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# An Experimental Study on the Deterioration of Paint Coatings in the Bilges of a Sea Vessel

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## ABSTRACT

Scantling and rolling tolerances have gradually improved. The durability of anticorrosive property of coatings is the critical factor in safeguarding the capital investment locked up in the structure of the vessel. Understanding of reduction in corrosion rate due to protective coatings and the breakdown point of the coatings is a vital part of safe vessel operation. In this paper, surface morphology of paint scheme used in bilges water, is measured by using both optical and AFM (Atomic Force Microscope) to prevent corrosion. Both the strategies are utilized to study natural practices of diverse coatings in addition to the impact of their film development and shades. The results demonstrate that undercoat epoxy utilized within bilges water has great resistance towards corrosion in bilges water immersion test. Surface attributes of distinctive layers are noticeably unique in relation to one another in surface morphology. Mild steel coated with epoxy under coat shows better surface characteristics whereas film of primer epoxy coat has many pits as observed by percentage surface imaging of the current bilges paint scheme.

**Key Words:** Corrosion, Bilges, Optical Atomic Microscope, Pitting, Topography.

## 1. INTRODUCTION

Gradual deterioration in the structural properties of metal by interaction with their environment is known as corrosion. It is a natural ongoing phenomenon. Engineers generally consider corrosion when dealing with metallic materials. However, none of the materials, such as plastics, rubber, ceramics, etc., are safe from this devastating process. However due to its high versatility and cost effectiveness, mild steel is used in many industrial applications and infrastructures [1-4]. Resistance to corrosion is very important to ensure the structural integrity of the vessel. Organic paint coatings

are widely used to ensure metal infrastructure integrity against erosion in atmospheric conditions [5].

In order to ensure structural integrity of a vessel, it's important to understand the phenomenon of corrosion resistance. Besides repair and maintenance loss, it is also a hazard for human safety. For corrosion prevention, organic coatings are applied to the material [6]. With the increasing demand of thermal-resistant coatings there is a need for further research work in the field of thermal stability of organic coatings. Mathivanan, et. al. [10] reported the

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failure of conventional organic coatings, such as epoxy, at high temperatures. The anticorrosion properties of thermal-resistant paint coatings are greatly affected due to the breakdown of polymer chains. This results in fractures, delamination, blisters and pore formation on the film of protective coating.

Considerable research work has been done in the field of thermal stability of paint coating. However, in high performance thermal applications organic materials alone can't be utilized due to their restricted properties. Consequently, thermal resistant fillers, such as carbon black [7], silicone [6,8], and silica [9], are frequently added into the epoxy paint system to overcome restraint. Ramesh, et. al. [8] and Mathivanan, et. al. [10] reported significant erosion protection for mild steel coated when coated with conductive epoxy resin composite filler in NaCl immersion test at 25°C.

Corrosion is a destructive natural process. It causes huge losses of money, material and natural resources. In a study of corrosion cost analysis jointly conducted by CC Technologies Inc., USA [11], FHWA (Federal Highway Agencies), USA [12] and National Association of Corrosion Engineers [13], material loss due to erosion was estimated to be around 24.278 trillion rupees, approximately 15.2% of the national gross domestic product. In recent research it is found that every new born baby in the world now has an annual corrosion debt of \$40 [14].

Corrosion in sea vessels is mostly, categorized as general and localized corrosion. Localized corrosion is witnessed on protected surfaces while general corrosion is a problem where there are no protective coatings. Generally, pitting corrosion is defined as localized corrosion [15]. Pitting corrosion has more adverse effect on structure than general corrosion. It initiates cracks leading to further fractures and damage [16-19].

Sea water covers about 70% of the earth's surface. It is considered to be the most corrosive of the natural environments [20]. The properties of seawater fluctuate impressively with geographical locations, climatic conditions and its depth. Generally, the corrosive property of sea water is due of its salt content. However, other factors also contribute to the corrosive property of seawater which include chlorides, sulphates, low pH, dissolved oxygen, high conductivity, and presence of microorganisms, bio fouling and putrefaction [21].

