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Evaluation Of Anticorrosive Coatings For Tanker Walls To Transport Oil In A High Salinity Environment, In The Presence Of Tension, Temperature And Co_2

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ABSTRACT

The offshore heavy oil project uses Floating Production, Storage and Offloading (FPSO) structural tanks to act as oil separators (washing tanks) a vital requirement. These tanks operate with a continuous layer of produced water at high operational temperatures and high residence time, creating a critical corrosive environment. This condition is far beyond typical conditions for tankers and makes the development of a special test necessary to qualify paint systems for that condition. Traditionally the qualification of paint systems in Brazil offshore units is based on NACE TM-0104 and ISO 20340 standards. But these standards have a test protocol based on physical/mechanical tests and corrosion tests. However, for this specific case, it did not suffice. Thus, a specific test was developed for washing tanks, which can evaluate simultaneously both corrosion and mechanical properties. This paper presents the development of a new test to simulate the behavior of paint systems submitted to cyclic tension in coatings in very corrosive environments (high salinity, CO_2, and high temperature).

Keywords: tankers, coatings, fatigue, heavy oil, salinity.

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INTRODUCTION

FPSO structural cargo tanks are not rigid structures. Shell plates are somewhat flexible and subjected to cyclical loads due to wave and cargo loading and offloading. This situation associated to very corrosive environment (high temperature, presence of carbon dioxide and high salinity of the produced water) is a challenge when a paint system to protect the carbon steel against corrosion must be chosen. Corrosion tests only were not considered enough, since the coating is subjected to high stress due the tank shell movements (some projects consider that the material must withstand tensile stress up to 80% of yield point). Consequently, the anticorrosion paint system must have sufficient flexibility and fatigue resistance in addition to good corrosion resistance.

Usually the test protocols like NACE TM -104, NACE TM-0404 and ISO 20340 have distinct tests for evaluating corrosion and mechanical/physical properties but not one evaluate at the same time both corrosion and mechanical properties. It was found that, for washing tanks, It could be more representative to test simulating both an aggressive environment and tensile tests the paint could be subjected during operation. With this goal, a test procedure based on cyclic stress condition plus a corrosive environment was developed.

TEST PROTOCOL CONCEPT

The developed test protocol concept was based on three-point flexural test applying a cycling load onto a painted carbon steel plate. The cyclic flexural load simulates the tankers wall deflections and subjects the paint system to the tension levels withstand by the tank walls.

Tension level applied must be representative of the worst conditions, so we selected the tension level which can stress the base material at 80% of material´s yield strength, and the number of cycles was select to 1,000,000 (considered a lifetime for a typical FPSO).

The corrosive environment means high salinity and high temperature (60ºC). Initially H_2S saturated solution was considered, but the costs and difficulties of managing H_2S could made the test protocol not practical and, more important, it could greatly increase the cost of the test protocol (the aim was, since the beginning, a low cost test protocol available to the paint manufacturers). So we changed to CO_2 saturated solution an aggressive reagent also found in oil fields.

This work presents new test to simulate the tensile stress in coating and to evaluate the fatigue resistance associated to very corrosive environments as: high salinity, CO_2, and high temperature in coatings applied on the walls of the tankers. The results can supply more appropriate information.

The test, nominated "Fatigue Resistance Test in Coatings", was carried out in synthetic seawater saturated with carbon dioxide at 60°C. Four different coatings were studied: (1) epoxy with glass flakes; (2) thermal spray aluminum (TSA), sealed with epoxy mist coat; (3) thermal spray aluminum (TSA), sealed with epoxy mist coat plus an additional layer of epoxy novolac with glass flakes and (4) thermal spray zinc-aluminum (TSAZ), sealed with epoxy mist coat plus an additional layer of epoxy with glass flakes, all of them applied on carbon steel panels.

