Chapter

Novel Antifouling and Self-Healing Eco-Friendly Coatings for Marine Applications Enhancing the Performance of Commercial Marine Paints

George Kordas

Abstract

Nanocontainers of the type CuO and CeMo were filled with bromosphaerol and 8-hydroxyquinoline, respectively, and incorporated into commercial marine paints. The generated paints with nanotechnology perform better in laboratory tests with respect to fouling and corrosion and test carried out via painting commercial ship traveling across the Adriatic Sea for a year than the currently used commercial paints. This is another application of nanotechnology that will someday find a commercial application. Since copper oxide is used for the current commercial paints and bromosphaerol is a natural biocide, there will be no need to pass the expensive approvals to use these antifoulants.

Keywords: nanocontainers, antifouling, marine paints, natural biocides, corrosion

1. Introduction

Biofouling is produced by immersing a surface (e.g., metal, net, etc.) in seawater where quickly a biofilm is formed first, composed of microorganisms, and then colonized by invertebrate animals. Next, corrosion is developed consisting of iron oxide, oxyhydroxides, green rust, etc. The metabolic activity influences further the corrosion process. All this generates problems to the structures exposed to the seawater with considerable consequences to energy consumption, speed of the ship, pollution of the environment, intervals between repairs, etc. [1]. This can be prevented using antifouling coatings composed of biocides and copper oxide preventing the organisms of settling. The total concentration of copper oxide in paints varies between 20 and 76 wt.% [2]. The biocides target microorganisms that produce a biofilm (typical bacteria). Biofouling is also a problem for all aquaculture industries, membrane bioreactors, offshore oil platforms, desalination units, cooling water systems, wind farms, oil pipelines, etc. Concerning antifoulants, tributyltin compounds (TBT $(C_4H_9)_3Sn$) were used for a long time and incorporated into marine paints [3]. It was determined that TBT was very toxic and prohibited to be used as antifoulant in 2008. This generated the demand to find natural antifoulants that are eco-friendly [4]. A number of marine metabolites show high-level antimacrofouling properties and were studied as additives for antifouling paints [5]. One of them, bromosphaerol, was identified that occurs in the red algae *Sphaerococcus coronopifolius*, inhibiting settlements of barnacles on marine paints [6]. Another strategy is to develop surfaces resembling that of shark because its surface is free of fouling [7].

It has been demonstrated that incorporation of nanocontainers loaded with inhibitors into coatings induces self-healing of paints after an external damage [8]. Among the various nanocontainer types, TiO_2 and CeMo exhibit also antimicrobial properties.

The present research was inspired by the previous successful use of nanocontainers loaded with inhibitors into paints (e.g., automobile and airplane multi-level protection of materials for vehicles by "smart" nanocontainers [9]) to tackle the replacement of chromium (VI) that is also carcinogenic. Since copper oxide is heavily used in marine paints as antifoulant, this inspired the production of copper oxide nanocontainers that were filled with bromosphaerol and SeaNine™211. The results of the laboratory work were encouraging and certified via painting two ships, the one traveling in the Adriatic Sea and the other in the Nord Sea for 1 year.

2. Experimental procedures

2.1 Experimental techniques

The nanocontainers were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The corrosion behavior of the samples was determined using a Solartron ModuLab XM MTS equipment. The size of the nanocontainers was determined by a Malvern Nano Series system.

2.2 Chemicals

We used cerium (III) acetylacetonate (Sigma-Aldrich Chemie GmbH), sodium molybdate (Panreac Quimica SA), copper (II) sulfate pentahydrate (Sigma-Aldrich Chemie GmbH), polyvinylpyrrolidone (PVP, Sigma-Aldrich Chemie GmbH), potassium persulfate (KPS, Sigma-Aldrich Chemie GmbH), sodium dodecyl sulfate (SDS, Sigma-Aldrich Chemie GmbH), sodium chloride (NaCl, Sigma-Aldrich Chemie GmbH), 8-HQ (Sigma-Aldrich Chemie GmbH), bromosphaerol (FORKYS AE Ichthyokalliergeies) and 1-BSA (Sigma-Aldrich Chemie GmbH).

