inhibitor	E,	$-\Delta G_{ads}(k\text{Irmof}')$					
conc.	(Klimol* -	Temperature (*C)					
(10 · molL ·))	30	- 40	50	60		
Blank	26.40	-	-	-	-		
4.5×10 ⁻⁴	31.37	32.88	33.84	34.84	35.53		
Equilibrium constant (K)		8405	7995	7761	6746		

The thermodynamic parameters for the corrosion of 6061 Al alloy 15 % (v) $SiC_{(p)}$ in the presence of PDOH are studied (Table 4).

The values of activation energy (E_a) are calculated using Arrhenius equation [14]

$$\ln\left(\frac{r^2}{r^1}\right) = -\frac{E_a\Delta T}{(R \times T_1 \times T_2)} \tag{4}$$

where, r_2 and r_1 are the corrosion rates at temperatures T_2 and T_1 respectively, R is the gas constant, T_1 and T_2 are the two temperature levels and ΔT is the difference in temperatures.

The equilibrium constant (K) is determined by the relation:

$$K = \frac{\theta}{c(1-\theta)} \tag{5}$$

where, θ is the degree of surface coverage on the metal surface and c is the concentration of the inhibitor in molL⁻¹.

The free energy of adsorption (ΔG_{ads}) is calculated from the following equation [15, 16].

$$\Delta G_{ads} = -RTln(55.5K) \tag{6}$$

where 55.5 is the concentration of water in solution in molL⁻¹ and T is the temperature in Kelvin.

The negative values of ΔG_{ads} indicate spontaneous adsorption and strong interaction of inhibitor molecules on to the surface of the composite. The ΔG_{ads} values for the optimal concentration (4.5×10⁻⁴ molL⁻¹) of PDOH are less than -40 kJ mol⁻¹. This indicates that the inhibition is governed by physical adsorption mechanism [17].

4. CONCLUDING REMARKS

- a) The corrosion rate decreased drastically in the presence of PDOH in both 0.5 and 1 M hydrochloric acid media over the temperatures studied (30-60 °C).
- b) PDOH has proved to be an efficient cathodic inhibitor for corrosion of 6061 Al alloy 15 % (v) SiC_(p) composite in 0.5 and 1 M hydrochloric acid media.
- c) The adsorption of the compound on the surface of 6061 Al alloy 15 % (v) $SiC_{(p)}$ composite obeys Temkin's isotherm and is governed by physical adsorption mechanism.
- d) % IE obtained by polarization techniques and weight loss method are in agreement.

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REFERENCES

- [1] G. O. Avwiri and F. O. Igho, "Inhibitive action of veronica amygdalina on the corrosion of aluminium alloys in acid media." *Marer. Lett.* 57(2003):3705.
- [2] K. A. Lucas and H. Clarke. "Corrosion of Aluminium based metal matrix composites." *Research studies Press Ltd.*, Somerset, U.K., 1993.
- [3] S. Wernick, R. Pinner and P. G. Shasby. *The surface treatment and finishing of Alumunium and its alloys*, 5th ed., 1.5(1987).

- [4] D. W. Berkeley, H. E. M. Sallam and H. E. M. Sallam and H. Nayeb-Hashemi. "The effect of pH on the mechanism of corrosion and stress corrosion and degradation of mechanical properties of AA 6061 and Nextel 440 fibre reinforced AA 6061 composite." *Corros Sci.*, 40(1998): 141.
- [5] B. Mernari, H. Elattari, M. Traisnel, F. Bentiss and M. Lefrance. "Inhibiting effects of 3.5 his (npyridyl)-4-amino-1, 2, 4-triazoles on the corrosion of mild steel in 1 M HCI medium." *Corros. Science* 40(1998):391.
- [6] K. Obesegum Abiola, N. C. Oforka and S. S. Angeye, "Corrosion behavior of aluminium in hydrochloric acid solution containing mercaptoacentic acid." *Materials Letters* 58(2004): 3461.
- [7] Suma Rao, Padmalatha, Jagannath Nayak and A. Nithyananda Shetty. "3-Methyl-4-amino-5 mercapto-1, 2, 4-triazole as inhibitor of corrosion of 6061 Al-15 Vol. pct. SiC(p) composite." *Journal of Metallurgy and Materials ScienceJ*,47.1(2005: 51.
- [8] Suma Rao A, Padmalatha, Jagannath Nayak A, Nithyananda Shetty and K. R. Hebbar, "Corrosion behavior of Al-15 Vol. Pct SiC (p) in Hydrochloric acid (A study of inhibitive effect of Allysl Thiourea)." *National conference on corrosion and corrosion control*, METCORR -NITK, Suraathkal, (2005): 100.
- [9] Arun M Isloor, PhD Thesis. "Study on the Synthesis and Biological activity of some pharmaceutically important Heterocyclic compounds." Mangalore University: 104, August 2001.
- [10] S. Divakara Sheety and Prakash Sheety. "Inhinition of mild steel corrosion in acid media using N-benzyl-N'-phenyl thiourea." *Indian Journal of Chemical Technology* 15.3 (2008): 216.
- [11] M. Abdallah. "Rodaninc Azosulpha drug as corrosion inhibitors of 304-stainless steel in hydrochloric acid solution." *Corrosion Science* 44(2002):717.
- A. E. Stayomova, E. I. Sololova and S. N. Roichara. "The inhibition of mild steel corrosion in 1 M HCI in the presence of linear and cyclic thiocarbamides-effect of concentration and temperature of the corrosion medium on their protective action." *Corrosion Science* 39(1997):1595.
- [12] Pandian, Bothi Raza and Mathur Gopalakrishnan Sethuraman, "Solanum Tuberosum as an Inhibitor of Mild Steel Corrosion in Acid Media", *Iran Journal Chemical and Chemical Engineering* 28.1(2009):77.
- [13] S. S. Abd El-Rehim, S. A. M. Refacy, F. Taha, M. B. Saleh and R. A. Ahmed. "Corrosion inhibition of mild steel in acidic medium using 2-amino thiophenol and 2-cyanomethyl benzothiazole." *Journal Applied Electrochemical* 31(2001): 429.
- A. K. Putilova, S. A. Balezin, Y. P. Borasanic, Metallic Corrosion Inhibitors, Pergomeon Press,Oxford, 1960.
- [14] M. A. Quaroishi and R. Sardar. "The effect of some nitrogen and sulphur based synthetic inhibitors on corrosion inhibition of mild steel in acid solution." *Indian Journal Chemical Technology* 11(2004):103.
- [15] B. Obot and N. O. Obi-Egbedi. "Inhibition of Aluminium corrosion in hydrocholoric acid using nizoral and the effect of iodide addition." *E-journal of chemistry* 7.3(2010):837.