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Coating **OPEN ACCESS**

Comparative Analysis of AquaSun Sol-Gel Coating and Commercial Antifouling Paint in Protecting Shipbuilding Steel in Port Seawaters

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Abstract The results of the first tests aimed to assess antifouling activity of new AquaSun sol-gel paint coated on shipbuilding steel immersed in highly polluted port seawaters, compared to a state-of-the-art self-polishing commercial silyl acrylate antifouling topcoat containing high amounts of cuprous oxide and copper pyrithione, are promising.

Keywords AquaSun, biofouling, antifouling, coating, shipbuilding steel

Introduction

The “AquaSun” sol-gel coating has shown biomolecule degradation and antifouling (AF) activity in laboratory experiments, first in the degradation of biomolecules[1] and then preventing adhesion of biofouling on a coated glass substrate immersed in Indian Ocean seawater for 122 days.[2]

Exploiting the unique versatility of the sol-gel route to organically modified silica (ORMOSIL) materials,[3] the original composition of AquaSun coating consisting of a fully methyl-modified silica[1] was subsequently modified to incorporate flower-like microparticles of visible-light photocatalyst Bi_2WO_6 suspended in a C18 1%/C8 49%/TEOS 50% silane solution in 2-propanol.[4] This second generation AquaSun coating (wherein C18 stands for *n*-octadecyltrimethoxysilane, C8 for *n*-octyltriethoxysilane and TEOS for tetraethylorthosilicate) was readily obtained via hydrolytic sol-gel polycondensation of the silane mixture under acidic conditions.[4]

AquaSun merges the solar-driven photocatalytic generation of powerful oxidizing species H_2O_2 and hydroxyl radicals once immersed in water and exposed to solar light,[5,6] with the foul release (FR) properties of undoped ORMOSIL xerogels.[7,8]

In light of forthcoming practical applications, it is also remarkable that the AquaSun glassy coating displays very high strength of adhesion to shipbuilding steel and lacks ecotoxicity.[4] Finally, the new coating is a less rigid material when compared to state-of-the-art commercial AF topcoat, but more adherent to the steel substrate, due to its lower viscosity and lower stiffness thanks to which the glassy organosilica sol containing plentiful Si-OH groups is able to chemically bind to the Fe-OH groups at the steel surface.[10] The strongly cohesive thin film is ideally suited to coat and protect the outer steel surface not only from corrosion,[9] but also from biofouling.[10]

To gain an insight on the practical viability of the new multifunctional (AF/FR) coating, we carried out the first real-life comparative investigation of the AquaSun performance in marine (harbor) waters, in comparison to a state-of-the-art commercial AF topcoat.

The waterborne AquaSun paint was deposited by simple brushing the liquid sol on the surface of shipbuilding steel rectangular (15 cm x 30 cm) substrates 5 mm thick, followed by curing at room temperature.

The commercial AF topcoat, a “self-polishing” silyl acrylate antifouling coating (SeaQuantum Ultra S)[11] purchased from Jotun (Sandefjord, Norway) was applied to shipbuilding steel by state-of-the-art three-step coating process consisting in sanding the steel substrate followed by spraying the i) primer, ii) tie-coat and iii) AF topcoat followed by curing at room temperature.

The specimens were thus fixed to metal array kindly developed *ad hoc* by Fincantieri, and immersed in the port waters of Palermo, Sicily (Figure 1). All were retrieved from water every month during the 3-month investigation between September 13 and December 6, 2022.

Figure 1 Shipbuilding steel specimens coated with different AF coatings immersed in Palermo’s port waters (left). Specimen testing system in immersed position (right).

Table 1 displays the date of each check in testing the shipbuilding steel substrates treated with commercial and experimental antifouling coatings in the seawater of Palermo’s harbor, alongside with the fact that specimens were immersed in water on September 13, 2022.

