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A new inhibitor cum sealant for Anodized Aluminium surfaces

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Abstract

A new inhibitor cum sealant for anodized aluminium has been used involving 1-cyclopropyl-6-fluoro-4-oxo- 7-piperazin-1-yl-quinoline-3-carboxylic acid [CPFP] drug in 3.5% NaCl. The corrosion resistance of the anodized aluminium surfaces could be improved by this new sealant cum inhibitor. The efficacy of the sealant film was assessed by potentiodynamic polarization and A.C impedance analysis. The calculations of quantum mechanical parameters viz., the localization of frontier molecular orbital's, EHOMO, ELUMO, energy gap (ΔE) and dipole moment (μ), indicated that this new compound retards the corrosion of Anodized aluminium surfaces through its effective adsorption of Al surfaces.

Key words: Anodizing, sealing, corrosion inhibition

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Introduction

The anodized aluminium is extensively used in the fields of aerospace, automobile, electronic products, etc. The life of the anodized film is short due to presence micro pores in the aluminium oxide which pervades the entry of foreign materials , when it is exposed to acidic and hard water media. Organic compounds containing sulphur, nitrogen and oxygen atoms are capable of reducing metallic corrosion. Several substituted thiourea and drugs compounds have been investigated as corrosion inhibitors [1-5] for the aluminium and its alloys. All the above studies reveal the one common observation that thiourea derivatives can be regarded as excellent corrosion inhibitors for aluminium. However , no systematic approach is available for the corrosion protection of anodized film using eco friendly sealing agent.The present paper describes a study of special sealing cum Inhibitor on the corrosion of anodized aluminium in 3.5% NaCl using potentiodynamic polarization and impedance methods. The quantum mechanical descriptors substantiate the performance of the CPFP antibiotics by forming a resilient adherent layer on the metal surface.

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Experimental details

Al 1200 specimens of compositions, Fe = 0.42%, Si = 0.23%, and Aluminium remainder, and of size 4 cm2x 2cm were used for anodizing and 1cm2 x 0.02 cm were used for electrochemical studies .

Al 1200 coupons were mechanically polished and then degreased with tri chloro ethylene. Then the coupons were subjected to anodizing by following the procedure as appended below:. Anode: Al 1200 coupons; Cathode: Lead ; electrolyte: 2M Boric acid + 2M Ammonium tartrate ; Voltage: 15 V ; Time : 12 minutes. Thickness: 35 microns. Colour of the anodized film: Bronze colour.

The sealing of anodized film was carried out by immersing the anodized plates into CPFP drugs solution of concentrations ranging from 5 to 15x10-4 M mixed with hot water.The duration of sealing process was 2 minutes.

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After sealing, the coupons were removed , washed , dried and characterized with electrochemical techniques. Both cathodic and anodic polarisation curves were recorded in 3.5% NaCl potentiodynamically (10 mv S-1) using corrosion measurement system BAS Model : 100A , computerised electrochemical analyser (made in West Lafayette, Indiana) and PL-10 digital plotter (DMP-40 series, Houston Instruments Division). A platinum foil(5 cm2) and Hg/Hg2Cl2 /3.5%NaCl were used as auxiliary and reference electrodes, respectively. Double layer capacitance (Cdl) and charge transfer resistance values (Rt) were calculated using AC impedance measurements (EG&G Princeton Applied research model:7310) as reported elsewhere10. Quantum chemical calculations were performed using Gaussian 03 software package. The energy of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and dipole moment (μ) of the inhibitor Cum Sealant were calculated.

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Results and Discussion:

Potentiodynamic polarization studies

Polarization curves for sealed anodized aluminium in 3.5% NaCl containing different concentrations of CPFP are given in figure-1. The values of corrosion potential (Ecorr) , corrosion current densities (Icorr), anodic tafel slope (βa) ,cathodic tafel slope (βc) surface coverage(θ) and inhibition efficiency (IE%) calculated using polarization curves are summarized in table-1.