2.3 Nanocontainer production

The nanocontainer reduction has been the subject of many of our papers. We sketch here the production of CeMo and CuO that we cannot claim an extensive description and advise the reader to search for more details in our literature [8].

2.3.1 CeMo nanocontainers

The CeMo nanocontainers were produced using a three-step process. The first process involves the formation of a core. This was accomplished by mixing 10.0 g styrene, 10.0 g potassium persulfate, 1.3 g sodium dodecyl sulfate in 900 g water in a 500 cm^3 container. The flask was purged under nitrogen for 18 h. The second step was the coating of the polystyrene core by $Ce(acac)_3$ and sodium molybdate aqueous solution in the presence of PVP. The third step was the drying of the powder at 60°C for 1 h and then heating at 550°C for 4 h. The process was described extensively in the literature [8].

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2.3.2 CuO nanocontainers

0.75 g of $CuSO_4{\cdot}5H_2O$ and 0.2 g of glucose were diluted in 0.2 L of distilled water. Then, 50 mL of $NH_3{\cdot}H_2O$ solution (0.04 M) and 50 mL of NaOH solution (0.20 M) were assorted slowly in 30 min. At the end, 0.100 mL of ascorbic acid (0.03 M) was added. After this, the color of the mixture from blue turned into yellow. Later, the color changed into orange. We centrifuged the solution at 8000 rpm for 5 min to receive the solids. We processed Cu_2O at 250°C for 2 h to observe a black solid of CuO hollow nanospheres via thermal oxidation. The hollow CuO nanocontainers were loaded via a vacuum facility with bromosphaerol.

2.3.3 Marine paints

We used two commercial paints for the experiments from Wilckens. The paints were free from any additives used for corrosion and antifouling protection (**Figure 1**).

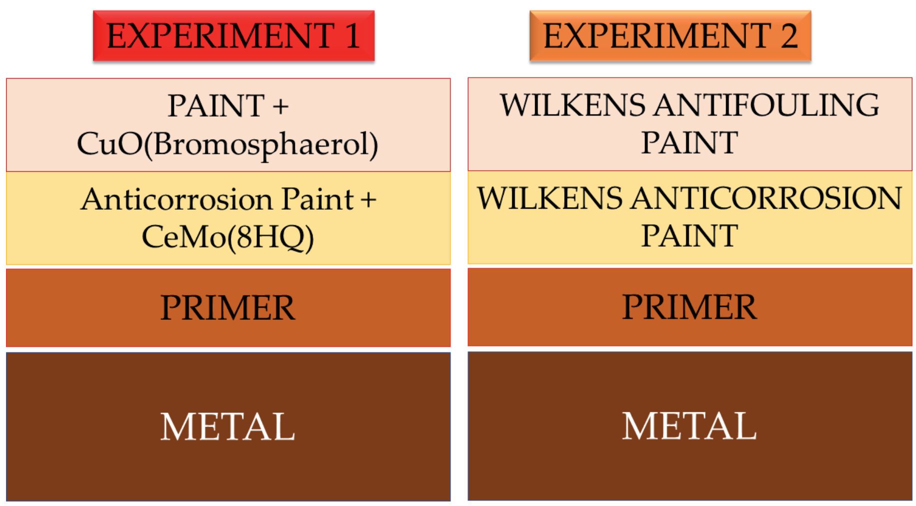

Figure 1.
Two experiments where metals were painted: the first with the primer (bottom), anticorrosion paint with CeMo(8HQ) (mittle), and paint with CuO(bromosphaerol) (top) (Experiment 1); and the second the primer (bottom), anticorrosion Wilckens paint (mittle), and paint with Wilckens antifouling paint (top) (Experiment 2).

Figure 2.
Tube with samples placed in Mikrolimano (Piraeus) for 3 months. The motion of a ship with 14 knots simulated using at the end of the tube a propeller.

2.3.4 FRA measurements

Metals used for ship hulls were painted in size 1 cm by 2 cm and were placed in a tube in the seawater in the Mikrolimano harbor (**Figure 2**). At the end of the tube, a propeller was placed inducing motion of water inside the tube corresponding to 14 knots. After 3 months of exposure of the samples in this custom-made facility, corrosion tests were conducted using the electrochemical impedance spectroscopy (EIS).

