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The corrosion resistance of mild steel submerged in seawater prior to coating and following the application of Asian paint

ABSTRACT

The corrosion resistance of mild steel submerged in seawater has been assessed through polarization studies, both prior to and following the application of Asian paint. The results of this evaluation will contribute to advancements in shipping technology. Key corrosion parameters, including corrosion potential (E_{corr}), Tafel slopes (β_c for cathodic and β_a for anodic), linear polarization resistance (LPR), and corrosion current (I_{corr}), have been determined. In the study of polarization, fundamental principles indicate that an increase in corrosion resistance corresponds with a rise in linear polarization resistance (LPR) and a decrease in corrosion current (I_{corr}). The findings of this research lead to several conclusions. Asian paints can be applied to hull plates constructed from mild steel to mitigate corrosion, particularly since these plates are consistently exposed to seawater. The surface morphology has been analysed by SEM. The results are in agreement with the results of the polarisation study.

Keywords: *Corrosion resistance, mild steel , seawater , before coating , after coating Asian paint*

INTRODUCTION

Corrosion is an inherent process that transforms a refined metal into a more chemically stable oxide. It involves the gradual degradation of materials, typically metals, through chemical or electrochemical interactions with their surroundings. The discipline of corrosion engineering focuses on the management and prevention of corrosion.

Corrosion protection painting refers to the application of protective paint systems on metal substrates. The primary aim of this process is to safeguard the metal from atmospheric corrosion, such as rust, while also providing the surface with the intended appearance and texture.

The industrial, commercial, and architectural sectors significantly depend on coatings to safeguard their assets. Broadly speaking, coatings are characterized as a thin layer of solid material applied to a surface, enhancing its protective, aesthetic, or functional attributes.

More precisely, these coatings consist of a liquid, liquefiable, or mastic formulation that transforms into a solid adherent film after being applied to a surface. Protective coatings serve to shield the substrate from corrosion. A highly effective method for preventing metal corrosion involves physically isolating the substrate from its environment through the application of protective coatings.

Coatings safeguard against corrosion by employing one of several methods: they either obstruct essential elements from interacting to initiate the corrosion process, actively inhibit the electrochemical reaction, or redirect the corrosion process in a manner that does not damage the asset.

Numerous studies have been released regarding the protection of metals using paint coatings. A selection of these works is provided below [1-10].

Sheng et al. [1] investigated the development of medetomidine/epoxy coatings aimed at combating marine corrosion and biological fouling. These issues pose significant obstacles to the advancement of the marine industry. Given that medetomidine (MM) has been demonstrated to

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promote hyperactivity and disrupt the settlement of barnacle larvae, we synthesized MM along with its derivatives: 4-(1-(3,4-dimethyl phenyl)ethyl)-1H-imidazole (MM-2), 5-(1-phenylethyl)-1H-imidazole (MM-3), and 4-(1-(3,4-dichlorophenyl)ethyl)-1H-imidazole (MM-4) to assess their antifouling properties in marine environments. These antifouling medetomidines were combined with an anticorrosive epoxy resin (EP) to create coatings that provide both antifouling and anticorrosion advantages. Among the evaluated compounds, the dichlorosubstituted medetomidine analogue (MM-4) emerged as the most effective option [1].

Barbosa et al. [2] conducted a comparative study on the effectiveness of corrosion inhibition between epoxy paint and organic varnish infused with aloe vera and elaeis guineensis oils, specifically in cooling systems. Air conditioning coils, typically made of copper, are recognized for their excellent corrosion resistance. However, in high-salinity environments, these coils are prone to corrosion, leading to issues such as refrigerant leaks, decreased efficiency, a reduced operational lifespan, and higher electricity costs. To mitigate coil corrosion, a public organization in São Luís-MA employs a highly toxic and costly epoxy polyamide paint [2].