Gardiner and Melchers [22] proposed that three factors explain the corrosion rates which are immersion time, salt deposition and temperature. Their experimental result concluded that atmospheric corrosion has a linear relation with temperature and salt deposition.

In this paper, optical spectroscopy of various organic coatings has been conducted to analyze the performance parameters of these coatings in bilges water such as their resistance towards corrosion, film formation and pigments.

## 2. EXPERIMENTATION AND DATA COLLECTION

The experimental material is MS (Mild Steel), AISI 1020, measuring 381x50.8x3 mm, coated with three different epoxy coatings was exposed to bilges water. Chemical composition of MS is given in Table 1.

TABLE 1. CHEMICAL COMPOSITION OF MILD STEEL (AISI 1020) [23-24]

Elements	Symbols	Contents (%)
Carbon	C	0.17-0.230
Iron	Fe	99.08-99.52
Manganese	Mn	0.30-0.60
Phosphorous	P	0:040
Sulfur	S	0:050

The primer coat contains epoxy resins with butane and xylene as major constituents. A detailed chemical composition is shown in Table 2. However, sealer coat is pigmented with aluminum in xylene epoxy resin as the fundamental substance of film shaping. The chemical composition of under coat is shown in Table 3. The under coat has alkyl glycidyl ether epoxy resin as a distinguishing element in film formation. Its chemical composition shown in Table 4. is applied at the end, composition data is taken from the marine paint guidelines.

TABLE 2. CHEMICAL COMPOSITION OF PRIMER COAT [25]

Ingredients	Weight (%)
Epoxy Resins	10-25
Butan - 1	10-25
Xylene	10-25
Ethylbenzene	1-2:5

TABLE 3. CHEMICAL COMPOSITION OF SEALER COAT [25]

Ingredients	Weight (%)
Epoxy Resins	25-50
Xylene	10-25
Aluminum	2:5-10
Butan - 1	2:5-10
Ethylbenzene	2:5-10
Solvent naphtha	2:5-10
Naphtha, hydrodesulfurized heavy	1-2:5

TABLE 4. CHEMICAL COMPOSITION OF UNDER COAT [26]

Ingredients	Weight (%)
Alkyl glycidyl ether	10-25
Benzyl alcohol	10-25
Butan - 1	10-25
Diethylenetriamine	1-2:5
Stoddard solvent	1-2:5

Coatings were applied to the elongated bar in such a way that bar 1 was coated with primer, bar 2 with primer and first coat, bar 3 with primer, first and second coat. Applied paint scheme is shown in the Table 5. These coatings have been utilized within bilges water to ensure the metal against erosion in practice. One of the bilges paint scheme is shown in Fig. 1.

Measurement of pitting rate for bilges coating scheme coated on mild steel was performed in bilges water. Each long coated bar was cut into 4 samples, measuring 76.2x50.8 mm, thus making 12 samples, referred as coated samples. Formation of samples is shown in Table 6. Figs. 2-3 show the abrasive cutter used for obtaining samples with a corresponding explanation given in Table 7.

Bilges water on boats is a mixture of discharge and spillage from a wide assortment of sources and regulated to the lowest part (least) compartment or bilge tank. The mild steel sheet coated with different bilge paints was exposed in the bilge water, which was used as an electrolyte at the room temperature of 25°C. Composition of bilges water sample is given in Table 8.

TABLE 5. PAINT SCHEME APPLIED TO EACH SAMPLE

Sample No.	Exposed Coating	Coating Scheme
1	Primer	Primer
2	Sealer	Primer + 1st Coat
3	Under Coat	Primer + 1st Coat + 2nd Coat

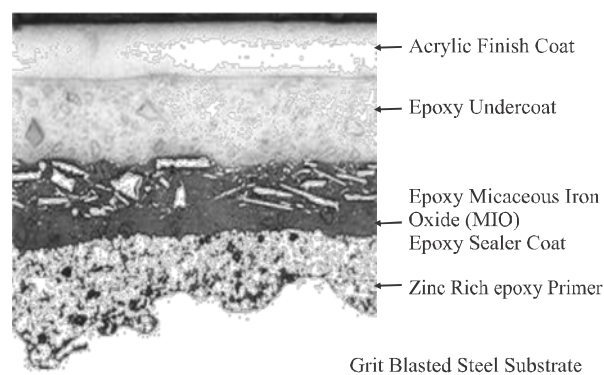


FIG. 1. BILGES PAINT SCHEME [27]