Table 1 Date and action in testing the shipbuilding steel substrates treated with commercial and experimental anti-fouling coatings in the seawater of Palermo's harbor

Date	Action
13-Sept-2022	Immersion of the specimens
27-Sept-2022	Check No.1
11-Oct-2022	Check No.2
25-Oct-2022	Check No.3
8-Nov-2022	Check No.4
22-Nov-2022	Check No.5
6-Dec-2022	Check No.6

Figure 2 Right side of the shipbuilding steel substrate protected (top) by commercial topcoat and (bottom) by the AquaSun at 5 wt% bismuth tungstate load (THA8-5) after 69 consecutive days in Palermo's harbor waters (13 Sept-22 Nov 2022).

Figure 2 shows on top the right side of the shipbuilding steel substrate protected by commercial topcoat, and on bottom the right side of the shipbuilding steel substrate protected by AquaSun doped with 5 wt% bismuth tungstate after 69 consecutive days of immersion in Palermo's harbor waters (13 Sept-22 Nov. 2022).

Both surfaces are fouled by barnacle larvae and algal spores tightly bound to the metal surface. Due to partial shadowing, fouling in the area beneath the supporting tube in the substrate coated with THA8-5 is more pronounced. Visual evidence of partial protection is shown also by complete contamination of the galvanized steel comprising the aforementioned supporting tube.

We briefly remind that the state-of-the art commercial paint tested (SeaQuantum Ultra S)[11] belongs to the AF class of "self-polishing" copolymer paints containing a large amount (785 g/L) of cuprous oxide (Cu_2O) as main biocide in combination with another biocidal species (the antifungal and antimicrobial complex copper pyrithione in 66 g/L concentration)[11] to broaden the spectrum of action against the widely different organisms (microbes, algal spores, algae, animal larvae, barnacles, mussels, dog teeth, *etc.*) comprising marine biofouling.[12] The product is commercialized to deliver long-term fouling protection "with a consistent 45 idle day ability".[13]

Five main factors combine to determine the rate and extent of biofouling which is a ubiquitous biological phenomenon involving first quick microbial surface colonization and biofilm development,[14] and eventually attachment of large and hard marine organisms such as mussels and barnacles: i) the temperature of water (high temperatures promote biofouling), ii) water depth and iii) distance from shore (as both increase, organisms will have more difficulty proliferating), iv) the presence of nutrients, and v) exposure to sunlight.

Figure 3 displays above the right side of the shipbuilding steel substrate protected by commercial topcoat, and on bottom the right side of the shipbuilding steel substrate protected by AquaSun doped with 5 wt% bismuth tungstate after 14, 28, 42, 56, 69 days of immersion (from left to right) in Palermo's harbor waters.

Figure 3 Shipbuilding steel substrate protected by commercial topcoat (top), and by AquaSun doped with 5 wt% bismuth tungstate (bottom) after 14, 28, 42, 56, 69 days immersion in Palermo's port waters (from left to right).

After 14 days, the specimen treated with the commercial AF coating did not show biofouling, whereas the substrate treated AquaSun showed moderate fouling. The difference is highest for samples observed after 28 days, when the steel substrate treated with AquaSun was significantly more colonized when compared to steel painted with the commercial AF paint. However, whereas for the steel substrate treated with the biocide-based commercial paint, colonization constantly grew with time of immersion, this was clearly not the case for the specimen treated with the AquaSun coating.

Indeed, after 42 days the amount of biofouling on the surface of the specimen treated with AquaSun decreased, pointing to enhanced photocatalytic activity indeed due to particularly sunny weather in Palermo between the end of October and the early days of November 2022 (Table 1). A modest increment in the amount of biofouling was observed after another 14 days by late November 2022, as mild and sunny weather in Palermo continued without interruption.

Only by the end of November 2022, clouds and rain started to characterize Palermo's weather. Cloudy weather lasted until December 10th, when another wave of sunny weather lasted until January 9, 2023.

With the exception of exposure to sunlight (indicative values for suspended solids in the experimental area of the port are 11 mg/L),[14] the other main parameters affecting biofouling (water temperature, distance from shore, nutrient concentration) in the highly polluted waters of Palermo's port between September and December all promote microfouling and macrofouling.[15] The water temperature in the mild Palermo's late summer weather when the experiments started was around 25 °C and at 16—17 °C when the test

ended. Distance from the shore and depth are negligible, whereas the abundance of nutrients is rendered by the 0.059 mg/L for N and 0.012 mg/L for soluble P concentration values found in 2010,[15] and since then considerably increased.

