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Multifunctional Hydrophobic Antifouling Coating for Marine Applications

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Abstract— **Non-toxic, economical and eco-friendly Antifouling coating for ship hull with multifunctional properties was successfully developed with silicone acrylic resin, Nano silica and other pigments like Titanium dioxide possessing functional properties. The physical and chemical properties of the coated film surface was characterized by SEM, FTIR, Contact angle measurement and Salt spray test. Moreover the antifouling property also was evaluated through field immersion studies in sea water. Hydrophobicity of the coating is substantiated from the water contact angle above 130˚. The anticorrosive property of the coating was predominant even after continuous exposure for several hours in the salt spray chamber. The antifouling behavior evaluated for a duration of 60 days of immersion in sea water confirms sustained antifouling protection without the use of biocides and toxic volatile compounds**.

Keywords—Multifunctional;Nanosilica;biocide free;hydrophobic; antifouling.

I. INTRODUCTION

The marine biofouling and corrosion on the immersed structures in seawater, are the major concern for the shipping industry. Biofouling is the accumulation and growth of micro and macro organisms on the immersed structures and this causes additional hydrodynamic drag which affects the fuel efficiency[1]. Moreover, it leads to corrosion of the immersed structures and causes failure at earlier stages. Ship hull is highly prone to biofouling due to continuous exposure in sea water. Macrofouling affects the economy of the shipping industry due to excess fuel cost, maintenance cost, frequent dry-docking, idle time due to hull cleaning etc. After the ban of toxic organotin compounds there has been continuous search for an effective antifouling paint. The usage of Foul - Release coatings and copper biocides has been limited owing to the toxicity that affects the marine environment. Due to several restrictions and limitations imposed by the regulations such as International Maritime Organisation(IMO), there is a need for a solution that does not affect the marine environment and also resists fouling for a long term[2]. The focus of this work lies in the development of a novel antifouling coating which is nontoxic and biocide free. The concentration lies in modifying the surface topography to resist fouling. The hydrophobic property resists fouling organisms and also prevents the surface from corrosion. The term superhydrophobic, refers to surfaces with a water contact angle (CA) greater than 150˚ and very low contact angle hysteresis which is obtained by controlling the surface roughness with low surface energy. The surface roughness plays a vital role in inducing hydrophobicity. The low surface energy reduces the ability of the organisms to adhere to the target surface. This lets the organisms to be released off easily from the surface when the ship moves with speed. The coating must possess better durability and stability as it has to withstand the heavy force of the hitting waves, hence Nano silica is added to enhance the wear resistant properties of the coating. All the pigments used in the synthesis of the paint are selected based on the expected functionality such as durability, anticorrosive, antifouling, water repellent, etc. Silicone-acrylic resin possesses excellent functionality like durability, water repellent, weather resistant, wear resistant, and heat resistant. It also has higher hardness, improved adhesion and excellent anticorrosion properties. Titanium dioxide is a multifunctional white pigment with enhanced wear resistance and it is widely used for its physicochemical properties in many industrial applications. Nano silica is added to improve the wear resistance and water resistance. Nano silica plays a major role in modifying the surface topography with considerable roughness. The coating preparation is also economical due to low cost materials and easy synthesis process. The application method is also simple. The nontoxic multifunctional coating with hydrophobic surface has become the major research area in recent years. This work has therefore been carried out with improving the properties of the coating by adding Nano particles.

II. MATERIALS AND METHODS

A. *Materials*

Commercially available mild steel plate with the composition of C - 0.12%, Si - 0.18%, Mn - 0.5%, P - 0.04%, S - 0.04%, Cr - 0.02%, Ni - 0.02% and balance Fe, was used as substrate. Commercially available Silicone- air drying resin (10304) and acrylic powder was used as resin. Pigments such as Nano silica, Titanium dioxide, Zinc oxide, Talc and silica were used.

B. *Synthesis of Antifouling Coating*

Initially the surface preparation of the mild steel specimen was done by pickling, to remove grease and rust present on the surface. The paint formulation reflects the performance of the surface which is a key factor for the functionality of the coating. Red oxide primer was applied on to the test specimen initially and allowed to dry for 24 hours. After curing, the mid coat was applied with Micaceous Iron Oxide as the major pigment for its anticorrosive property and was allowed to dry for 24 hours. The top coat was prepared by mixing silicone acrylic resin with Titanium dioxide, hydrophobically modified Nano silica, Zinc oxide, Talc, silica and plasticizer in an attritor for 60 min. The final coat was applied by spray painting and cured at room temperature for a week. The dry film thickness obtained was 300 to 350 µm.