TABLE 6. TOTAL NO. OF SAMPLES

Sample No.	No. of Coatings Applied	Obtained Samples
1	1	4
2	2	4
3	3	4
Total Samples =3	Total Coatings = 3	Total Samples = 12



FIG. 2. ABRASIVE CUTTER



FIG. 3. CUTTING OF PLATE WITH ABRASIVE CUTTER

All the samples were vertically immersed in the bilges water, so that surface will remain perpendicular to the flow of water. In order to achieve the desired purpose, holes were drilled in each sample to enable suspension with the help of nylon string. As bilges is a closed compartment i.e. no direct access to the sunlight however sea water can penetrate into it, in order to develop such environment experiment was performed in closed container at 25°C with an assumption that temperature remains constant. The samples were recovered after two, four, six, and eight weeks i.e. a total of two months.

All samples were dipped in such a way that all the twelve pieces of the same sample i.e. same coating were immersed in batches of four in the bilges water. Total immersion time was two months. One sample each, of the same paint coating, from the three waters, was taken out fortnightly and analyzed under microscope. Two samples of the same coating were left still in water. Similarly one sample each from all the three coatings were removed after first two weeks. A total of three samples were thus removed after two weeks. Then again after a period of two weeks, one more sample of same paint coating and a total of three samples of three different coatings were removed from bilges water and analyzed under microscope. The same procedure was applied for another month. Recovery scheme of samples is given in Table 7.

TABLE 8. BILGES WATER COMPOSITION

No.	Composition	Fresh Water
1.	pH	6.95
2.	Chloride (ppm)	180
3.	Sulfate (ppm)	132
4.	Oil traces	Nil

TABLE 7. SAMPLES RECOVERY SCHEME

Sample No	No. of Samples Immersed in Bilges Water	Recovered Samples after 2 Weeks	Recovered Samples after 4 Weeks	Recovered Samples after 6 Weeks	Recovered Samples after 8 Weeks
1	12	1	1	1	1
2	12	1	1	1	1
3	12	1	1	1	1

These samples were then washed with fresh water and detergent. However black protective film formation was observed on 2nd and 3rd coatings after 30 days. This film had been removed with the help of engine oil in order to observe the underlying formation of film pit. Images were taken under optical and atomic force microscope. Images were then analyzed for the number of pits and the size of pits with respect to time. Characteristics of these tested organic coatings have been analyzed by the help of AFM and optical microscopes as shown in Figs. 4-7.

The corrosion behavior of mild steel was studied using optical microscope. Images of all the 12 samples were taken. Number of pits and their respective diameters were calculated. The equations derived by Newton's forward analysis method, and further verified by correlation factor, for predicting numbers of pits from the collected data are as follows:

In these equations no of pits are represented by variable  $y$  and no of immersion days by variable  $x$ . All equations stood good for the existing data.

Equation (1) for the number of pits for single coated plate (sample 1) is:

$$y = 7 \times 10^{-18} x^3 + 0.0079 x^2 - 0.0429 x + 0.1714 \quad (1)$$

Equation (2) for the number of pits for double coated (sample 2) plate is:

$$y = 4 \times 10^{-6} x^4 - 0.0007 x^3 + 0.0391 x^2 - 0.4389 x - 3 \times 10^{-11} \quad (2)$$



FIG. 4. ATOMIC FORCE MICROSCOPE (AFM)