3. Results

Figure 3 shows the SEM micrographs of the CuO and CeMo nanoparticles. One can perceive a size of ~420 and ~350 nm for the CuO and CeMo nanocontainers. The term "nanocontainers" is used instead of "nanoparticles" because the nanomaterial produced here is hollow inside as one can perceive from **Figure 2**.

The CuO and CeMo nanocontainers were filled with bromosphaerol and 8-hydroxyquinoline, respectively. This was accomplished using a special for this purpose vacuum facility. The question is how much of bromosphaerol and 8-hydroxyquinoline the containers were filled. We used thermogravimetric analysis (TGA) to answer that question. **Table 1** gives the results for the encapsulation efficiency (EE) and loading capacity (LC) for the two systems.

Figure 4 shows the SEM micrographs of the three coatings: (a) the primer, (b) primer plus anticorrosion, and (c) the primer, anticorrosion, and antifouling layers. The thickness of the primer is 50 μm, of the anticorrosion layer 140 μm, and of the antifouling layer 130 μm.

The samples were placed for 3 months in the facility in Mikrolimano (Piraeus) and then soaked in 0.5 M NaCl solution for 48 h. The FRA spectra of the two samples the one painted with our technology (Experiment 1) and the other painted with the commercial paints (Wilckens Experiment 2) are shown in **Figure 5**. One can perceive from **Figure 5** that the nanotechnology paints are more stable in the seawater for 3 months than the commercial paint.

The nanotechnology paints were tested using one passenger ship (Sea Anemos) traveling daily between Ancona (Italy) and Patras (Greece). **Figure 6** shows the

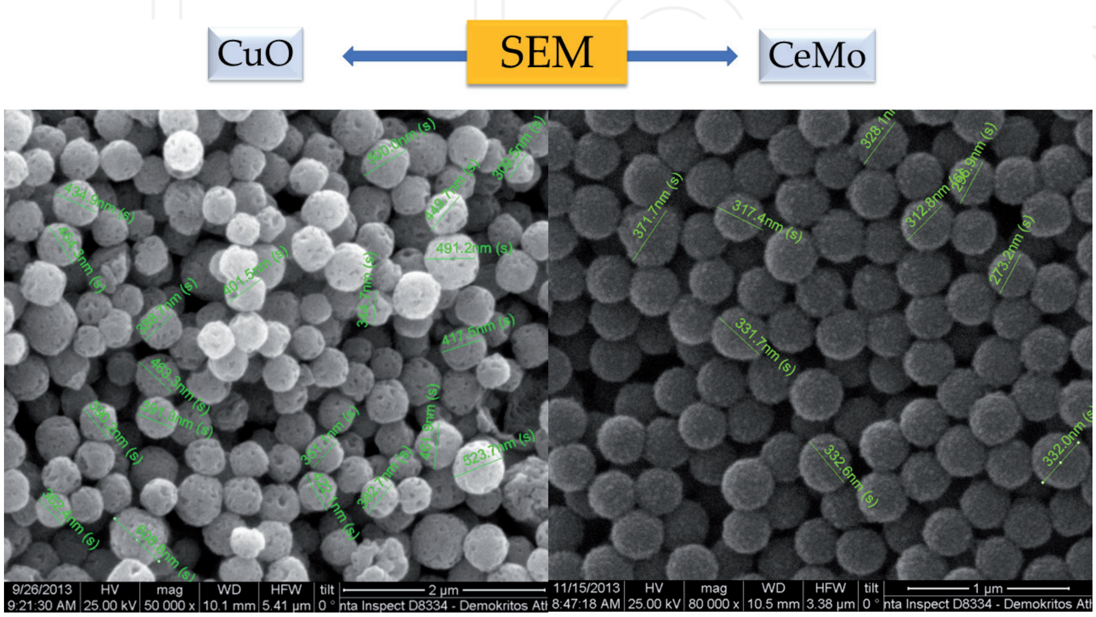

Figure 3.
SEM of CuO and CeMo.