III. CHARACTERIZATION

The surface morphology of the multifunctional coating was characterized by means of scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDAX) using Hitachi model S-3000H. SEM images were obtained at different magnifications from a secondary electron detector with an accelerating voltage of 5.00kV.

For elemental analysis FTIR spectra were recorded on a Fourier transform infrared spectrum analyzer TENSOR 27 (Bruker Optik GmbH, Germany) in the range of 4000 to 400cm^{-1}.

Water contact angle was measured by using goniometer OCA 35 model equipped with charge coupled device camera at room temperature. According to a sessile drop method, deionized water droplets of 4-5µL were allowed to drop onto the coated surface from a micro syringe and contact angles formed at the solid liquid interface was measured at different locations over the coated panel and the average is listed.

Salt spray (fog) testing was used to determine the corrosion resistance of the coated panels. It was done as per the standards of ASTM B117. The samples were kept in an enclosed chamber where the temperature was maintained at 45˚ to 49˚C and salt solution was allowed to spray continuously. The panels were monitored at regular intervals for formation of rust or blisters.

Field exposure test was performed to assess the antifouling property by immersing the panels in sea water. The panels were threaded to a PVC frame and suspended in seawater wells located at OPMEC (Offshore platform and marine electrochemistry center), Tuticorin. These panels were inspected every week to verify the degree of fouling over the surface. The attachment of biofilm and other organisms to the surface of the specimen were analyzed for few months to determine the rate of fouling.

IV. RESULTS AND DISCUSSIONS

A. *SEM Analysis*

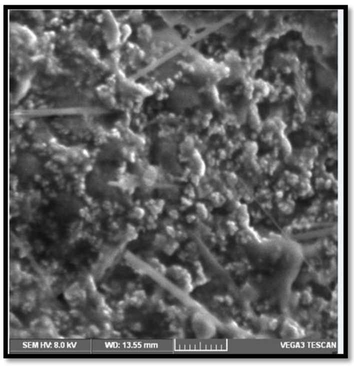

Fig. 1. SEM image of the antifouling coating with nanoridges at a magnification of 5X.

Clearly from the SEM image it is evident that the surface of the substrate is covered homogenously by the coating. The surface is rough with Nano ridges and Nano valleys which makes it hydrophobic. This phenomenon is due to the presence of Nano silica particles with low surface energy. This property makes it tough for the microorganisms to adhere to the surface. The functional coat therefore resists fouling due to the surface property alone, without any biocide or toxic elements.

B. *FTIR Analysis*

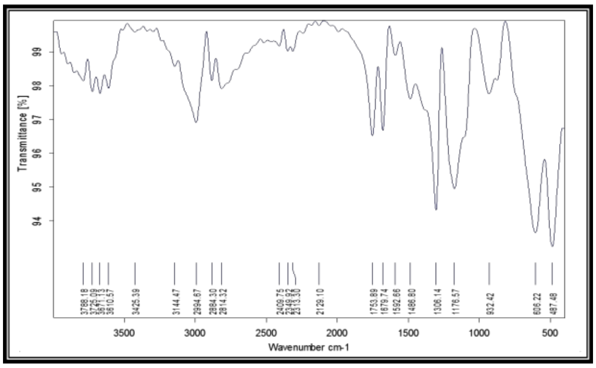

Fig. 2. FTIR spectra of the antifouling coating.

From the IR spectra of the thin film, characteristic absorption peak at 1176 and 1306 cm^{-1} confirms the presence of Si-O-Si and Si-C bond. The sharp peaks at 1753 and 1679 cm^{-1} indicates the presence of C=O symmetric stretching vibration. The hydroxyl groups are found to exist from the absorption peaks at 3425 cm^{-1} [10]. The presence of free O-H groups is shown by the stretching vibration peaks around 3500 to 3700 cm^{-1}. Peaks at 1486 and 1592 cm^{-1} indicates the presence of Si-CH3 [11]. C-H bending is found to be present at 605 cm^{-1} in the finger print region of the spectra.