FIG. 5. PLACEMENT OF SAMPLE UNDER AFM MICROSCOPE

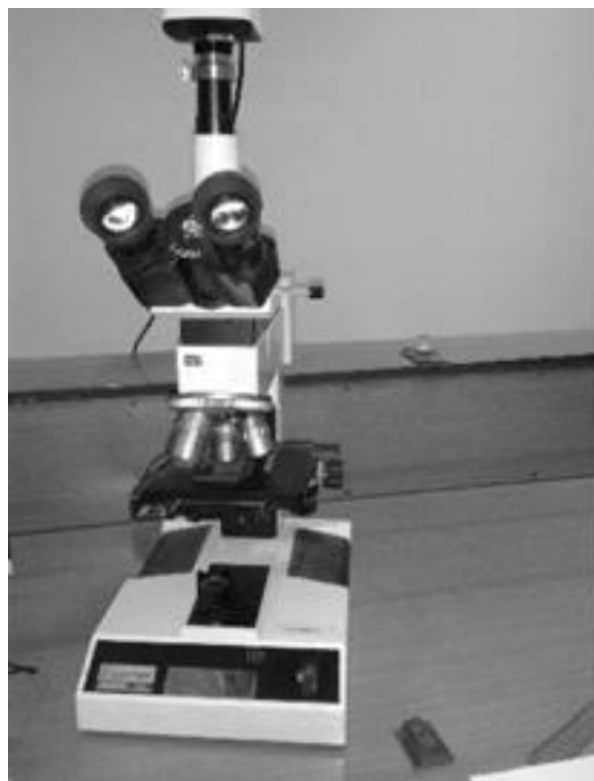


FIG. 6. OPTICAL MICROSCOPE

Equation (3) for the number of pits for triple coated (sample 3) plate is;

$$y = 4 \times 10^{-6} x^4 - 0.0006 x^3 + 0.0302 x^2 - 0.3278 x - 2 \times 10^{-11} \quad (3)$$

### 3. RESULTS AND DISCUSSIONS

Fitting results of the current experimental data are shown in Figs. 8-11 which are in accordance with the results obtained by Liu, Equivalent circuit model [28-29] of the results is shown in Fig. 8, which explains the dynamic processes of under film coating. If the coating resistance has a large value and small capacitance then the coating will act as a capacitor. Water penetration level can be determined by the capacitance value. This serves as an evident that coatings have good barrier ability in bilges at the boundary of metal-coating. As the immersion time increases the water absorption also increases. Deviation in the pitting graph is being observed which shows that coated film behavior changes from fully capacitive to resistive with water diffusion. This implies that after short immersion in bilges water there is decline in coating resistance against corrosion due to water uptake in the coated film. This reveals that



FIG. 7. PLACEMENT OF SAMPLE UNDER OPTICAL MICROSCOPE

water diffusion rate is the major controlling factor of erosion reaction of painted metal in bilges water. The anticorrosive characteristics of marine protective coatings can be represented by coating resistance [28]. Both are directly proportional to one another.

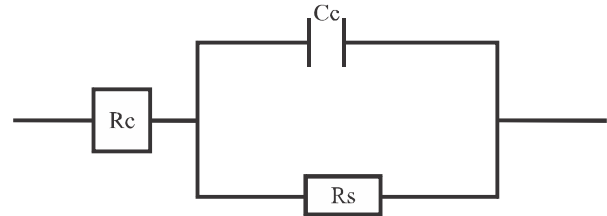


FIG. 8. ESI MODEL OF COATED CARBON STEEL MODIFIED FROM [28]