Cui et al. [3] have investigated a dual-purpose approach for self-healing marine coatings that possess both antifouling and anticorrosion characteristics. Metal materials exposed to marine environments endure severe conditions, with damage from marine gravel significantly impairing their functionality. A potential solution is the development of self-healing integrally antifouling and anticorrosion coatings (SIAAC) utilizing epoxy resin (EP). However, achieving a balance between these properties proves to be difficult, often leading to the prioritization of one characteristic over the other. To overcome this challenge, 2D nano-fillers (GB@MMT) were created by incorporating benzimidazole (BIA), which exhibits antifouling and anticorrosion properties, onto montmorillonite (MMT) through cation exchange. This was then dispersed in silicone-grafted EP to produce a composite coating known as SiEP-3GB@MMT. The SiEP-3GB@MMT coating demonstrates outstanding antifouling capabilities and a high resistance to protein adsorption, with a surface energy of 17.05 mJ/m^2, comparable to that of silicone [3].

Liu et al. [4] have explored GNP/Ag@PDA Incorporated Waterborne Epoxy Coating with Excellent Corrosion Resistance and Antifouling Performance.

Corrosion and fouling present significant challenges for devices operating in marine environments. Nevertheless, most current solutions fail to provide simultaneous protection against both corrosion and fouling. In response to this issue, a novel waterborne epoxy (WEP) composite coating has been developed, demonstrating exceptional resistance to both corrosion and fouling. This WEP-based composite incorporates a nanohybrid filler, which is created by depositing silver (Ag) nanoparticles onto the surface of graphite nanoplatelets (GNP) through a straightforward in situ hydrothermal synthesis process, followed by polydopamine (PDA) modification. The PDA modification significantly enhances the dispersion and compatibility of the GNP/Ag@PDA (GAP) within the WEP matrix[4].

Królikowski [5] has examined a subjective perspective on the evolution of the railway in Poland, particularly focusing on corrosion challenges and the solutions that have been developed to address them.

Over the course of its 200-year history, the railway sector has faced numerous corrosion-related issues, making the prevention of such damage crucial for the progress of this transportation method. In the 19th century, significant problems arose from stress corrosion cracking in steam boilers and the wear of bearings in carriage wheels. The range of corrosion issues in the 20th century grew substantially, encompassing infrastructure corrosion due to stray currents following the adoption of electric traction, the use of copper steel and paint coatings to inhibit rust in steel carriages, fretting corrosion of bolted tie plates on railway tracks, and galvanic corrosion occurring in carriages where steel, aluminum, and composite materials interact. Effective strategies were implemented to mitigate these corrosion-related damages. Additionally, the role of Polish innovations in the history of railways and insights into the future of this transportation mode were also addressed [5].

Morsy et al.[6] conducted an extensive study on oxygen/graphite carbon nitride smart nano coatings aimed at sustainable maintenance and sacrificial anode protection for mild steel. This research focuses on enhancing the corrosion resistance of mild steel (MS) by integrating photo-catalyst-doped graphitic carbon nitride ($g\text{-}C_3N_4$) nano-sheets infused with silver (Ag) and oxygen (O_2) into a solar light-activated photo-electrochemical anticorrosion paint formulated with polyester (PE). The primary goal is to achieve sacrificial anode protection through activation by visible light. The resulting paint creates a consistent film on the surface of the mild steel, effectively delivering anodic protection when exposed to visible light. Various characterization methods, such as energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), and UV–Vis spectroscopy, validate the molecular structure of the nano-sheets [6].

The hydrophobic and anticorrosive characteristics of secondary doped polyaniline-modified basalt flake composite epoxy coatings have been investigated by Yu et al.[7].

Oceans cover 71% of the Earth's surface, with an average depth of around 3,700 meters, and 90% of the ocean's depth surpassing 1,000 meters. Besides being rich in mineral resources, the ocean also holds significant reserves of natural gas, combustible ice, and oil. Consequently, it has emerged as a key strategic area for the exploration and utilization of Earth's natural resources. Robust anticorrosion coatings are essential for ensuring the safe operation of marine engineering and equipment. The failure of these coatings in aggressive marine environments poses a serious risk to the reliable functioning and long-term safety of marine equipment. However, conventional anticorrosion coatings exhibit a low water contact angle in the atmosphere and demonstrate inadequate long-term protective performance in severe corrosive marine conditions. The active epoxy groups present in the molecular structure of epoxy resin enable it to crosslink with various curing agents, resulting in a three-dimensional polymer network structure [7].