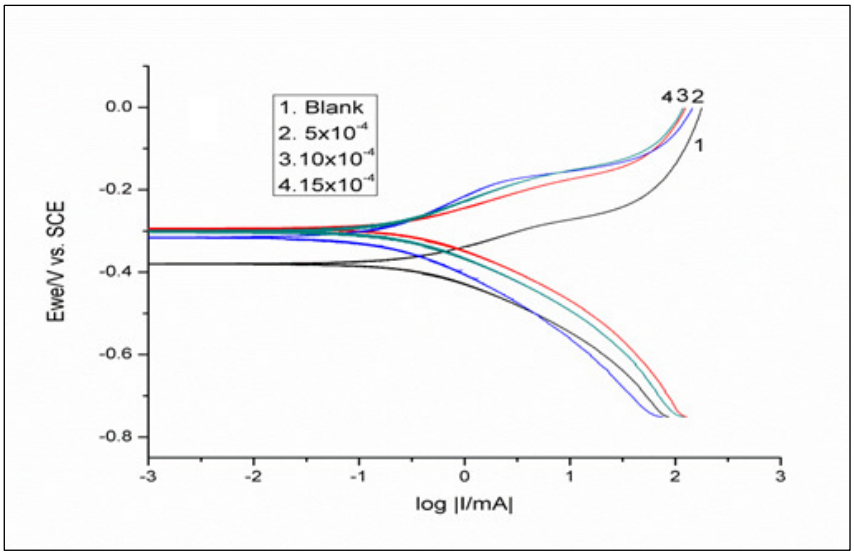

Fig. 1: Polarization curves of Al surfaces in 3.5% NaCl in absence and presence of different concentrations of sealant

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According to the results, corrosion current (Icorr) value decreases with increase in the concentration of the sealant on Al surfaces . The inhibition efficiency (IE %) and surface coverage (θ) increases with increase in antibiotic concentration. The maximum inhibition efficiency is achieved at 15x10-4 M concentration. Both βa and βc are reduced, but the values of βc are decreased to a greater extent. This indicates that the sealing compound behaves as cathodic inhibitor.

Table 1: Potentiodynamic polarization parameters for Anodized Al surfaces immersed in 3.5% NaCl in absence and presence of different concentrations of sealant.

Inhibitor Con. [M]	E_{corr} [mV vs SCE]	I_{corr} [μA cm^{-2}]	β_a [mV dec^{-1}]	β_c [mV dec^{-1}]	Inhibiton efficiency [%]	Surface coverage [θ]
Blank	-376.12	548.57	82.9	135.3	-	-
$5x10^{-4}$	-264.05	195.77	64.1	144.2	64.31	0.6431
$10x10^{-4}$	-259.95	125.42	57.9	134.7	77.13	0.7713
$15x10^{-4}$	-255.21	80.26	51.9	132.4	85.36	0.8536

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Electrochemical impedance studies

The Nyquist representations of impedance performance of sealed anodized aluminium in 3.5% NaCl containing different concentrations of CPFP are given in figure 2. A large capacitive circle at higher frequency range is observed at all concentrations of the sealing compound. The higher frequency capacitive loop is due to the adsorption of inhibitor molecule [28].The results are presented in table 2.

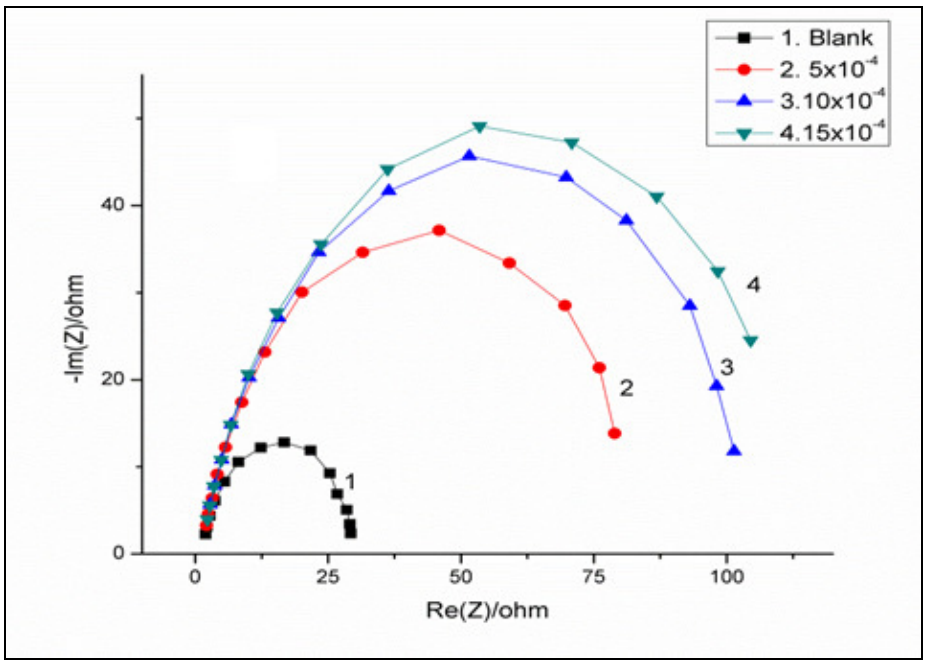

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Table 3: Electrochemical impedance parameters for sealed anodized aluminium in 3.5% NaCl containing different concentrations of CPFP