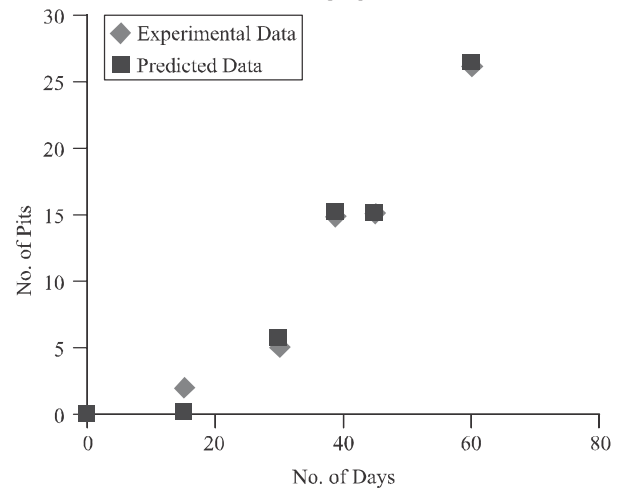


FIG. 9. COMPARISON BETWEEN EXPERIMENTAL DATA AND PREDICTED DATA ACCORDING TO EQUATIONS FOR PRIMER COAT

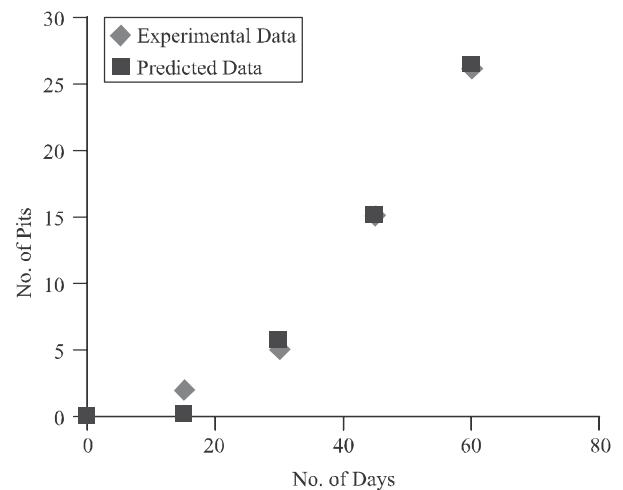


FIG. 10. COMPARISON BETWEEN EXPERIMENTAL DATA AND PREDICTED DATA ACCORDING TO EQUATIONS FOR SEALER COAT

Our main focus of study was to investigate the deterioration of protective coatings in bilges water. Corrosion behavior of mild steel coated with three different coatings which are primer, sealer and under coat immersed in bilges water at 25°C was measured. The tested results are shown in Figs. 9-11.

As shown in the Figs. 12-14, all the coatings exhibit the same behavior during the initial time of immersion. With an increase in immersion time the pitting increases; however the minimum pitting is observed in the last coated sample. Highest pitting along with the largest diameter is observed in the film of primer coated sample. Sealer coated film exhibits the same behavior as the other two, the only variation is the deposition of a black colored protective coating at the surface of the film due to aluminum pigmentation, which slows down the rate of water uptake hence reduces corrosion rate. This is due to high concentrations of chloride and sulfate ions in addition to higher conductivity of bilge water [20], as well as low pH and dissolved oxygen contents which results in localized corrosion. Presence of microorganisms is also a contributing factor in pitting corrosion [21]. The presence of water content in the film of coated material can enact the corrosion process or may cause damage to its protective coating by blister formation or weakling

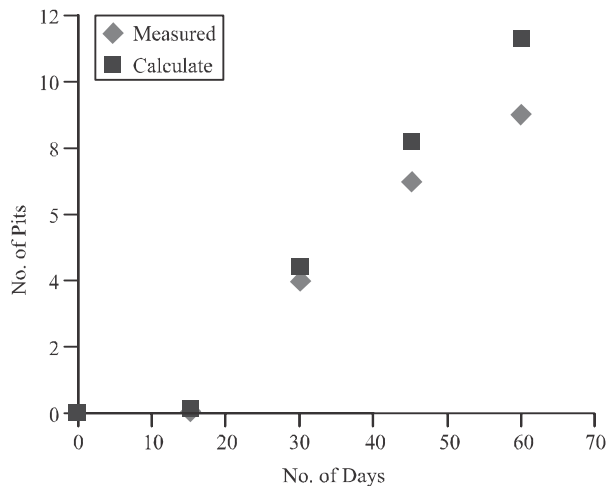


FIG. 11. COMPARISON BETWEEN EXPERIMENTAL DATA AND PREDICTED DATA ACCORDING TO EQUATIONS FOR SEALER COAT

adhesion characteristics [28]. For such a case anti-corrosive property of bilge water becomes very important.