	EE	LC
Bromosphaerol in CuO	50%	25%
8-OH quinoline in CeMo	80%	40%

Table 1.
EE and LC for bromosphaerol and 8-OH quinoline in CuO and CeMo, respectively.

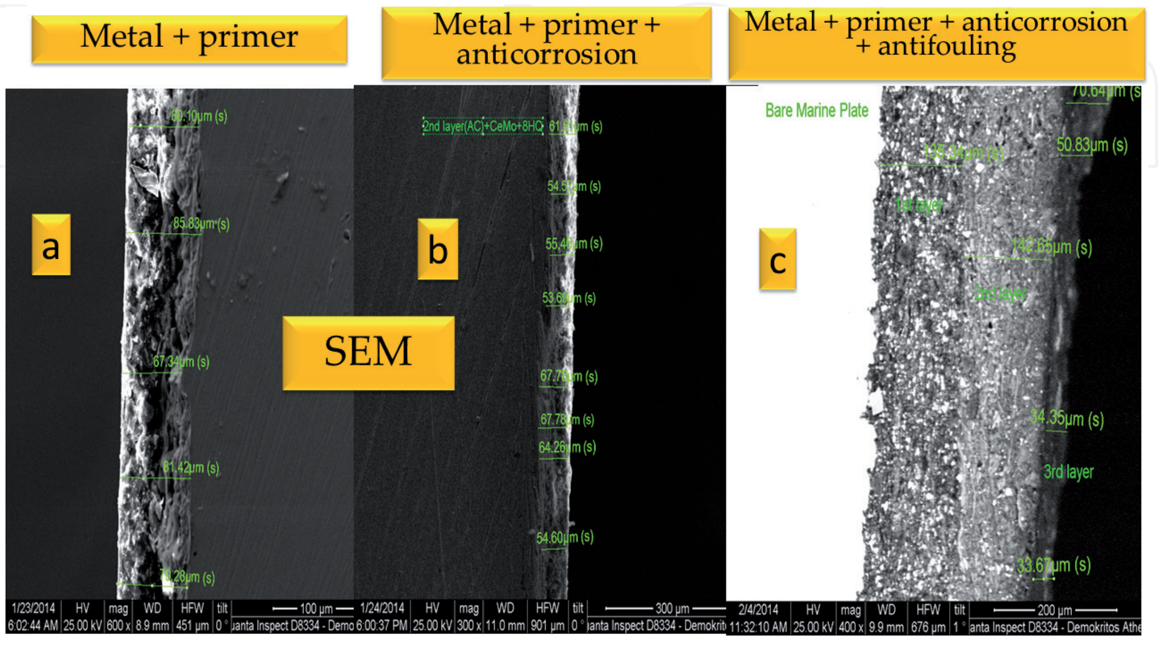

Figure 4.
SEM of primer, anticorrosion, and antifouling layers.