C. Contact Angle Measurement

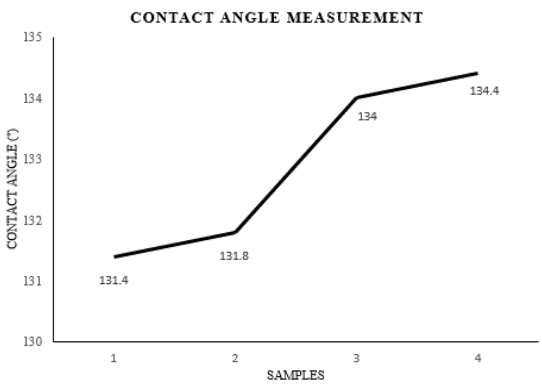

Fig. 3. Contact Angle Measurement of four different coated samples are plotted.

Determining the water contact angle provides essential information on the wettability of the multifunctional coating. The under coat and mid coat were hydrophilic with a contact angle below 100˚.The top coat was hydrophobic with a contact angle of maximum 134˚.The increase in surface roughness is evident from the SEM image Fig 1, which is a key factor in determining the wettability of the coating. This hydrophobic surface inhibits corrosion and fouling growth over the surface and acts as a good barrier devoid of toxic biocides.

D. Salt Spray Test

The coated panels were exposed to a controlled corrosive environment in a fog chamber. The exposure zone was maintained at a temperature of 46˚C. The panels were inspected at regular intervals for the occurrence of rust or blisters. Even after continuous exposure for 3 months there was no rust or blister formation on the coated surface. The presence of anticorrosive pigments have acted well, being impermeable to corrosive medium and made it a completely functional coating even after continuous exposure for several hours. This functionality helps in reducing maintenance cost and also increases the life of the substrate.

E. Field Exposure Test

The panels were exposed in sea water at OPMEC, Tuticorin, in the well openings on the platform facilitated with suspension of rafts. The panels immersed under static condition showed no slime or microfouling until two weeks of immersion. After a month light slime formation occurred but there was no macrofouling on the surface. Even after two months of immersion there was only microfouling found on the surface and not macrofouling.

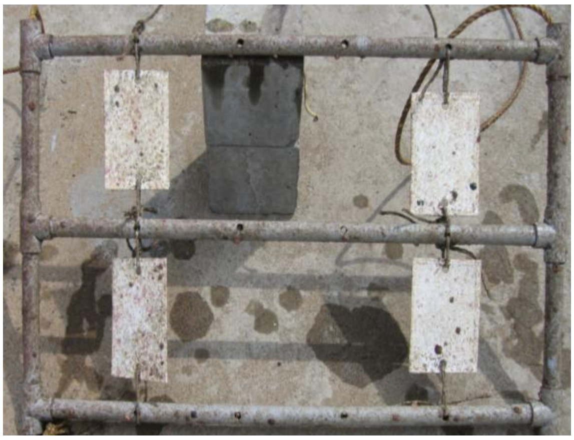

Fig. 4. Image of panels exposed in sea water for 3months.

After 3 months of immersion there were only one or two tiny barnacles found on the surface which easily gets removed off in dynamic condition due to the hydrophobic nature of the surface. The adhesion of the barnacles to the surface will be very low so that when a ship travels at a particular speed these fouling organisms get detached by themselves from the surface. This helps in maintain a lower drag and increase the efficiency of the ship.

V. Conclusion

Antifouling and anticorrosion paints are essential for the protection of ship hulls from fouling and corrosion. In summary, an effective and economical Multifunctional coating was prepared with Nano Silica and Titanium Oxide as the main pigments that has good adhesion to the substrate. It possesses low surface energy and resists fouling organisms without the use of biocides and other toxic elements. The anticorrosion property is superior which is evident from long term exposure in corrosive medium. The field exposure studies prove that the coating provides sustained protection from the accumulation of fouling organisms on to the surface and also due to sea water impermeability the surface is free from corrosion. These functionalities are obtained from using nontoxic substances which is an added advantage as it prevents pollution of marine environment. The results obtained from the experimental studies were satisfactory. The current work can be further developed to achieve superhydrophobicity with enhanced durability. This coating is not only restricted to ship hulls. It can also be used for other offshores structures, solar panels, equipment used underwater and various other applications.

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