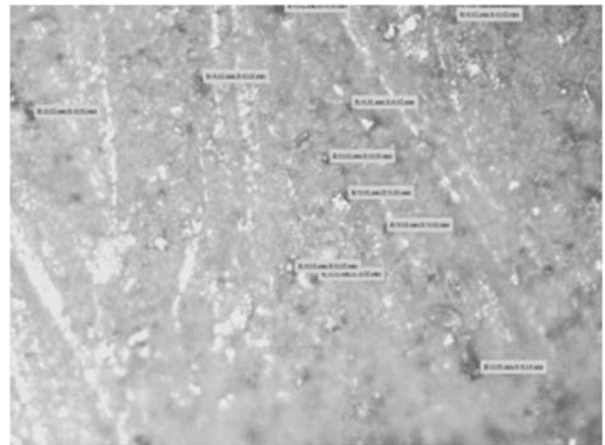


FIG. 12. OPTICAL PHOTO OF PRIMER EPOXY COAT

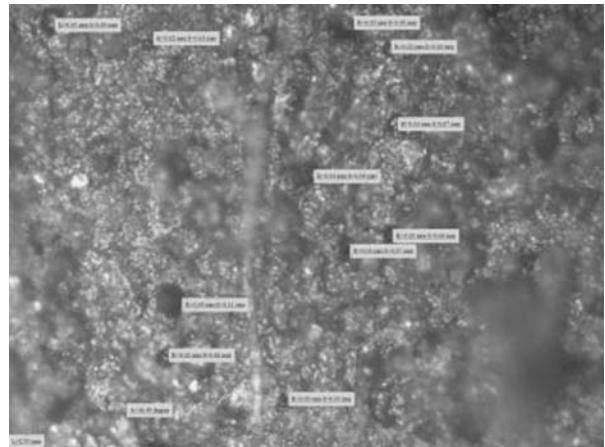


FIG. 13. OPTICAL PHOTO OF SEALER EPOXY COAT

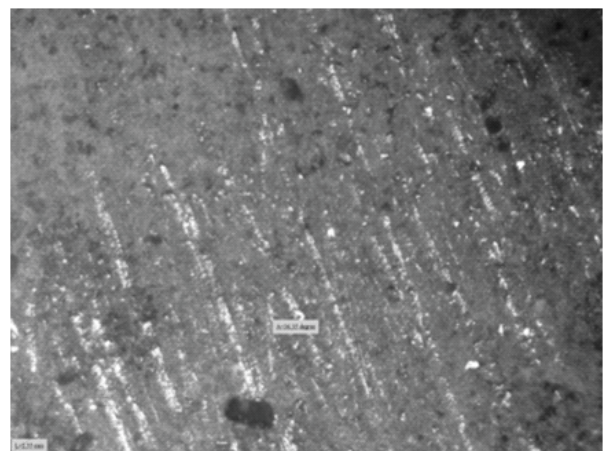


FIG. 14. OPTICAL PHOTO OF EPOXY UNDERCOAT

### 3.1 Microscopic Observation of Topography

Corrosion behavior of different coatings was measured in order to establish a relationship between their performance and terrain. To further examine the surface morphology, micro scale observation was also conducted, which revealed the correlated variations in the sample because of the different types of the coating. Surface morphology of three coatings was observed. In the Figs. 12-14, all the different layers exhibit the same film formation characteristics on their surface i.e. relatively uniform, even and smooth. While the appearance characteristics of these layers are not quite the same as one another. However, with respect to topography for different coatings a quiet variance was observed on their surfaces. The film of Fig. 14 is more compact and uniform than other layers and there are no noticeable cavities on the foundation. As the aluminum pigmented epoxy coating is exposed to a lot of pigments, its surface is relatively coarse and uneven, and can be seen in Fig. 13. Form of the pigments is similar to the ferric oxide i.e. slice like. Pigments are uniformly scattered on the surface of the epoxy film. At the point where aluminum is exposed to the wet environment, the enveloped film exhibits feeble resistance towards corrosion which is visually noticeable. However, even at this point of experiment, the sealer coating with such a pigment still shows a good anti-corrosion protection. There are many noticeable pits on the background of the primer coat Fig. 12 while its surface is more smooth and compact. This is in agreement with the correlation factor obtained earlier. Water can easily penetrate through protective coatings and trigger the substrate metal whenever the protective coating becomes permeable to water.