METHODOLOGY USED TO CALCULATE THE TENSION

The corrected applied tensile level was a great concern. The first step was to made tensile tests to discover the yield point of uncovered carbon steel. Another challenge was the methodology to apply the tension. The methodology used to apply the tension in the sample was based on a three-point device in agreement with ASTM G 39, shown in Figure 1. There is a relationship between the deflection and the applied tension that is given by Equation (1). In this arrangement, the maximum tension occurs exactly at the middle point of the distance between the supporting points and it decreases linearly to nil at the edge.

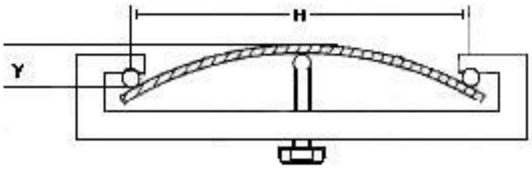

FIGURE 1 - Schematic representation of the three-point device used to define the relationship between deflection and tension.

$$\sigma = \frac{6\,E\,t\,y}{H^2} \qquad (1)$$

Where:

σ = maximum tensile stress;

E = modulus of elasticity of the test material;

t = thickness of the sample;

y = maximum deflection;

H = distance between supporting points of the sample.

Equation (1) is valid for small deflections, typically for y/H smaller than 0.1. According to this equation, once the yield point of the material as well as parameter E; t and H are known, it is possible to apply different deflection levels corresponding to different percentages of yield point of the material.

The sample of carbon steel used as a substrate was tested to determine the yield point of the material. Then the deflection corresponding to 80 % of yield point was calculated, using Equation (1).

To assess the validity of these assumptions, a strain gauge was coupled on the metallic plate made, with the same material and with the same dimensions as the sample to be tested, and the sample subject a deflection corresponding to 80% of the yield point of the material. The monitored areas of the sample are illustrated in

Figure 2 and they correspond to 80 %, 68 %, 56 % and 35% of the yield point of the material. The relationship between the deflection and the tension is shown in the Figure 3 and confirms the linear relationship assumption.

EQUIPMENT

The equipment was developed by Laboratory of Corrosion and Protection of Institute for Technological Research of Sao Paulo State. Figure 2 shows the equipment. Some components of the equipment are presented below and in Figure 3:

- Tank 50 cm width, 45 cm length and 30 cm depth;
- The up-and-down mechanism to apply cyclical deflection;
- The electric resistance to warm the solution. The resistance was made of resistant material against corrosive environment;
- Rocker arm with mandrel of stainless steel with adjustable cable to apply cyclical tension. The mandrel width is similar to the sample width, for good tension uniformity;
- The frequency control system;
- The system for gas injection, with a C-ring of stainless steel. The C-ring contains some holes to improve the gas distribution inside the tank;
- Stainless steel support for holding the sample;
- The cycle counter;
- The thermocouple;
- The temperature recorder;
- The graduated meter to adjust the deflection in the sample.

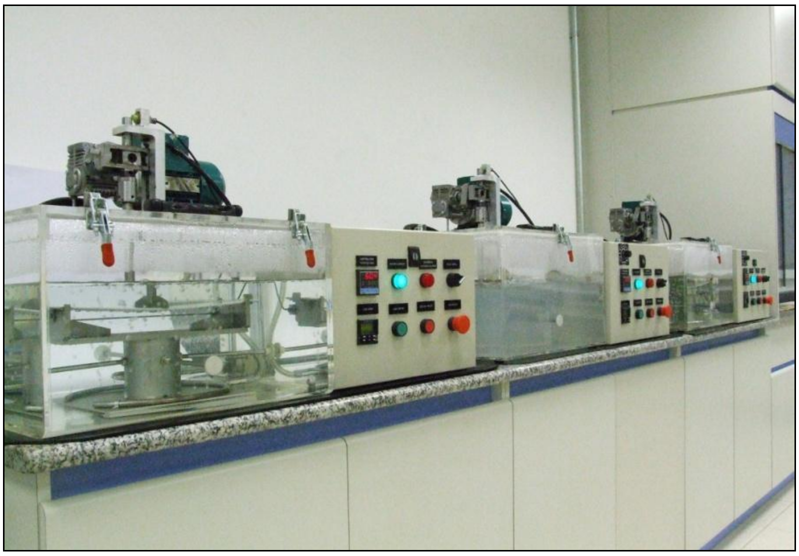

FIGURE 2 - Equipment developed for fatigue resistance test in coatings.