Xu et al. [8] have documented the development and efficacy of a low surface treatment coating that incorporates rust conversion and corrosion inhibition. In marine environments, metal structures are highly susceptible to corrosion, resulting in significant maintenance challenges and elevated costs. Traditional low surface treatment coatings generally provide limited benefits, primarily focusing on superficial improvements. These coatings often fail to deliver sufficient long-term protection against corrosion. Although rust converters and corrosion inhibitors effectively address surface rust and protect the underlying materials, they face challenges such as inadequate paint penetration and compatibility issues with waterborne coating systems. This research aims to create an innovative low surface treatment coating that integrates long-lasting anti-corrosion properties, effective low surface treatment functions, and improved penetration capabilities. The new formulation seeks to optimize the interaction between the rust converter, corrosion inhibitor, and waterborne coating to achieve synergistic and multifunctional advantages [8].

Bargout et al. [9] investigated the development of a cellulose acetate poly acrylonitrile (CAPA)–SiC/epoxy coating aimed at reducing copper corrosion in chloride-containing environments. A novel conducting polymer composite, CAPA–SiC, was synthesized through an in situ oxidative polymerization method in an aqueous solution. Silicon carbide (SiC) was derived from Cinachyrella sp. as a carbon and silicon source, processed at 1200 °C in an argon atmosphere via catalytic reduction. The characterization of the CAPA–SiC composite's structure and morphology was conducted using various techniques, including surface area analysis (BET), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and surface morphology assessments (SEM & TEM). To enhance copper protection, the synthesized CAPA–SiC composite was blended with commercial epoxy paint through a casting method, resulting in a coating applied to the copper surface using the three-component CAPA–SiC/epoxy paint mixture. The effectiveness of the CAPA–SiC/paint coating in inhibiting corrosion was evaluated through electrochemical impedance spectroscopy and Tafel polarization measurements in a 3.5 wt% NaCl solution [9].

Zarki et al. [10] have explored the topic of "Grafted Sepiolite as a Smart Nanocontainer for Daphne Gnidium Plant Extract: pH-Dependent Controlled Release and Effective Green Anti-Corrosion Coating." This research aims to enhance the creation of environmentally friendly and effective active anti-corrosion coatings for metal surfaces across various engineering fields. A novel smart anti-corrosive container was engineered using fibrous sepiolite clay (Sep). Initially, Sep underwent a grafting process with 3-Aminopropyl-diethoxy-methylsilane (APDEMS). The resulting grafted sepiolite (Sep-G) was then utilized to incorporate a Daphne Gnidium plant extract (DGE), serving as a natural corrosion inhibitor. The modification of Sep was meticulously monitored and characterized using techniques such as Zeta potential analysis, scanning electron microscopy, X-ray diffraction, UV/visible spectroscopy, and Fourier transform infrared spectroscopy. The findings demonstrated successful modification of the clay, with a silane loading of 7.68% and an adsorption capacity for DGE of approximately 58 mg/g. The release behavior of DGE from the developed nanocomposite (Sep-G@DGE) was examined at various pH levels, revealing distinct pH-dependent release patterns [10].

In the present work the influence of Asian paint Apex Floor Guard on the corrosion resistance of mild steel immersed in seawater has been evaluated. Polarization study has been used for this purpose. The findings will be used to protect hull plates which are always in contact with seawater [11-14].

EXPERIMENTAL

Composition of mild steel

The composition of mild steel used in this study is given in Table 1.