### 3.2 AFM Imaging

AFM has been adapted to analyze the detailed surface topography of the bilges paint and metal-coating interface. AFM is considered a very important tool in understanding the behavior of protective coatings [30]. AFM was used to inspect the surface morphology of different surface coatings. Figs. 15-17 shows us the AFM captured images of these coatings. The surface permeability and roughness

is shown in the captured images. It can be seen from the images obtained, at the view of the height, the surface morphology of coatings differs from each other. The porous nature of primer coating shows that the degradation of the coating occurs at the exposed reactive points at first. While other epoxy pigmented coatings show comparatively less surface roughness and blister formation. Therefore, they are better anti-corrosive coats which exhibit good non-permeable characteristics towards liquid diffusion, despite the fact that AFM tip can't locate nanoscopic pathways [31] that might exist in these films.

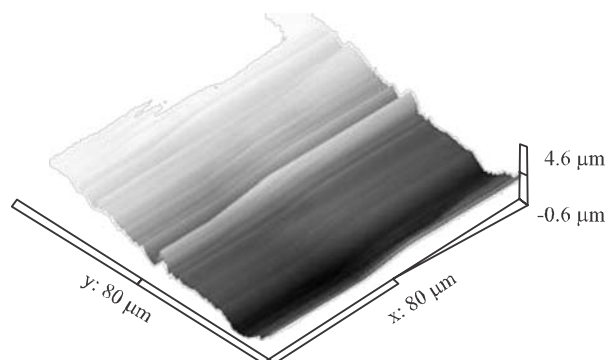


FIG. 15. AFM TOPOGRAPHY OF PRIMER COAT

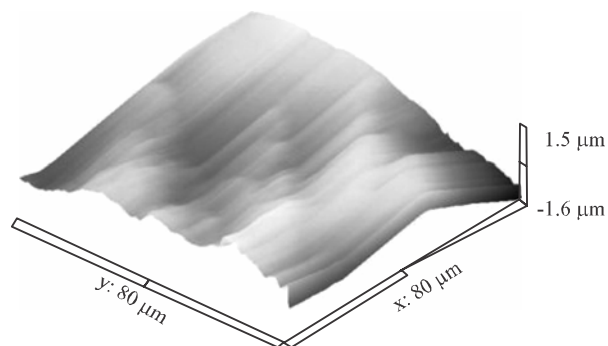


FIG. 16. AFM TOPOGRAPHY OF PRIMER COAT

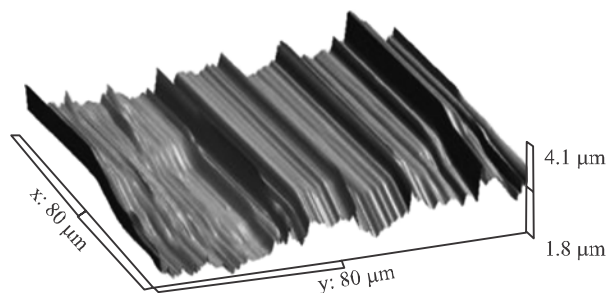


FIG. 17. AFM TOPOGRAPHY OF PRIMER COAT



#### 4. CONCLUSIONS

It is evident from the experimental result that pitting in undercoat is minimal and in primer it is maximal for these three tested coatings. It can be concluded from the experimental result that all the coatings exhibit good protection against corrosion in bilges water immersion test. Meanwhile, the under coat is the best; sealer is medium; and primer coating is weakest. In a nut shell, pitting decreases with the application of existing paint scheme.

Surface topography of tested coatings reveals that surface characteristics of the three coatings are visibly distinguishable from one another. Numerous pits have been observed on the primer coating, while the film quality of under coat is better than other layers.

Corrosion rate expected in future can be estimated for establishing repaint time span.

In this study, AFM was used as secondary evidence in analyzing the effects of surface topography on behavior of these coated samples. AFM results are also in accordance with the previous results obtained from optical microscopy.

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