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

Rosaria Ciriminna,* a Salvatore Vacante, b Antonino Scurria, a Gabriella Di Carlo, a Mario Pagliaro, a and Annamaria Visco* a,b

a Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via U. La Malfa 153, 90146 Palermo, Italy
b Cetena, via dei Cantieri 75, 90142 Palermo, Italy
c Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via Salario km 29.3, 00015 Monterotondo RM, Italy
d Dipartimento di Ingegneria, Università di Messina, C.da Di Dio, 98166 Messina, Italy
e Istituto per i Polimeri, Compositi e Biomateriali, CNR, via P. Gaifami 18, 95126, Catania, Italy

Email: rosaria.ciriminna@cnr.it (R. C.); annamaria.visco@unime.it (A. V.)

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 Bi2WO6 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-octadecytrimethoxysilane, 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 H2O2 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 simply 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 Sj)[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 a 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).
Cloudy weather lasted another wave of sunny weather started to characterize Palermo’s weather. Cloudy weather continued without interruption.

After 14 days, the specimen treated with the commercial AF coating did not show biofouling, whereas the substrate treated with AquaSun showed moderate fouling. The difference was 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), 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. 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, and since then considerably increased.

Indeed, even the AF coating releasing plentiful Cu²⁺ ions and copper pyrithione biocidal “booster” molecules 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. Besides deposition speed being the fastest amid all methods including roll coating, waste of coating sol is minimized, 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 μm thickness, a relatively high roughness of 2.13 μm, and a Young contact angle of 91.9° that makes it hydrophobic. 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.

The flower-like Bi₂WO₆ 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 Bi₂WO₆ 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.

In conclusion, following the sustainability analysis of AquaSun production and commercial uptake, 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.

Further applied research aimed to 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 will be reported soon.

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Conflict of Interest

The authors declare no conflict of interest.

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[18] The FE-SEM photographs were taken as described in Ref.4 using a Carl Zeiss, apparatus equipped with an energy dispersive X-ray spectrometer (EDS) INCA 450 and a four sector back-scattered electron and secondary electron detectors, under an acceleration voltage of 20 kV.


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