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MARINE BIOFOULING TESTING OF EXPERIMENTAL MARINE PAINTS: TECHNICAL CONSIDERATIONS ON METHODS, SITE SELECTION AND DYNAMIC TESTS



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ABSTRACT

There is need to optimize testing protocols for marine coatings and develop improved accelerated test systems that best simulate the erosion process on marine paints as ships travel. The selection of a marine environment with aggressive biofouling conditions is necessary to obtain early results on the performance of experimental antifouling coatings. Simulation of the erosion of the coatings on the hull is an important tool in evaluating the efficacy of novel formulations. Procedures in marine exposure testing, criteria in the selection of ideal sites with aggressive fouling conditions and a proposal for a modified dynamic test system are described.

INTRODUCTION

The marine paint industry is undergoing dynamic change in redefining the benchmark technologies used in the coatings market. From the 1970's through the end of the century, tributyl tin (TBT) and self-polishing coatings dominated the industry and provided the market with effective, reasonably priced, high performance protective paint systems for ships to avoid fouling of their underwater surfaces. With the then looming ban on TBT by the International Maritime Organization (IMO), new resin technologies and coating formulations were developed, using cuprous oxide in combination with booster biocides to achieve the same goal. On January 1, 2003, the IMO treaty confirmed this TBT ban which effectively ended the manufacturing of TBT-based paints followed by a ban in 2008 on the presence of TBT on all ships. Although it still requires the signature of 25 nations to activate this treaty, the industry has already realized that the use of toxic components that are indiscriminately released into the marine environment by leaching from marine paints is a thing of the past. There is also the possibility that other substances, such as cuprous oxide, though considerably less toxic than TBT, may eventually prove to be harmful to the marine ecosystem.

Marine paint formulators are under pressure to develop new coating systems with reduced copper, preferably metal-free systems, and versatility in color (apart from the traditional red imparted by the cuprous oxide binder) without sacrificing the performance targets required by the shipping industry. Innovation within the industry is fueling the race to develop a superior marine paint. This is clearly apparent from the numerous patents being issued for novel paint systems in the last few years. However, progress in the development

of commercial products is hampered by the typically long duration of marine exposure panel tests that is required to verify efficacy of an experimental formulation before undertaking ship tests on oceangoing vessels. There is therefore a need to either optimize the testing protocols or develop improved accelerated test systems that best simulate the erosion process as the ship travels.

STATIC PANEL IMMERSION

The American Society for Testing Materials (ASTM) has published a guide referred to as D 3623 "Standard Test Method for Testing Antifouling Panels in Shallow Submergence," which served to standardize the procedures used for testing of marine coatings in the aquatic environment [1]. In this system, the coated panels are submerged in a heavily fouled marine environment, typically port areas, and left for periods of time to determine the degree of resistance provided by the test coatings against attachment of hard (barnacles, oysters) and soft (algae, seaweeds, sponges, etc) fouling. Although most major companies maintain their own marine test stations in various port areas, fouling conditions tend to vary from site to site. Testing in major ports, such as in Singapore and Los Angeles, provides a representation of the performance of coatings at these ports of call. However, there is considerable variability in the degree of fouling even within the same port.

To best evaluate the performance of the test coatings, site selection is critical in ensuring that coatings are screened quickly enough so that modifications can be made if the coating performed poorly. Besides the usual characteristics of convenience for experimentation, protection from adverse climactic conditions and accessibility, there are several conditions that are important to consider. The most important is a year-round warm water environment that allows for continuous fouling conditions of known biofoulers. Another consideration is predictable salinity conditions. The two conditions ensure the presence of the desired fouling organisms and enable the researcher to predict the cyclical fluctuations and the abundance of the various fouling communities at the particular site. In subtropical environments, the wider fluctuation in temperature and salinity generally produces variability in fouling organisms from month to month. Hence, the time of the year the panels are immersed will determine what type of fouling pressures those panels will experience. If one desires to see the effect of barnacle fouling, it is likely that the paint chemist may miss the opportunity if there is incomplete information on the ecology of the chosen location.



It is best to illustrate these concepts by introducing two marine research stations in the United States and India.

