3-1-2020

Influence of Paint Type on Steel Corrosion for Marine Applications.

Abdou Abdel-Samad
Production Engineering and Mechanical Design Department., Faculty of Engineering., El-Mansoura University., Mansoura 35516., Egypt.

Yaser Soud
Production Engineering and Mechanical Design Department., Faculty of Engineering., El-Mansoura University., Mansoura 35516., Egypt.

M. Zaki
Akhbar El-Yom Academy., Production Engineering and Printing Technology Department., 6th of October., Egypt., mostafazaki8@hotmail.com

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Influence of Paint Type on Steel Corrosion for Marine Applications

تأثير نوع الطلاء على صدأ الصلب للتطبيقات البحرية

Abdou Abdel-Samad[a], Yaser Soud[b], M. Zaki[c]

a. Mansoura University, Faculty of Engineering, Department of Production Engineering and Mechanical Design, Mansoura 35516, Egypt
b. Research Student, Faculty of Engineering, Department of Production Engineering and Mechanical Design, Mansoura 35516, Egypt
c.   Akhbar El-Yom Academy, Department of Production Engineering and Printing Technology, 6th of October, Egypt

ملخص

حيث أن هياكل السفن مصنعة من الصلب فإنها تكون معرضة للصدأ نتيجة تعرضها للأجواء البحرية مما أدى إلى وجود اهتمام متزايد من الباحثين وصناع السفن لإيجاد سبل لمنع أو تقليل الصدأ. أن البحث الحالي يهدف إلى اختبار ثلاث أنواع حديثة من الطلاء للصلب وذلك تبعا للمواصفات القياسية للاختبارات من حيث التصاق الطلاء بسطح الصلب وقياس معدل الصدأ عند التعرض للماء المالح سواء بالغمر أو الرش. ولقد أوضحت النتائج المعملية أن وجود الطلاء عموما يؤدي إلى خفض معدل الصدأ مقارنة بسطوح الصلب غير المطلية. النتائج أوضحت أيضا أن أحد أنواع الطلاء المستخدمة تعطى أقل معدل صدأ ويمثل قيمة 0.8 مم/للعام مقارنة بقيمة 2.1 مم/للعام للصلب غير المطلي. ولقد تم فحص سطوح العينات ميكروسكوبيا عند فترات زمنية مختلفة للصدأ أثناء التجارب المعملية. وقد أوضح الفحص المجهرى زيادة التآكل بالنظر مع زيادة معدل الصدأ.

Abstract

The majority of naval ships are constructed of mild steel. Corrosion is a major concern in a maritime environment. This particular type of material degradation has recently received more attention by the marine industry. The present work aims to investigate the effect of recent coatings used in marine ship surfaces for preventing corrosion. Experiments were performed according to standard tests to evaluate and measure the coating adhesion to steel and to measure the corrosion wear rate if any for three types of coatings. An accelerated corrosion test was conducted to duplicate in the laboratory the field corrosion performance of a product. The results indicate that all under investigated types of paint have resulted in a reduction in the corrosion rate compared with the uncoated steel. A minimum corrosion rate of 0.8 mm/year was obtained for the coat "Hempadur 52140" compared to 2.1 mm/year for the uncoated steel. A microscopic examination of the corroded steel surfaces was conducted which prevailed pitting behavior with different degree. The minimum corroded surface exhibited few pitting attack in comparison to other specimens. Although the pitting attack of the surface layer (paint), one can drive a conclusion that sample surface without coating is aggressively attacked by pits.

1- INTRODUCTION

Marine atmosphere with its high level of salinity and humidity is very corrosive, and the effects of corrosion are allegedly responsible for 30% of failures on ships and other marine equipment. It has been estimated that the total cost of marine corrosion worldwide is between $50-80 billion every year [1]. The coating industry is almost 40% of the total direct costs, and the largest portion of this cost (88%) is attributed to organic coatings [2].

The corrosion rate in an open natural system is controlled by the diffusion rate of oxygen from the bulk solution to the steel surface and the composition of the carbon steel that is being attacked has no effect on rates [3]. Initially the corrosion rates are higher and are at least 2.5 times the subsequent steady state rate that begins earlier than one month following exposure according to some studies [4].