Table 1. Composition of mild steel

Element	Average, %	Abs. Std. Dev.	Ref. Std. Dev.	1	2
C	0.101	0.0014	1.4	0.102	0.1
Si	0.055	0.0021	3.89	0.053	0.056
Mn	1.629	0.0057	0.35	1.633	1.625
P	0.0087	0.0003	3.25	0.0085	0.0089
S	0.0028	0.0003	10.1	0.0026	0.003
Cr	0.036	0.0014	3.93	0.037	0.035
Mo	0.0086	0.00007	0.83	0.0086	0.0085
Ni	0.033	0.0007	2.18	0.033	0.32
Cu	0.0063	0.00007	1.13	0.0062	0.0063
Al	0.044	0.0014	3.21	0.043	0.045
As	0.0011	0	0	0.0011	0.011
B	0.0027	0.0005	18.68	<0.00010	<0.00010
Bi	<0.00010	0.00002	84.85	<0.0025	0.003
Ce	0.0032	0.0013	42.65	0.0041	0.0022
Co	0.011	0	0	0.011	0.011
Mg	0.0003	0	0	0.0003	0.0003
Nb	0.03	0.0007	2.4	0.029	0.03
Pb	0.0081	0.0013	15.71	0.0072	0.009
Sb	0.004	0.0004	8.95	0.0037	0.0042
Sn	0.0034	0	0	0.0034	0.0034
Ta	0.03	0.0071	23.57	0.025	0.035
La	0.0071	0	0	0.0071	0.0071
Ti	0.0035	0	0	0.0035	0.0035
V	0.138	0.0014	1.02	0.137	0.139
W	0.071	0,0078	11.03	0.076	0.065
Zn	0.0024	0	0	0.0024	0.0024
Zr	0.0051	0.0002	0.2	0.0052	0.0049
Se	<0.0005	0.0001	4.42	<0.0005	<0.0005
N	0.0093	0.00007	0.76	0.0092	0.0093
Ca	0.0014	0.0001	10.1	0.0013	0.0015
Te	0.0026	0.0025	97.91	<0.0010	0.0044
Fe	97.74	0	0	97.74	97.74

Sea water

The study examined the corrosion resistance of mild steel in seawater both prior to and following the application of coating. The composition of the seawater utilized in this research is detailed in Table 2. The seawater samples were gathered from the Bay of Bengal, specifically at Kanampadi along the East Coast Road in Chennai, India, in proximity to AMET University, Chennai.

Electrochemical study

In the present work the corrosion resistance of mild steel specimens immersed in various test solutions was measured by Polarization study.

Polarization study

Polarization studies were carried out in a CHI Electrochemical work station model 660A. It was provided with automatic iR compensation facility. A three- electrode cell assembly was used (Figure 1). The working electrode was mild steel. A SCE was the reference electrode. Platinum was the counter electrode. From polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = b_a and cathodic = b_c and LPR (linear polarisation resistance) values were derived.

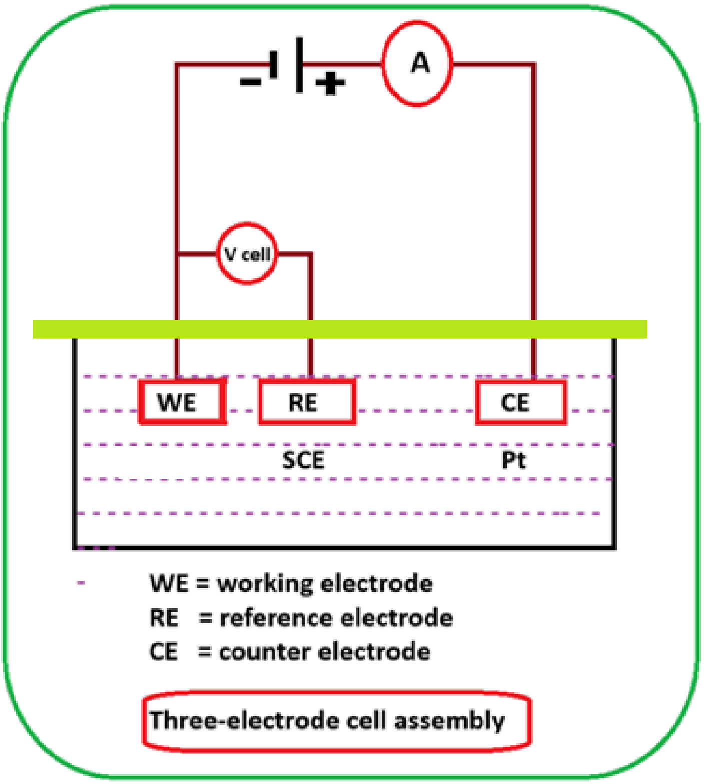

Figure 1. Three- electrode cell assembly

Table 2. Composition of sea water used in this study (all the values, except pH, are in ppm).