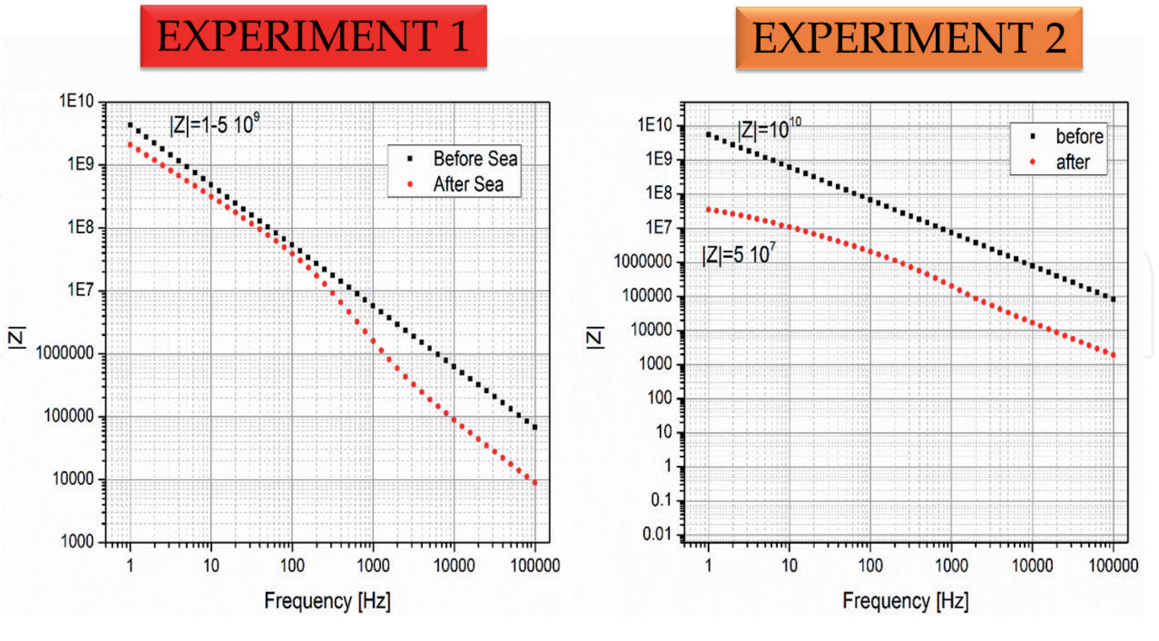

Figure 5.
FRA of the nanotechnology-based coating (Experiment 1) and of the commercial paints (Experiment 2).

stripe that was painted, and the rest of the ship was painted with the commercial coatings (primer, anticorrosion, and antifouling paints). After a year, the ship was taken out in a shipyard near Piraeus (Skaramagas shipyard, in a port town in the western part of Athens), and the result is shown in **Figure 6**. To our surprise, the

Figure 6.
Ship painted with nanotechnology.

stripe we painted with the "nanotechnology paints" was nearly without fouling as compared with the rest of the ship painted with the "commercial paint."

4. Discussion

In the last few years, polymer-based nanocomposites incorporating nano-sized fillers have been studied extensively. The merits of this approach are that the nano-sized particles provide a larger interface for interactions with polymer matrix leading to improved properties. The control of the surface topography at nano level leads to new types of coatings with targeted properties, like antifouling. It is important to mention here the "nanostructuring" of surfaces can alter the wetting properties of the surfaces, the so-called lotus effect, leading to self-cleaning or super hydrophobic coatings. The presented biomimetically inspired surface topography Sharklet AF™ containing 2 μm wide rectangular-like periodic features spaces at 2 pm that reduced Ulva settlement by 86%. This is a convincing demonstration that antifouling can be achieved by the topography of the paint surfaces inhibiting accumulation of marine algae. When spacing above 5 μm this feature, the inhibitory response is not achieved. There is under development a new class of antifouling coatings called "biomimetic" resulted from the skin of shark consisting of overlapping plates in nanoscale size with parallel-oriented ridges preventing shark from becoming fouled even standing. Many investigators were inspired by this fact that is formulated by the engineering roughness index (ERI) given by Eq. (1):

$$\text{ERI} = \frac{\boldsymbol{r} * \boldsymbol{n}}{\mathbf{1} - \boldsymbol{\varphi}} \tag{1}$$

where r is the Wenzel roughness ratio, n is the number of individual surface features, and φ is the area segment of the dissimilar surface topographies. When the surface is completely smooth, ERI is zero. The Sharklet AF exhibits an ERI of 9.5 due to 3D dimensions in microstructural differences. Due to this patterning, Sharklet AF conveys a 77% decrease in microfouling.

Considering the fact that the nanostructure impacts the topography of the surfaces, one can use these observations to explain the outcome of the paintings of the ship with and without nanocontainers on the surface shown in **Figure 6**. Another contribution arises from bromosphaerol included in the nanocontainers given in **Table 1**. It has been demonstrated that bromosphaerol inhibits settlements of barnacles on painted substrates [6]. Bromosphaerol is released from the nanocontainers via their porosity shown in **Figure 3** or via wearing out the nanocontainers by the friction with the seawater while the ship is moving in the sea. It is known that copper oxide is also an antifoulant. The commercial paints include copper oxide in the amounts of 20–76 wt.% in the paints. Here, we used 4 wt.% CuO in the form of nanocontainers. Though the amount is small, one has not to neglect the antimicrobial properties observed in nanocontainers [10]. All these factors together may lead to the outstanding outcome of **Figure 6**. Here, the contribution arises not only by one property, namely, the shark skin effect, but from the contribution of the bromosphaerol that is a natural occurring diterpene from the red algae *Sphaerococcus coronopifolius,* which can inhibit settlement of barnacles on painted substrates and the antimicrobial contribution of the CuO nanocontainers. All three components lead to a superb technology not to be achieved by other methods.