Accidents involving ships that carry environmentally dangerous cargo, such as oil tankers, can have severe consequences for the environment. In many accidents, the ship structure had been weakened by corrosion [5-6-7]. Maritime safety and the prevention of accidents require a sound ship structure. As such, the prevention of corrosion is a key priority for safe shipping. Today's coating systems work well and have a sufficient lifetime when they are applied according to the coating producer's specifications [8-9-10].

There are organic and metallic protective coatings, other common methods for preventing and controlling corrosion include; corrosion-resistant alloys, plastics and polymers; corrosion inhibitors; and cathodic protection. Coatings used for maintenance purposes on vessels will account for 65%, and 20% for offshore drilling and platforms [11]. The effects of corrosion are expensive costs to vessel, structural and equipment operations,

compounded by the financial penalties on breakdowns, outages, and repairs. These problems have challenged the industry for years, but it needs to remain proactive in preventing in controlling marine corrosion. The many types of marine corrosion, their possible interaction, and the need to review the entire system when considering changes highlight the importance of tackling the problem through design, selection of materials, construction, use and maintenance. Sharing knowledge of research findings and the expertise of those developing modern engineering systems are vital to controlling the damaging effects of the marine environment [12-13].

Paints used in marine environments are usually constituted by a polymeric resin (typically epoxy, alkyd or polyurethane), organic solvents and wide variety of organic and inorganic additives (as pigments, biocide, fillers, etc.) [14-15-16-17]. Active anticorrosive pigments like metallic chromates passivates metal surface by covering it with an oxide film. However, these agents are preferably kept out of the environment due to the toxicity of heavy metals.

On the other hand, metals like zinc, which are usually employed as anticorrosive additive in epoxy paints, prevent discharge of current from substratum (naval steel) to electrolyte by electrochemical attachment of a less passive anode, i.e. it covers the paint into a sacrificial coating. In recent years a new generation of paints that employ water as solvent has emerged. However, their anticorrosive performance is poor with respect to that of the organic-based paints they intend to replace. This is a critical problem for the shipbuilding industry, which requires high specifications due to the aggressive marine environment. In spite of this, promising results have been

reported for different ecological water-based paints that incorporate zinc phosphates as non-contaminant anticorrosive additive. Thus, the entry of water through the coating produces a zinc film that passivates the metallic substratum. However, once the anticorrosive additive has been exhausted, there is a complete loss of the protective properties of the paint because of its high porosity making difficult the practical use of this type of paints in aggressive environments. Regarding to the barrier protection, this consists in protect the metal surface blocking the passage of oxygen and water. Usually, the protection by barrier effect provided by a coating is evaluated using immersion assays, in which both the volume of

water and oxygen that enters into the system and the rate of penetration are measured [18-19]. The structure of the polymers is essential to decide the extent of permeation through it. Indeed, the relationship between structure of polymers and their permeability has been successfully exploited in applications like membranes and packaging. However, in coating applications the presence of pigments and additives can alter the porosity and adherence of the films modifying their protective action. For instance, pigments reduce the porosity of the coatings; the smaller the pigment particles, the lower the porosity.

2- EXPERIMENTAL PROCEDURE

2.1- Materials

Three different coatings were painted (Table 1) on 5mm thickness steel plates. The chemical composition of the steel substrate is

shown in Table 2. Prior to coating the substrates were prepared according to ISO 8501-4:2006 [20-21].

Table 1. Tested Paint Types

Coat No.	Name	Description
1	HEMPADUR MASTIC 45880	Two-component polyamide adduct cured, high solids, high build epoxy paint.
2	HEMPALIN ENAML 52140	Glossy alkyd
3	HEMPATHANE TOPCOAT 55210	Two-component glossy acrylic polyurethane

Table 2. Chemical Composition of the Steel Substrate (wt %)

Element	C	Si	S	P	Mn	Ni	Cr	Al	Cu
wt %	0.06	0.01	0.010	0.015	0.49	0.016	0.009	0.049	0.02

2.2- Experimental Tests

2.2.1- Adhesion test

Adhesion Pull-Off and Tape(X-Cut test +Cross Cut test) tests were measured according to ASTM D 4541 and ASTM D 3359 standard tests respectively (ISO 4624 and ISO 2409 tests). The results of the adhesion test are illustrated in Table 3.