S. No.	Physical Examination	Acceptable Limit	Permissible limit	Sample Value
1	Colour	–	–	Unobjectionable
2	Odour	Unobjectionable	Unobjectionable	
3	Turbidity NT Units	1	5	0.2
4	Total Dissolved Solids mg/1	500	2000	29400
5	Electrical Conductivity micro mho/cm	–	–	42000
6	pH	6.5–8.5	6.5–8.5	7.46
7	pH Alkalinity as $CaCO_3$	–	0	0
8	Total Alkalinity as $CaCO_3$	200	600	140
9	Total Hardness as $CaCO_3$	200	600	4000
10	Calcium as Ca	75	200	1200
11	Manganese as Mn	30	100	240
12	Iron as Fe	0.1	1	0
13	Magnesium as Mg	0.1	0.3	NT
14	Free Ammonia as NH_3	0.5	0.5	0.48
15	Nitrite as NO_2	0.5	0.5	0.104
16	Nitrate as NO_3	45	45	25
17	Chloride as Cl	250	1000	15000
18	Fluoride as F	1	1.5	1.8
19	Sulphate as SO_4	200	400	1170
20	Phosphate as PO_4	0.5	0.5	1.47
21	Tds Test 4hrs as O_2	–	–	NT

RESULTS AND DISCUSSION

In the present study, polarization analysis has been employed to evaluate the corrosion resistance of mild steel when immersed in various test solutions. The primary parameters considered in the polarization analysis are corrosion potential (E_{corr}), corrosion current (I_{corr}), linear polarization resistance (LPR), and Tafel slopes, which are comprised of anodic (β_a) and cathodic (β_c) components.

Corrosion potential

Corrosion potential refers to the ability of both metallic and non-metallic surfaces to lose electrons when they come into contact with an electrolyte. This corrosion process inherently creates two electrodes: a cathode and an anode. The electrode potential of a metal serves as a measure of its tendency to dissolve and corrode in a specific electrolyte. Commonly known as Ecorr, the corrosion potential is regarded as one of the most significant parameters assessed in corrosion research and in monitoring corrosion in complex field environments.

Corrosion potential is defined as a mixed potential, often referred to as open-circuit potential or rest potential. At this specific potential, the rate of anodic dissolution of the electrode matches the rate of cathodic reactions, leading to a situation where there is no net current entering or exiting the electrode. The corrosion current is characterized as the dissolution current that takes place at this corrosion potential. [15,16].

Corrosion current

Corrosion current density measures the rate at which metal degrades in a given environment. It reflects the flow of electrons from the metal to the surrounding electrolyte during the corrosion process. [17,18].

Linear polarization resistance

A linear polarization resistance (LPR) test is utilized to assess corrosion rates and offers valuable information regarding the corrosion resistance of materials in aqueous settings. These tests can be performed under static conditions as well as during reciprocating motion.

The linear polarization resistance method entails the use of small voltage variations, typically under 30 mV, applied to the metal, both above and below its corrosion potential. Within this narrow range around the corrosion potential, the current response remains linear.

Measurements of polarization resistance (Rp) are utilized to evaluate the effectiveness of electrodeposited coatings in providing protection, as the obtained Rp values are inversely related to the corrosion current (indicating that a higher polarization resistance corresponds to a lower corrosion current). Polarization resistance is defined as the resistance of the specimen to oxidation when subjected to an external potential. The corrosion rate is directly linked to Rp and can be calculated from it [19].

Tafel slopes

Tafel slopes are a well-established metric for assessing the rates and mechanisms of electrocatalytic reactions. Fundamentally, the Tafel slope quantifies the millivolts (mV) required for a tenfold increase in current, represented in mV/dec. Therefore, a lower Tafel slope indicates a more efficient catalyst, as it reflects the need for a smaller overpotential to achieve a higher current density (see Figure 2). Furthermore, under certain conditions, the Tafel slope can provide kinetic insights, including the identification of the rate-determining step [20-23].