Sacred Heart Marine Research Center (Tuticorin, India)

Tuticorin is a port city in the southern tip of India where the Bay of Bengal, Indian Ocean and the Arabian Sea converge. The confluence of these major ocean environments results in a wide diversity of marine life. The location was selected because it fitted the criteria described above. The site is located within the Tuticorin port area called Karrapad Creek, an inlet that connects to Tuticorin Bay. The environmental profile of Karrapad Creek is shown in Fig. 1. The site has no major freshwater rivers to dilute the seawater so that salinity is reasonably stable except during the monsoon season [2]. Water temperature is typically 28o to 30o C, with a minor decline during the monsoon season. The major fouling organism is the barnacle, *Balanus amphitrite* Darwin, the predominant barnacle in all major ports worldwide. The worldwide

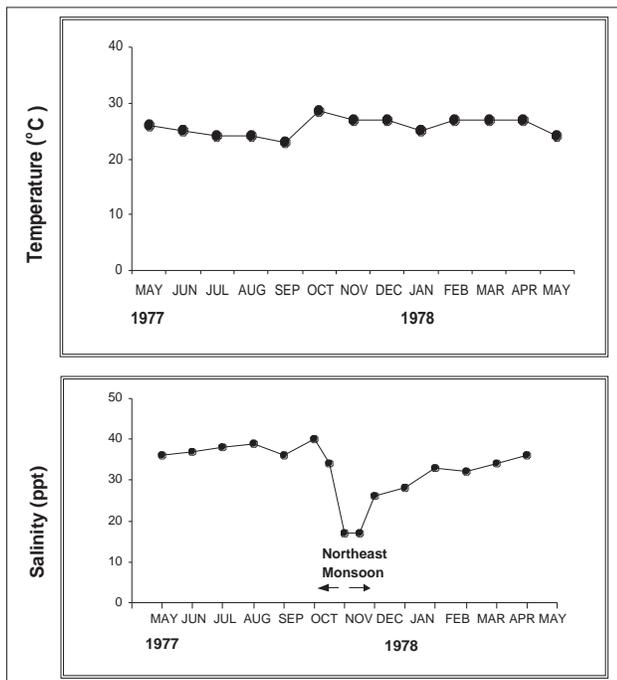


Figure 1. Salinity and temperature variation in Karrapad Creek (Tuticorin, India)

preponderance of *B. amphitrite* in port area likely resulted from introduction from ships centuries ago. In Tuticorin, *B. amphitrite* spawns year round and the high nutrient load of the water promotes massive growth of algae that serves as food for the barnacles. Marine sponges occur seasonally and can overgrow the barnacles for short

periods of time. Fig. 2 shows the pattern of fouling on test rods in Tuticorin. Coating failures can be observed as early as 1 month from immersion due to presence of juvenile barnacles on the surface.

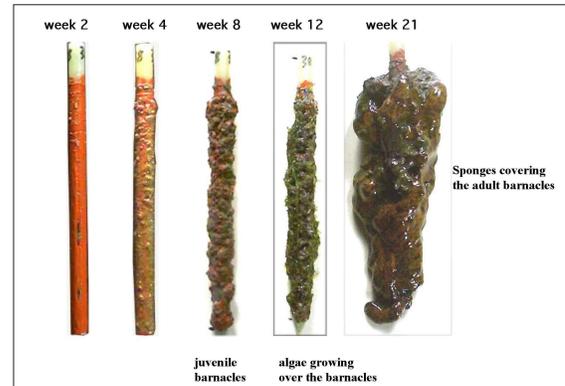


Figure 2. The pattern of fouling observed on test rods with low cuprous oxide concentration in Karrapad Creek (Tuticorin, India). Note that within one month, juvenile barnacles were already very prominent and the test rods were fully encrusted by three months of exposure in the marine environment.

Poseidon Marine Biological Station (Fort Pierce, Florida, USA)

In contrast to Tuticorin, Fort Pierce is a subtropical location in lower Florida. The site chosen is Link Port, a manmade inlet used to service the ships of the Harbor Branch Oceanographic Institution (HBOI). Fig. 3 shows the wide fluctuation in salinity and temperature in Link Port coinciding with the rainfall pattern. Also note that the relative abundance of major foulers is not continuous throughout the year [3]. The placement of panels at wrong periods will result in missed opportunity for heavy barnacle fouling pressure. However, the Link Port Station is an important test site because of the greater diversity of hard and soft fouling organisms, thus providing the researcher with a broader understanding about the efficacy of the coating against different types of fouling organisms.