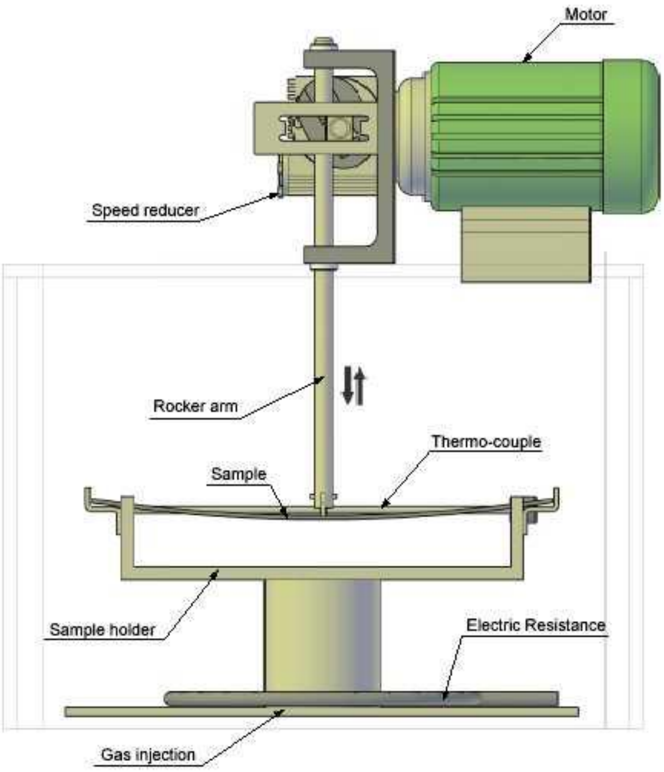

FIGURE 3 – Parts of the equipment.

SAMPLES

Carbon steel panels SAE 1020, 30 cm length; 10 cm width and 2 mm thick were blasted with bauxite up to the visual standard Sa 2 ½ of ISO 8501-1. Four different coatings were studied; all of them applied on carbon steel panels.

- Coating A – Thermal Spray Aluminum – TSA, 200 µm thickness sealed with epoxy mist coat;
- Coating B – Epoxy novolac with glass flakes, 900 µm DFT;
- Coating C – Thermal Spray Aluminum – TSA, 200 µm thickness plus epoxy novolac with glass flakes, 900 µm DFT;
- Coating D – Thermal Spray Aluminum-Zinc – TSAZ, 200 µm thickness plus epoxy novolac with glass flakes, 900 µm DFT.

CHARACTERIZATION TESTS

Initially, the samples were submitted to Holiday Detector test and to Pull-Off test. Holiday Detector Test was done in agreement with ASTM G 62(07) - Standard Test Methods for Holiday Detection in Pipeline Coatings. In this test method, an electrode was positioned on the coating and another terminal was connected at a substrate to make electric contact. Then 5,000 V was applied between the electrode and the substrate. A characteristic sound indicates that there are pores or cracking in the coating.

Pull-Off test was done in agreement with ASTM D 4541(09) using an epoxy based adhesive system with a bonding strength to 3,000 PSI. This test method uses a class of apparatus known as portable pull-off adhesion testers. They are capable of applying a concentric load and counter load to a single surface so that coatings can be tested even though only one side is accessible.