The nanotechnology strategy of this work has also another implication regarding the anticorrosion properties of the paints. Experiments 1 and 2 of **Figure 5** show the response of the paints including CeMo(8HQ) into the anticorrosion paints (Experiment 1) in contrast to the commercial paints of Wilckens (Experiment 2). One can perceive from **Figure 5** a Rp of 10^{10} Ω for the as painted substrate (Experiment 1), and it remains about the same after exposure of the samples for 3 months into the seawater in the Mikrolimano. On the contrary, the commercial paint has Rp equal to 10^{10} Ω before immersing the sample into the seawater and is reduced almost three orders of magnitude after 3 months in the seawater, the Rp equal to 5×10^7 Ω. Again, the nanotechnology-produced samples exhibit superior properties. The difference between the value of Rp of the commercial paint and the Rp of the paint with CeMo(8HQ) can be attributing to self-healing effect offered by the CeMo(8HQ) nanocontainers. The new technology is dynamic instead of static paints. The result of the painted ship tells us that the technology is not good for the laboratory but ready to be exploited with many implications not only for the ship hulls but also for aquaculture nets, oil drilling platforms, pipelines, etc.

Nanotechnology will contribute to many areas with outstanding impact in nanomedicine, energy, energy storage, thermal energy conversion, etc. Here, we demonstrated a contribution in the field of preventing biofouling. If one considers the impact to economy, air pollution reduction, increase of the time between repairs of the ship hulls, reduction of cost of paints due to the reduction of the use of copper oxide, increase of speed of travel due to the increase of the contact angle of seawater reducing the drag resistance, and many other benefits, we are experiencing a new revolution in technology arising from nanotechnology. Nanotechnology will not be like other technologies where money was wasted experiencing a boom with many expectations. Any investment in nanotechnology science and technology will deliver a multiple return to the investment with results benefiting the societies like cancer therapy, energy storage, self-healing of materials, etc.

5. Conclusions

The present technology will compete with existing technologies of reputable maritime companies. Sigma developed the product SYLADVACE™ 700 built upon pure silyl acrylate binder. This product exhibits self-smoothing characteristics of the silyl acrylate binder reducing the leached layer and average hull roughness. International Paint Ltd. (AkzoNobel) developed the lntersleek™900 product, yielding a smooth, slippery, low-friction surface onto which fouling organisms attach very difficult. Chugoku Marine Paints, Ltd. has the Seaflo Neo™ SL products in the market attaining an ultrasmooth surface with good self-leveling performance.

HEMPEL established a self-polishing antifouling paint named Clobic™ NCT based on nanocapsule technology. HEMPEL has also the HEMPASIL™ X3 87,500 with high solid content. JOTUN has the SeaQuantumPlus™ S in the market for faster vessels. NIPPON has launched the A- LF-Sea™. By incorporating this into NIPPON PAINT'S excellent self-polishing copper silyl acrylate antifouling, long-term low friction performance is ensured, and 10% more reduction of fuel consumption is guaranteed.

The nanotechnology developed in the Sol–Gel laboratory of NCSR "D" will not be able to break through these technologies of the big companies in the field. This work offers a brainstorming approach that these companies consider such an interesting approach because this technology offers self-healing technology together with excellent antifouling properties. This new technology will not need permissions to use in various countries as we all know how much time consuming they are and also expensive. The present work uses natural products as biocides and nanocontainers like CuO that is used to an amount of 4 wt.% instead of 20–76 wt.% of the current technology. Our technology uses less amount of copper oxide reducing significantly the cost of the paints.

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Author details

George Kordas
Sol-Gel Laboratory, INN, NCSR Demokritos, A. Paraskevi Attikis, Greece

*Address all correspondence to: gckordas@gmail.com

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