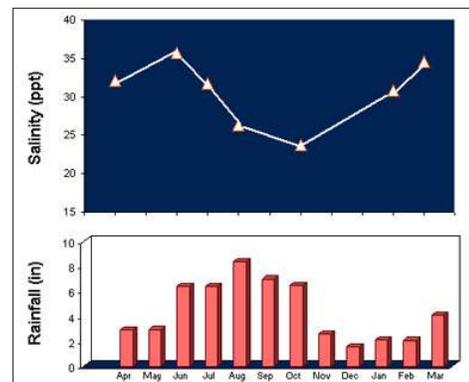


Figure 3. Salinity and rainfall pattern of hard fouling organisms in Link Port (Fort Pierce, Florida, USA)



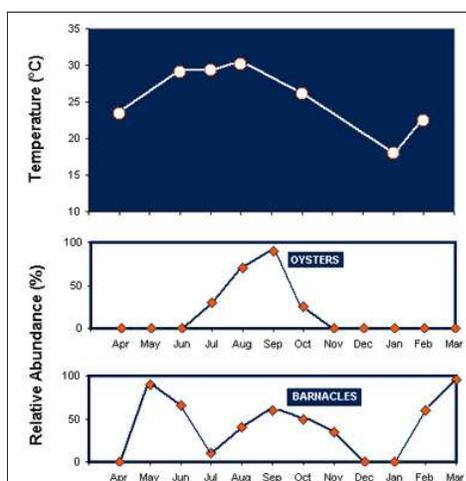


Figure 3 (cont.). Temperature and relative abundance of hard fouling organisms in Link Port (Fort Pierce, Florida, USA)

To illustrate further how site selection can affect the speed of evaluation, Fig. 4 shows the fouling conditions of test rods immersed at the same time in Florida and Tuticorin. Note that after 3 months, the test rods immersed in Karrapad are heavily fouled while the same rods immersed in Florida remained clean. While it is very important in the validation of coating performance to expose test panels in various sites around the world, it is equally important for scientists who need quick answers as to the performance of coatings to select the best site that provides a more aggressive year-round fouling environment.

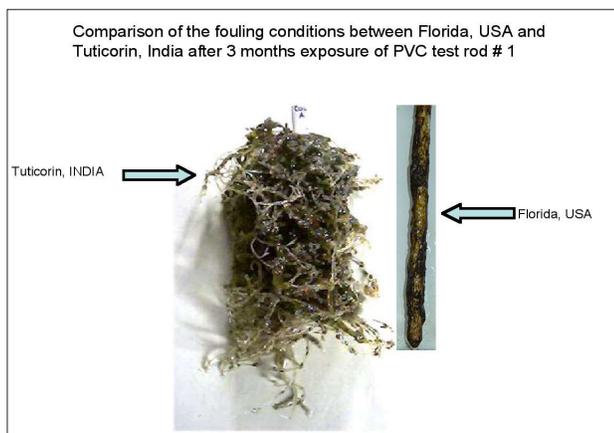


Figure 4. Comparison of the fouling conditions between Florida and India marine exposure sites.

Static Immersion Testing

The ASTM D 3623 provides an excellent guideline for evaluating the condition of the panels after immersion. With the advent of digital photography and internet, it has become easier to obtain real time

data on the conditions of the panels. However, these are subjective methods that can vary from one observer to another. Visual records are quite helpful but oftentimes, paint chemists do not have any idea what organisms they are looking at on a panel. For this reason, a marine biofouler guide is available, enabling paint chemists to identify the types of fouling organisms that are present in their test panels [4].