TEST CONDITIONS

50 liters of synthetic seawater were used. The water was prepared in agreement with ASTM D1141 (see chemical composition in Table 1). It was saturated with

carbon dioxide during the test. The agitation was done by carbon dioxide bubbles and by oscillatory movement of the sample.

It is known that the salinity of the petroleum-water is higher than the synthetic sea water. Even so, it was used because it is a standardized water and it would enable repeating the test whenever desired.

The test solution temperature was heated to 60 ºC using an electric immersion heater and measured with a thermo-couple installed close and parallel to sample. The test duration was 1,000,000 cycles and the oscillation frequency was 2 Hz. The pH of the solution was monitored. Initial pH was 7.5 e after CO_2 injection stabilized in 5.1.

TABLE 1
Composition of synthetic sea water (ASTM D 1141)

Reagents	Concentration (grams per liter)
NaCl	24.53
$MgCl_2$	5.20
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.695
$NaHCO_3$	0.201
KBr	0.101
H_3BO_3	0.027
$SrCl_2$	0.025
NaF	0.003

APPLIED TENSION

The maximum deflection applied on the sample corresponded to 80% of the yield point of the material. The deflection was calculated according to Equation (1) and the adjustment was made through a scale of 0.01 mm resolution.

Supposedly the coating would not be able to withstand the deflection corresponding to 80% of the yield point of the material, another four areas of the sample were monitored with strain gauges. Thus, the highest deflection withstood by the coatings could be determined. Monitored areas of the sample are illustrated in Figure 4 and they correspond to 80%, 68%, 56% and 35% of the yield point of the material. The relationship between the deflection and the tension is shown in Figure 5.

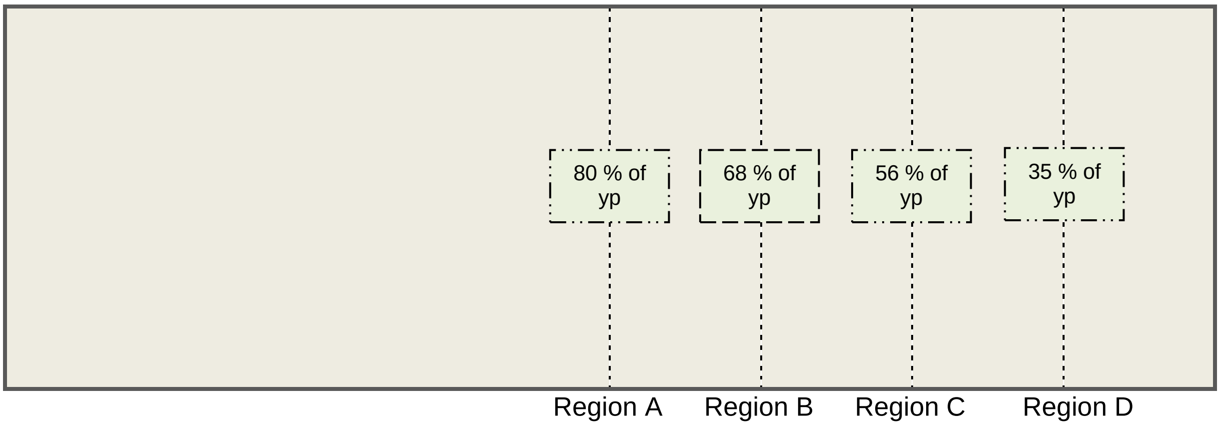

FIGURE 4 - Schematic representation of the monitored positions of the samples.