2.2.2- Salt spray test

To evaluate surface layer for the three different painted samples, unpainted sample as reference Gravimetric test and Visual and optical inspection were done. Atmospheric marine test (ASTM B287-62) is used (Fig. 1), where chloride atmosphere attack the samples. Chloride atmosphere mainly comes from the reaction between acetic acid and Sodium chloride with different concentration (as standard), at 40 °C and aeration. Duration of the test is about 54 hours; each 2 hrs a weight change (ΔW) was estimated. Finally, the change in the weight was plotted versus time. Visual inspection and optical microscopy was done to investigate the surface layer attack and the formed corrosion product. As well as, pitting initiation and propagation was inspected.
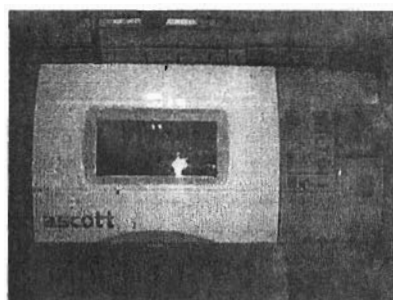
2.2.3- DC electrochemical polarization tests

All tests were carried out using Autolab Potentiostat/Galvanostat (PGSTAT 30) specified for electrochemical measurements Fig. 2. A conventional three-electrode cell, (a single compartment- glass cell of 250 ml capacity was used with stainless steel as counter electrode). The working electrodes were the coated specimens with an exposed area of 0.785 cm^2. All potentials were measured with respect to saturated calomel electrode (SCE). The electrolyte consisted of 3.5% NaCl solution made up from distilled water and reagent grade NaCl (Fisher scientific). Experiments were carried out at room temperature. Linear polarization technique was carried out by subjecting the working electrode to a potential range of 20 mV below and above corrosion potential (E_{corr}) at a scan rate of 0.0125 mV/sec. The current within this range varied linearly with applied potential. The polarization resistance, R_p (Ω), was determined from the slope of the plots of the applied potential against the measured current. The corrosion current I_{corr} (A) can be calculated using the Stern-Geary relationship: ($I_{corr}= B/R_p$) , where $B = \beta a \beta c /2.3 (\beta a+\beta c)$ where, βa and βc are the anodic and cathodic Tafel constants in (v/decade).
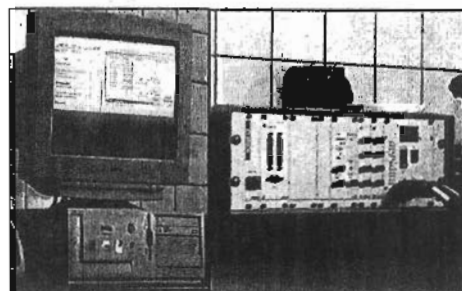

Fig. 1 Salt Spray Test Cabinet

Fig. 2 Autolab Potentiostat/ Galvanostat

By this technique, controlled potential scan (0.5mv/s) was typically applied to the sample starting at E_{corr} and extending in both anodic and cathodic directions for a few hundred millivolts (about ± 250mv from E_{corr}). When the resultant potential-current data were plotted as shown in Fig. 3, it characteristically exhibited linear regions on both anodic and cathodic branches. The slope of these linear regions in v/decade of current is known as the Tafel constants β_a and β_c respectively. The corrosion rate C.R. in mpy (millimeter per year) can then be calculated from Faradays law by:

$$C.R = 0.13 \; i_{corr} \; EW/d$$

Where, EW and d are the equivalent weight (g) and density (g/cm3) of steel and i_{corr} is the corrosion current density (mA/cm^2) that obtained from $i_{corr} = I_{corr}$ / exposed area.
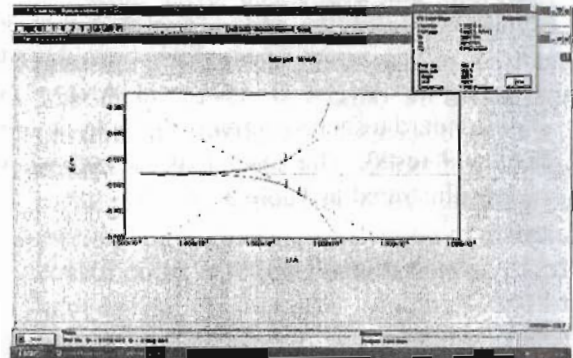

Fig. 3 Results of Potential-Current Data

3- RESULTS AND DISCUSSION

The results of the adhesion tests are shown in Table 3. From table 3.