Objective evaluation is a very difficult process since fouling on a panel typically represents a diverse fouling community present at each site. The most reasonable fouling evaluation that provides suitable objective data is to use a gravimetric method to get a relative fouling abundance. An example of data generated from weighing the panels before and after immersion is depicted in Fig. 5. A good correlation

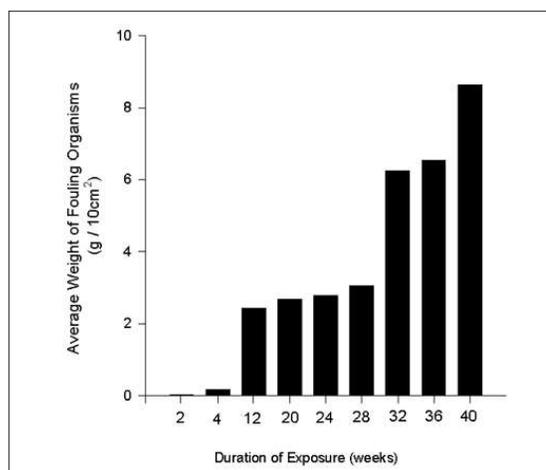


Figure 5. Total weight of fouling on metal panels exposed in seawater in Karrapad Creek (Tuticorin India)

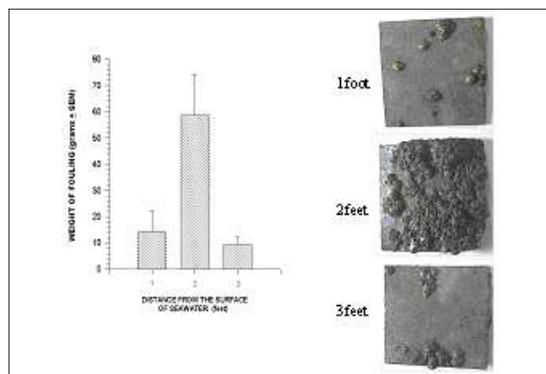


Figure 6. Variation in fouling abundance at different exposure depths in Karrapad Creek (Tuticorin, India)

has been found between weight of fouling and fouling resistance. This gravimetric measurement method is a useful complement to the subjective evaluations using the ASTM method and the digital photographic records. Fig. 6 shows that the positioning of the panels within the water column can be an important consideration. The



preferred location of the barnacle larvae is generally influenced by a number of factors, such as current, light, etc., so that optimum fouling for each given site may differ considerably. This should be included in any survey to optimize the fouling pressure. As in the Tuticorin site, the optimum location was at 2 ft. from the water surface. Above or below that level showed reduced fouling abundance.

DYNAMIC TESTING

ASTM D 4938 describes the use of high velocity seawater flowing through a channel with coated panels to simulate erosion of the coatings as the ship travels through the water [5]. Another version of the test is described in ASTM D 4939, commonly referred to as the rotating drum test, used for similar simulations [6]. A diagrammatic presentation of the rotating drum system is illustrated in Fig. 7. These test systems serves as the workhorse of the industry and allows for a better simulation of the stress on the coatings. By retrieving the panels after a period of time and immersion in a fouling environment one can then determine how the antifouling coating is performing. Again, it becomes critical that the right environment is selected for this purpose so as to shorten the marine exposure test and return the panel to the machine for continued erosion tests. The use of high velocity water has some drawbacks, such as the high cost of construction and operation of the system. The rotating drum test equipment can also be expensive, requires use of curved panels and accommodates a smaller number of test panels per drum. Another disadvantage of the current dynamic test system in use today is that the machine simulates erosion only at one speed at any one time so that testing at various equivalent ship speeds will require change in rotation of the drum or the velocity of the water during the course of the erosion testing.

The Poseidon Dynamic Test System

This dynamic test method has been designed to address critical issues related to the dynamic test—increased number of panels, use of flat panels, and simultaneous simulation at multiple ship speeds. A diagrammatic representation of this new system is shown in Fig. 8. Instead of mounting curved panels vertically on the outer surface of “drum,” flat panels are oriented horizontally on a disc, using bolts to hold the panel on the edges. It is then possible to construct multiple discs that can be rotated at a fixed speed on a central shaft. Since the velocity experienced by the panel depends on the distance from the center of the disc, the panels placed at various positions on the disc

will therefore experience different velocity and shear stress. Fig. 9 and Fig. 10 shows the positioning of the panels on the disc and the equivalent ship speeds when the disc is rotating at 40 miles per hour.