Inhibitor Con. [M]	Rct [Ω cm2]	Cdl [F cm-2]	Inhibition efficiency [%]	Surface coverage[θ]
Blank	28.1	0.489	-	-
5x10-4	82.1	0.381	65.77	0.6577
10x10-4	112.6	0.277	75.04	0.7504
15x10-4	176.32	0.143	84.06	0.8406

Quantum chemical calculations

Quantum chemical calculations were carried out to investigate the adsorption and inhibition mechanism of the inhibitor. Figure 3 showed the optimized structures of inhibitor cum sealant. The values of calculated quantum chemical parameters i.e. EHOMO (highest occupied molecular orbital), ELUMO (lowest unoccupied molecular orbital), ΔE (energy gap), μ (dipole moment), σ (softness) etc. are summarized in table-3.

EHOMO is associated with the electron-donating ability of the molecule. Several researchers have shown that the adsorption of an inhibitor on metal surface can occur on the basis of donor-acceptor interactions between the π-electrons of heterocyclic atoms and the vacant d-orbitals of the metal surface atoms [9-11].

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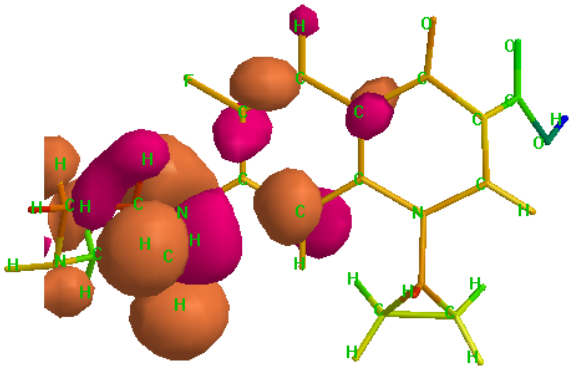

Fig.3a. HOMO of CPFP

A high value of E_{HOMO} indicates a tendency of a molecule to donate electrons to acceptor molecules with low energy empty molecular orbital. Increasing values of E_{HOMO} facilitates the adsorption and increases the inhibition efficiency by influencing the transport process through the adsorbed layer [46].

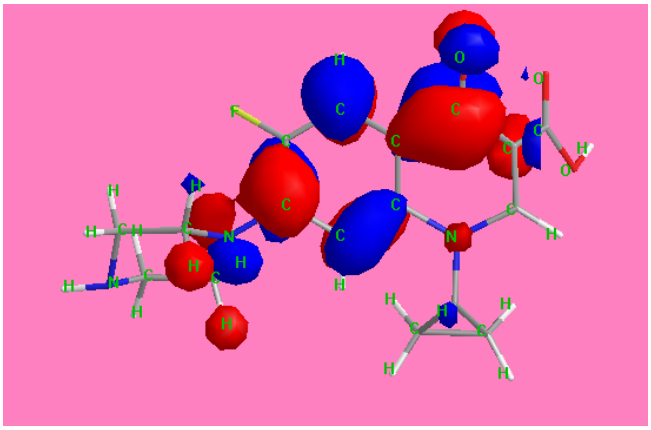

Fig.3b. LUMO of CPFP

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E_{LUMO} indicates the ability of the molecule to accept the electrons, hence these are acceptor states. The lower the value of E_{LUMO}, the more probable is that the molecule can accept electrons and increase the inhibition efficiency.

Table 3: Quantum mechanical parameters for sealants on the corrosion of anodized Al

Inhibitor	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol-1)	Dipole moment (Debye)
CPFP	-1.234	-9.442	8.208	4.9

Regarding ΔE (ELUMO-EHOMO) lower values of energy difference will cause higher inhibition efficiency because energy to release electron from last occupied orbital will be low. When dipole moment is concerned higher values of μ, will favours a strong interaction of inhibitor molecule with the metal surface .

Conclusions

A new inhibitor cum sealant has been use of 1-cyclopropyl-6-fluoro-4-oxo- 7-piperazin-1-yl-quinoline-3-carboxylic acid (CPFP) as sealing compound in 3.5% NaCl was thoroughly studied using, potentiodynamic polarization and impedance The quantum mechanical studies substantiate the performance of CPFP as excellent corrosion inhibitor for mild steel in 1M H2SO4.

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