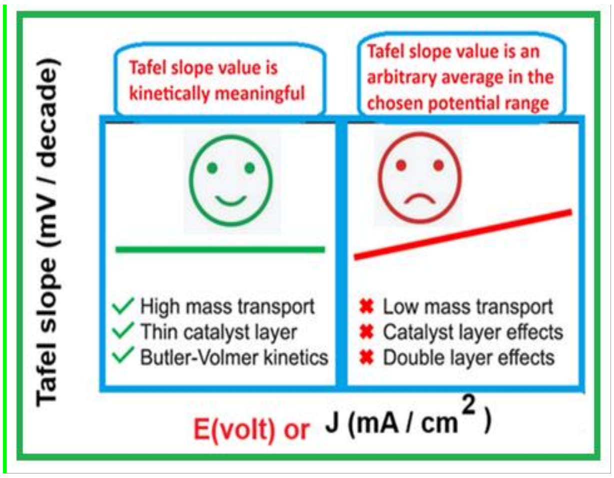

Figure 2. The meaning of Tafel slope

RESULTS AND DISCUSSION

The corrosion resistance of mild steel submerged in seawater and in a simulated concrete pore solution (SCPS) was assessed through polarization studies, both prior to and following the application of Asian paint. The results of this evaluation will be beneficial for advancements in shipping technology.

In polarization study, the basic principles say that , when corrosion resistance increases, the linear polarization resistance (LPR) increases whereas corrosion current (Icorr) decreases (Figure3).[24-28].

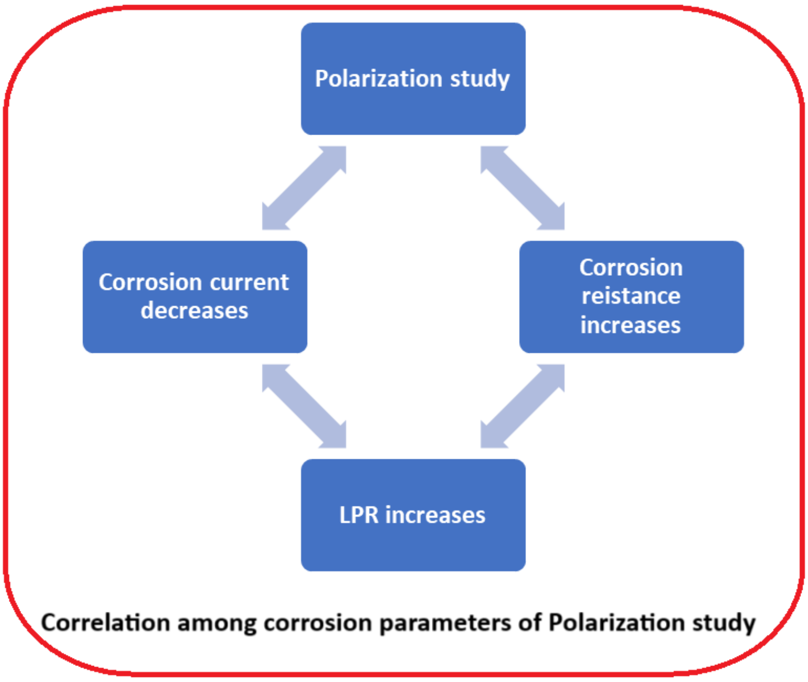

Figure 3. Correlation among corrosion parameters of Polarization study

The polarization curves of mild steel immersed in various systems are shown in Figures 4 and 5.

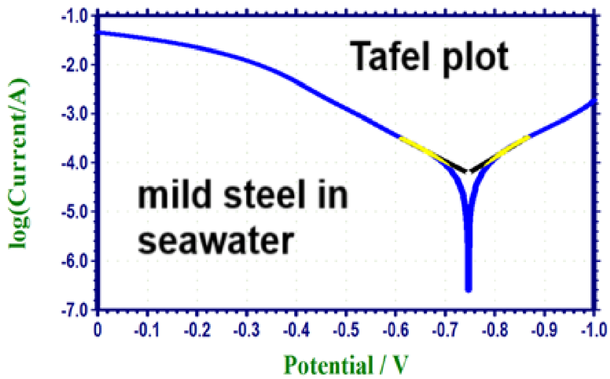

Figure 4. Tafel plot of mild steel in seawater

The various corrosion parameters namely, corrosion potential (Ecorr), Tafel slopes (βc =cathodic, βa = anodic), linear polarization resistance (LPR) and corrosion current (Icorr) are given in Table 3 .The corrosion parameters are compared in Figures 6-8.