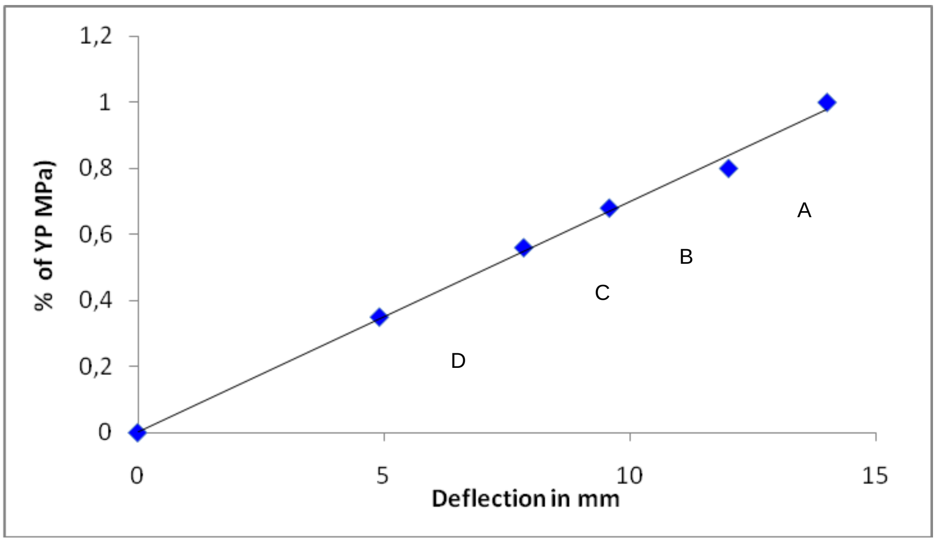

FIGURE 5 - Relationship between the deflection and the percentage of the yield point of the substrate material.

TEST RESULTS

After the test, a visual inspection with 40x magnification was done. The TSA sealed with epoxy presented white corrosion products because of its thinness; so, it was not possible to evaluate other defects in the coating. In the other coatings: epoxy novolac with glass flakes, TSA sealed plus epoxy novolac with glass flakes and TSZA sealed plus epoxy novolac with glass flakes, no damage was observed. Other inspections were done using Holliday Detector and Pull-off tests. Figures 6 to 12 show the coatings after Pull-Off test and after fatigue resistance test. The results are presented as follows.

Coating A – Thermal spray aluminum – TSA Sealed With Epoxy

- Pull-Off test before the fatigue resistance test: 7.0 MPa (only TSA);
- Holiday Detector test before the fatigue resistance test, with 5,000 V: no pores and no cracking;
- Visual examination after the fatigue resistance test: white corrosion products from aluminum were observed due to low thickness of sealing layer. Thus, it was not possible to evaluate the cracking and pore formation in the coating (see Figure 6).

FIGURE 6 - Coating A - TSA sealed with epoxy after the fatigue resistance test. White corrosion products were observed.

Coating B – Epoxy Novolac With Glass Flakes

- Pull-Off test before the fatigue resistance test: 5.4 MPa - cohesive failure;
- Pull-Off test after the fatigue resistance test: 5.4 MPa – cohesive failure (Figure 7);
- Holiday Detector test before the fatigue resistance test, with 5,000 V: no pores and no cracking;
- Holiday Detector after the fatigue resistance test, with 5,000 V: no pores and no cracking;
- Visual examination after the fatigue resistance test: there was no cracking or any other defects in the coating (Figure 8).

FIGURE 7 – Coating B – Epoxy novolac with glass flakes. Pull-Off test, after fatigue resistance test – cohesive failure.