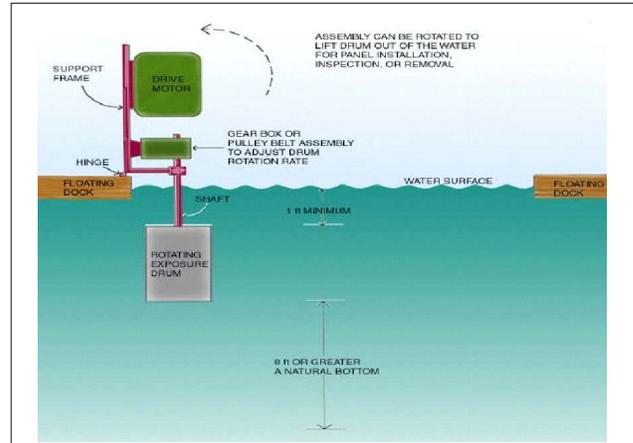


Figure 7. The above represents a diagrammatic representation of the rotating drum design for dynamic testing (ASTM D- 4938).

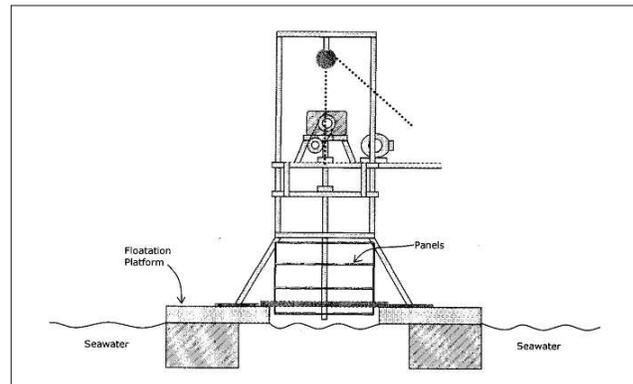


Figure 8. Schematic of the proposed dynamic system placed on a floating platform.

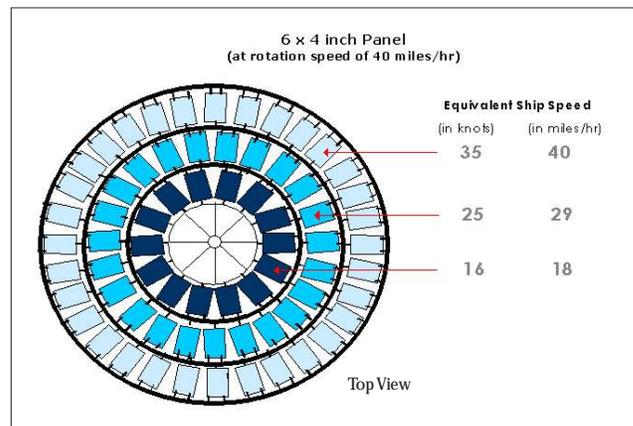


Figure 9. The positions of the 4 in X 6 in panels on each ‘disc’.



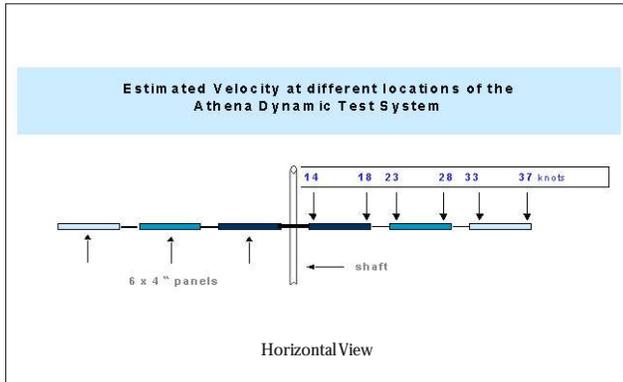


Figure 9 (cont.). The corresponding estimated velocity at the center of each panel.



Figure 10. Schematic drawing of the dynamic test system showing all the discs and panels.



Figure 11. The proposed dynamic system in actual operation.

This method offers the opportunity to investigate the shear stress on the coating at ship speed of 18 to 40 miles per hour or higher speeds by simply changing the speed of rotation. Flat panels can then be used to permit erosion tests on both sides of the panels. This dynamic testing machine, with a capacity of 280 standard panels (4 in x 6 in), was constructed with these specifications and has been in operation for one year in seawater simulating over 100,000 miles of travel (Fig. 11). A patent is now pending for this design, with two facilities (India and USA) coming into operation by the fourth quarter of 2003.

CONCLUSION

By combining the optimum site with aggressive fouling condition for marine exposure testing and a versatile dynamic system, it is now possible to accelerate the evaluation of experimental coatings to create improved marine coatings for the future.

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