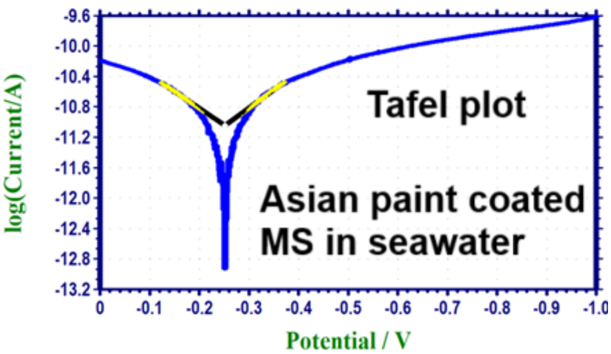

Figure 5. Tafel plot of Asian paint coated mild steel in seawater

Table 3. Corrosion parameters of mild steel immersed in seawater and also in SCPS (prepared in seawater) before and after Asian paint coating

System	E_{corr} mV vs SCE	β_c mV/decade	β_a mV/decade	LPR Ohm.cm^2	I_{corr} A/cm^2
MS in Seawater	-746	161	186	487	7.727×10^{-5}
Asian paint coated MS in Seawater	-251	209	226	3354506240 (IE = 99.99 %)	1.406×10^{-11}
Implication	*Asian paints can be coated on hull plates made of mild steel, to prevent the corrosion of hull plates which are always in contact with seawater.*				

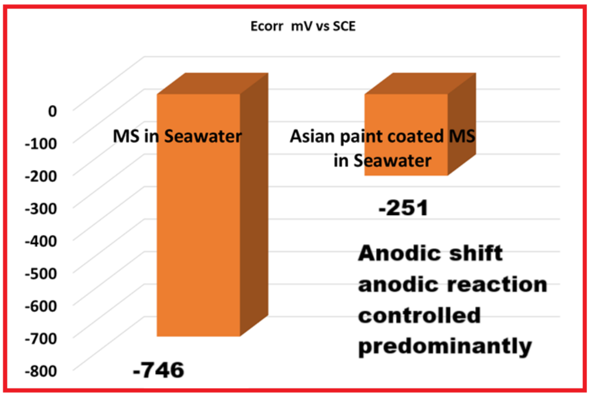

Figure 6. Comparison of corrosion potential values

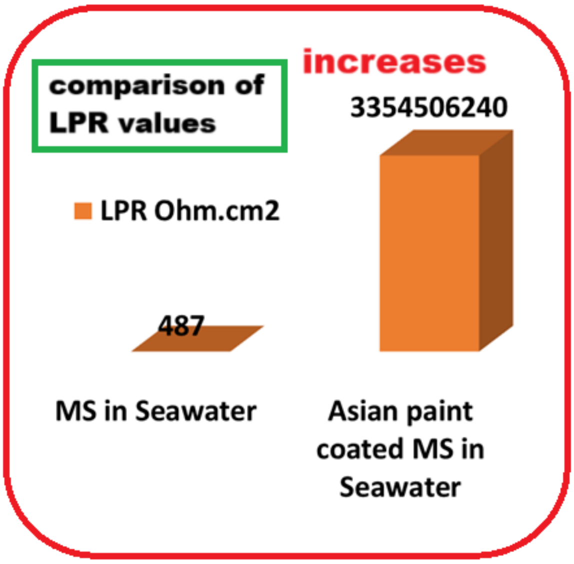

Figure 7. Comparison of LPR values

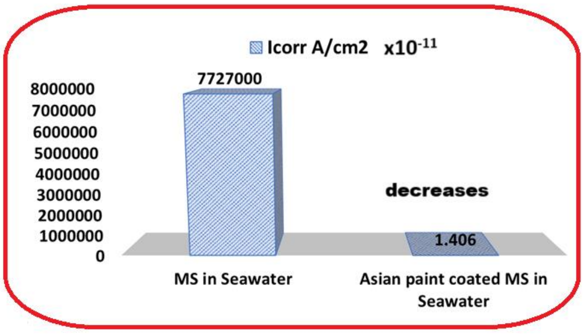

Figure 8. Comparison of corrosion current values

The data are interpreted under the following headings

Corrosion resistance of mild steel in seawater before and after coating

When mild steel is immersed in seawater the corrosion potential is -746 mV vs SCE. The LPR is 487 Ohm.cm^2. the corrosion current is 7.727 x10^{-5} A/cm^2.