Indeed, even the AF coating releasing plentiful Cu^+ ions and copper pirythione biocidal "booster" molecules[16] into seawater was not able to prevent fouling of the immersed substrate already after 28 days (Figure 3).

It is also remarkable that the AquaSun coating exerted AF activity even if quickly applied as a thin film ~50 μm thick by brush in a one coat paint (thanks to the very low viscosity of the waterborne paint (similar to water, 5—6 cP), and not by more effective spray coating. The latter method indeed is the optimal process to deposit sol-gel coatings using a spray gun under modest (10 psi) pressure.[17] Besides deposition speed being the fastest amid all methods including roll coating, waste of coating sol is m¢inimized, and the coating step is suitable for establishing an in-line process.

We remind that the same AquaSun coating deposited on shipbuilding steel has been extensively characterized. The coating has a 216 mm thickness, has a relatively high roughness of 2.13 mm, and a Young contact angle of 91.92° that makes it hydrophobic.[4] Figure 4, furthermore, displays the field emission scanning electron microscope (FE-SEM) photographs and the energy dispersive X-ray spectra (EDS) of selected coating regions unveiled by the SEM photographs.[18]

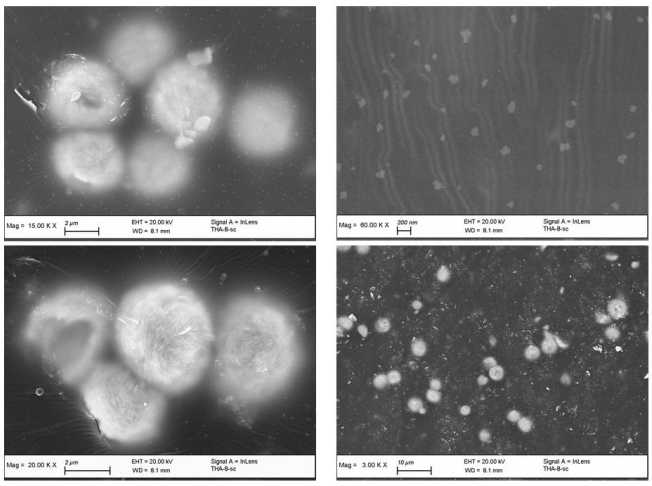

Figure 4 FSE-SEM photographs (×3,000, ×20,000, ×15,000 and ×60,000 in clockwise order from bottom right) of the AquaSun xerogel deposited on glass, and EDS spectra of encapsulated Bi_2WO_6 microparticle (white spots in the SEM photograph) and regions free of embedded microparticles.

The flower-like Bi_2WO_6 microparticles are embedded in the xerogel AquaSun matrix, often in clusters close to each other. The EDS signals confirm the presence of Bi, W, O, Si and C of the ORMOSIL-entrapped Bi_2WO_6 xerogel comprising the AquaSun structure (bottom of Figure 4, left), whereas coating regions free of dopant species are also clearly visible by FSE-SEM at very high magnification (×60,000) coupled to EDS analysis (bottom of Figure 4, right).

In conclusion, following the sustainability analysis of AquaSun production and commercial uptake,[19] the first results of testing the AquaSun coating under real life conditions in highly polluted port seawaters show that the xerogel ORMOSIL coating is able to exert antifouling function also under stationary conditions in highly polluted waters.

Under these demanding conditions, biocide-free ORMOSIL sol-gel coatings minimizing the surface energy of the coated surface are not able to drive the foul release mechanism that reduces the initial stages of fouling development and facilitates cleaning of the biofouling layer.[7,8]

Further applied research aimed to further improve the AF activity of AquaSun, for instance by replacing empirical brush coating with spray coating carried out according to state-of-the-art application methodology,[17] will be reported soon.

Conflict of Interest

The authors declare no conflict of interest.

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