Table 3. Adhesion Test Results

Coat No.	1	2	3
Pull Off Adhesion Test			
Average DFT (µ)	150	19	55
Pull Off Value (MPa)	9.0	7.5	7.0
Result	40% adhesion failure, 60% glue failure	45% adhesion failure, 55% glue failure	100% glue failure
Adhesion by Tape Test			
1-X-Cut test	Level 5A No peeling or removal	Level 5A No peeling or removal	Level 5A No peeling or removal
2-Cross Cut test	Level 5B Edges are smooth	Level 5B Edges are smooth	Level 5B Edges are smooth

DC electrochemical polarization test results are shown in Table 4 and the corrosion rate of the samples are shown in Fig. 4.

In general coating improves the corrosion resistance of uncoated steel. It is clear that coat number 2 and 3 show much lower corrosion resistance than coat number 1.

Table 4. DC Electrochemical Polarization Test Results

Coat No.	1	2	3	uncoated
I corrosion (A)	1.168E-6	5.861E-7	4.98E-7	3.687E-6
I corrosion (A/cm^2)	1.488E-6	7.466E-7	6.345E-7	4.697E-6
Bc (V/dec)	0.163	0.068	0.216	0.05
Ba (V/dec)	0.141	0.113	0.18	0.103
Rp (Ohm)	8.515E+3	5.699E+3	3.397E+4	6.006E+2
E corr, abs (V)	-0.554	-0.516	-0.496	-0.699
E corr, calc (V)	-0.556	-0.519	-.0502	-0.696
E-begin (V)	-0.605	-0.548	-.0558	-0.722
E-end (V)	-0.501	-0.475	-0.421	-0.675
Corrosion rate (mm/year)	1.115E-2	5.595E-3	4.754E-3	3.52E-2
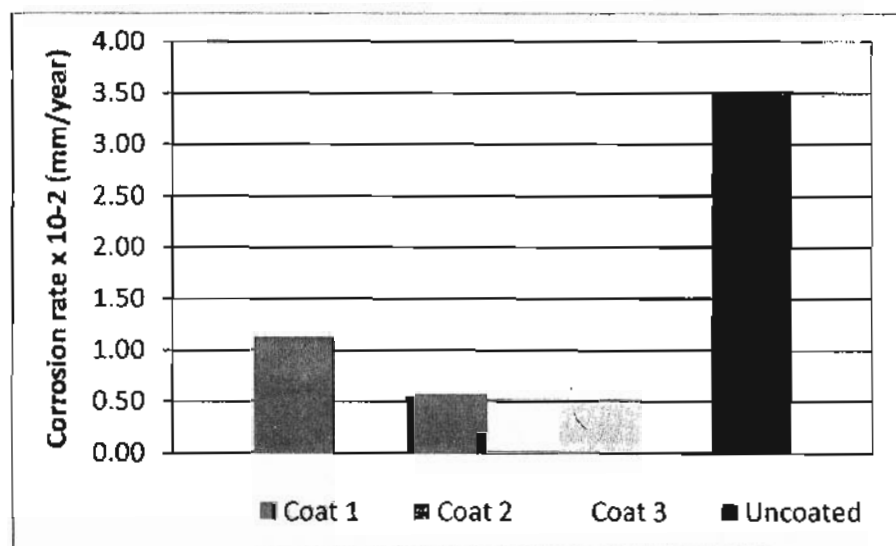
Fig. 4 Corrosion Rate of Coated and Uncoated Samples

The weight change (mg/cm^2) of the three samples coated with different types of paint was measured in chloride atmosphere at 40 °C for about 54 hrs. These results are plotted in Fig 5. From this figure, it is clear that sample 2 could withstand 54 hours without aggressive attack while the other two samples 1 and 3 show significant changes in the weight gain. Higher weight gain was obtained for samples 3 and 1 than sample 2. In comparison to the reference sample (without surface coating), lower weight gain was recorded. The values of

the corrosion rates in mm/yr after 54 hours from the experimental results is calculated using the relation (Corrosion rate $= K\ W/\rho At$) as shown in table 5.