When mild steel coated with Asian paint is immersed in seawater the corrosion potential shifts to anodic side (-251mV vs SCE). This indicates the anodic reaction of metal dissolution ($Fe \rightarrow Fe^{2+} + 2e^-$) is controlled predominantly. This results in increase in LPR value and decrease in corrosion current value. It is inferred that after paint coating , the corrosion resistance of mild steel in seawater increases.

Implication

Asian paints can be coated on hull plates made of mild steel, to prevent the corrosion of hull plates which are always in contact with seawater.

Calculation of inhibition efficiencies

Corrosion inhibition efficiency can be calculated from the following formula

$$IE = [(LPR2- LPR1)/LPR2] \times 100 \%$$

Where , LPR1= LPR before coating; LPR2 = LPR after coating

For Asian paint coated MS in Seawater, the inhibition efficiency is 99.99 %

Analysis of SEM images

Analysis of SEM images has been used in corrosion inhibition studies [29- 33].

When the corrosion protection is high the surface of the film is relatively smooth. The film will be uniform.

On the other hand, when the system undergoes corrosion or when the corrosion protection is relatively small then the surface becomes rough. Pits will be formed. The film will not be uniform. Based on these facts and a look at Figure 9 , reveals that in the presence of mint juice alone ever silver undergoes corrosion. On the other hand in the presence of salt (sodium chloride 5000 ppm) the surface becomes smoother. Corrosion resistance increases. This is in agreement with the results of the electrochemical study, namely, AC impedance spectra.

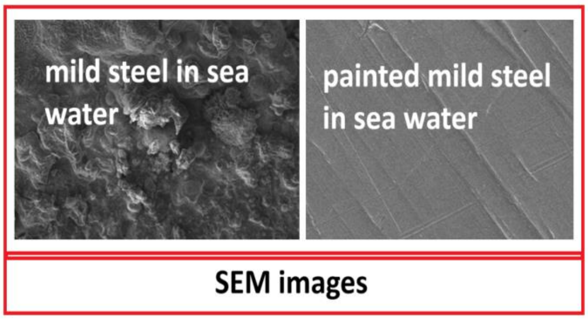

Figure 9. SEM images of various surfaces

SUMMARY AND CONCLUSION

- The corrosion resistance of mild steel immersed in seawater before coating and after coating Asian paint has been evaluated by polarization study.
- The findings will be useful shipping technology .The corrosion resistance has been evaluated by polarization study.
- The various corrosion parameters namely, corrosion potential (E_{corr}), Tafel slopes (β_c =cathodic, β_a = anodic), linear polarization resistance (LPR) and corrosion current (I_{corr}) have been derived.
- In polarization study, the basic principles say that , when corrosion resistance increases, the linear polarization resistance (LPR) increases whereas corrosion current (I_{corr}) decreases.
- The study leads to the following conclusion: Asian paints can be coated on hull plates made of mild steel, to prevent the corrosion of hull plates which are always in contact with seawater.
- The surface morphology has been analysed by SEM. The results are in agreement with the results of the polarisation study.

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IZVOD

OTPORNOST NA KOROZIJU MEKOG ČELIKA POTOPLJENOG U MORSKU VODU PRE PREMAZIVANJA I NAKON NANOŠENJA AZIJSKE BOJE

Otpornost na koroziju mekog čelika potopljenog u morsku vodu procenjena je kroz studije polarizacije, kako pre tako i nakon nanošenja azijske boje. Rezultati ove evaluacije doprineće napretku u tehnologiji brodarstva. Određeni su ključni parametri korozije, uključujući potencijal korozije (Ecorr), Tafelove nagibe (bc za katodni i ba za anodni), linearni polarizacioni otpor (LPR) i struju korozije (Icorr). U proučavanju polarizacije, osnovni principi ukazuju da povećanje otpornosti na koroziju odgovara povećanju linearnog polarizacionog otpora (LPR) i smanjenju struje korozije (Icorr). Rezultati ovog istraživanja dovode do nekoliko zaključaka. Azijske boje mogu se primeniti na ploče trupa izgrađene od mekog čelika kako bi se ublažila korozija, posebno zato što su ove ploče stalno izložene morskoj vodi. Morfologija površine analizirana je SEM-om. Rezultati su u skladu sa rezultatima studije polarizacije.

Ključne reči: *Otpornost na koroziju, meki čelik, morska voda, pre premazivanja, posle premazivanja, azijska boja*

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