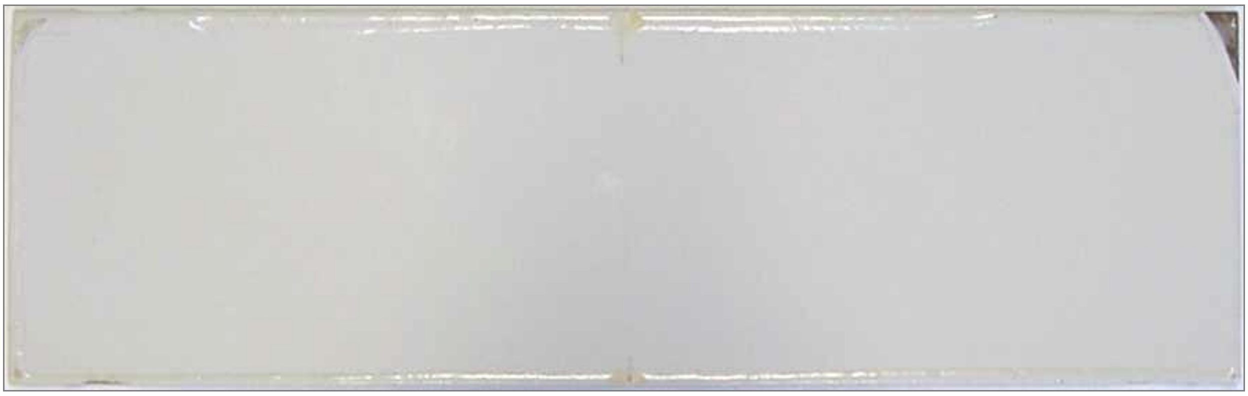

FIGURE 8: Coating B – Epoxy novolac with glass flakes after fatigue resistance test. There was no cracking in the coating.

Coating C – Thermal Spray Aluminum (TSA) Plus Epoxy Novolac With Glass Flakes

- Pull-Off test before the fatigue resistance test: 4.4 MPa – cohesive failure;
- Pull-Off test after the fatigue resistance test: 4.4 MPa – cohesive failure (epoxy novolac with glass flakes) (Figure 9);
- Holiday Detector test before the fatigue resistance test, with 5,000 V: no pores and no cracking;
- Holiday Detector test after the fatigue resistance test, with 5,000 V: no pores and no cracking;
- Visual examination after fatigue resistance test: there was no cracking and no other defect in the coating (Figure 10).

FIGURE 9: Coating C – TSA plus epoxy novolac with glass flakes. Pull-Off test, after fatigue resistance test – cohesive failure.

FIGURE 10: Coating C – TSA plus epoxy novolac with glass flakes, after fatigue resistance test. There was no cracking in the coating.

Coating D – Thermal Spray Zinc-Aluminum (TSAZ) Plus Epoxy Novolac With Glass Flakes The results are presented as follows.

- Pull-Off test, before the fatigue resistance test: 4.4 MPa – cohesive failure;
- Pull-Off test, after the fatigue resistance test: 4.4 MPa – adhesive failure (Figure 11);
- Holiday Detector test, before the fatigue resistance test, with 5,000 V: no pores and no cracking;

- Holiday Detector test after the fatigue resistance test, with 5,000 V: no pores and no cracking;
- Visual examination after fatigue resistance test: there was no cracking and no other defect in the coating (Figure 12).

FIGURE 11 – Coating D - TSZA plus epoxy novolac with glass flakes. Pull Off test, after fatigue resistance test – adhesive failure.

FIGURE 12: Coating D – TSZA plus epoxy novolac with glass flakes, after the fatigue resistance test. There was no cracking in the coating.

CONCLUSIONS

The test and the methodology were considered appropriate to evaluate paint systems subjected to cyclical tension and harsh corrosive environment (high salinity, high temperature and carbon dioxide environment). In this test method, coatings: B – epoxy novolac with glass flakes; C – Thermal Spray Aluminum plus epoxy novolac with glass flakes and D – Thermal Spray Aluminum-Zinc plus epoxy novolac with glass flakes presented good performances for cyclical deflection up to 80% of yield point of the substrate material. Coating A – Thermal Spray Aluminum sealed with epoxy mist coat did not present a satisfactory performance. It was observed white corrosion products from aluminum, probably due to low thickness of sealing layer.

REFERENCES

ASTM G 39 - Standard Practice for Preparation and Uses of Bent-Beam Stress-Corrosion Test Specimens

ASTM G 62(07) – Standard Test Methods for Holiday Detection in Pipeline Coatings

ASTM D1141 – Standard Practice for the Preparation of Substitute Ocean Water

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