Table 5 Salt Spray Test Results

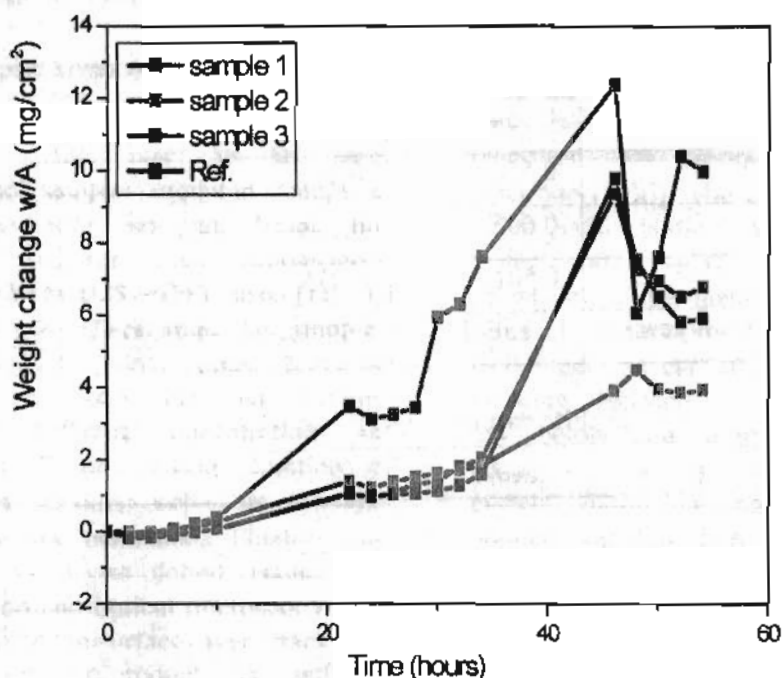| Sample no.	1	2	3	Blank
Corrosion rate (mm/yr)	1.4	0.8	1.2	2.1

Figure 5 Salt Spray Corrosion Rates

To support our result, visual inspection as well as optical micrographs was carried out during exposure time. In general, all the samples showed pitting behaviour with different degree according to the type of surface layer. The micrograph of sample 2 represents few pitting attack in comparison to sample 1 and 3 and also the reference sample. Although the pitting attack of the surface layer (paint), one can drive a final conclusion that sample surface without coating is aggressively attacked by pits. Larger and wider pits are formed on that surface. In all cases dark brown corrosion product was formed around the pits. Some selected micrographs are shown in Fig 6 for sample 1, 2 and 3 and also for comparison, reference sample (without coating) after 54 hrs.
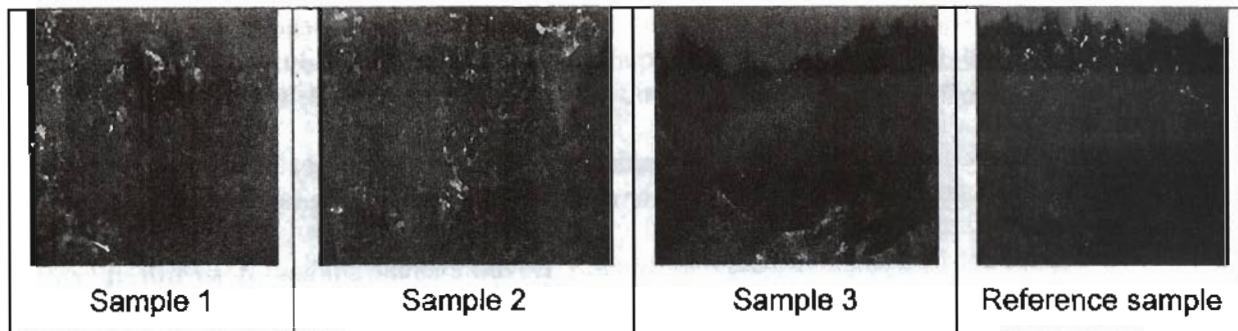
Figure 6 Optical Micrographs for Salt Sprayed Surfaces after 54 hours

4- CONCLUSION

From the present experimental study and the obtained results, it can be concluded that:

1. Polymeric coating for steel structure for marine application is essential to reduce salt water corrosion. A corrosion rate reduction of about 77% was realized for coated surfaces compared to uncoated steel surface.
2. The pull-off adhesion test for the coat Hempalin Enaml resulted in lower glue failure than other investigated coating layers.
3. Minimum corrosion rate of 0.8 mm/year was exhibited by the coat " Hempalin Enaml 52140" over a salt spray test duration of 54 hours.
4. Optical micrographs have shown that oxidation and pitting of dominate the corroded surfaces.

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