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Environmentally Benign Sol–Gel Antifouling and Foul-Releasing Coatings

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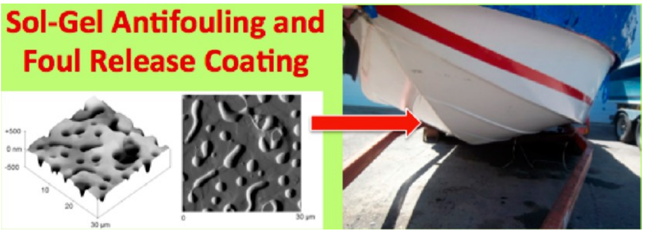

Biofouling on ships and boats, characterized by aquatic bacteria and small organisms attaching to the hull, is an important global issue, since over 80000 tons of antifouling paint is used annually. This biofilm, which can form in as little as 48 hours depending on water temperature, increases drag on watercraft, which greatly reduces their fuel efficiency. In addition, biofouling can lead to microbially induced corrosion (MIC) due to H_2S formed by the bacteria, especially sulfate-reducing bacteria.

When the International Maritime Organization (IMO) international convention banned the use of effective but environmentally damaging coatings containing tributyl tin in 2008, the development of clean and effective antifouling systems became more important than ever. New nonbiocidal coatings are now in high demand. Scientists have developed new polymers, materials, and biocides, including new elastomeric coatings that they have obtained by improving the original silicone (polydimethylsiloxane) formulation patented in 1975. However, the high cost of silicones, especially of fluoropolymer-modified silicones, has generally prevented their large-scale diffusion. In 2009, traditional antifouling coatings using cuprous oxide formulated in copolymer paints still represented 95% of the global market volume of anti-fouling paints.

The sol–gel nanochemistry approach to functional materials has emerged as an attractive candidate for creating low fouling surfaces due to the unique structure and properties of silica-based coatings and of hybrid inorganic–organic silicas in particular. Sol–gel formulations easily bind to all types of surfaces, such as steel, fiberglass, aluminum, and wood. In addition, they can cure at room temperature and form thin glassy coatings that are markedly different from thick silicone elastomeric foul-releasing coatings. Good to excellent performance against biofouling, low cure temperatures, enhanced and prolonged chemical and physical stability, ease of application, and the waterborne nature of sol–gel coatings all support the diffusion of these paints to efficiently reduce the accumulation of fouling layers on valued surfaces immersed in marine or fluvial waters. Furthermore, sol–gel glassy coatings are transparent and can be effectively applied to optical devices, windows, and solar panels used in lake, fluvial, or marine environments.

Sol–gel technology is eminently versatile, and the first generation sol–gel paints have already shown good performance. Even so, vast opportunities still exist for chemists to develop novel sol–gel derived coatings to both prevent biofouling and enhance the hydrodynamic properties of boat and ship hulls. Moreover, researchers have prepared and applied multifunctional sol–gel coatings providing protection against both biofouling and corrosion. They have tested these in the marine environment with good preliminary results.

In this Account, we discuss some of our new strategies for the controlled functionalization of surfaces for the development of efficient antifouling and foul-releasing systems and summarize the main achievements with biocidal and nonbiocidal sol–gel coatings. We conclude by giving insight into the marine coatings and sol–gel products markets, providing arguments to justify our conclusion that the sol–gel coatings technology is now a mature platform for the development of economically viable and environmentally friendly antifouling and foul-release formulations of enhanced performance.

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1. Introduction

The development of environmentally benign and economically viable technologies to control biofouling on ship and boat hulls is an urgent issue of global relevance because more than 80000 tons of marine antifouling paint are used every year.[1] In the marine and fluvial environments, bacteria, diatoms, algae, and invertebrates rapidly attach to any submerged metal, wood, or polymer surface causing increased hydrodynamic drag. Depending on water temperature, bacteria naturally present in seawater colonize immersed surfaces and form a biofilm within 48 h. These biofilms, especially those induced by sulfate-reducing bacteria, also lead to microbially induced corrosion (MIC) due to H_2S formed by the bacteria.

A fouled hull becomes rough and roughness leads to increased drag and thus either to increased fuel consumption or to reduced speed. After six months, a ship without antifouling (AF) paint will use 40% more fuel due to additional hull drag from fouling.[2] Fuel consumption accounts for up to 60% of the operating costs of a ship. Hence, the benefits of AF paint are readily calculated in energy and monetary terms.[3]

Coming into force in 2008, the 1999 International Maritime Organization (IMO) International Convention[4] on the Control of Harmful Antifouling Systems on Ships currently prohibits the use of tributyl tin (TBT) antifouling coatings that have been used since the end of the 1950s for their excellent antifouling efficiency. By the middle of the 1980s, 80% of the world's commercial fleet ships were painted with the TBT oxide/self-polishing copolymer paint affording optimal constant leaching rates (the bond between methyl methacrylate and ester-bonded TBT groups in seawater hydrolyzes, and the hydrophobic copolymer matrix slowly releases TBT) and longer service life.[5]

The negative aspects of TBT usage became noticeable in 1980, first in France with shell abnormalities in oysters and then in Britain with development of male genitalia in female gastropods causing reproductive failure. Leached TBT was causing global pollution of the seas (and thus of the food chain).[6] Adopted in 2001, the IMO convention prohibiting all application of TBT-containing antifoulants required consent of at least 25 states, representing 25% of the world's merchant shipping tonnage. This was achieved on September 2008. Four years later, the Convention went into force also in the United States.

Not only does it ban the use of toxic tin biocides but it also establishes a mechanism to prevent the potential future use of other harmful substances in antifouling systems. Yet, cuprous oxide, which has largely replaced TBT, is already banned in parts of Scandinavia, and pressure is already high to ban its use also in the US.[7]

In this context, intense research programs aimed toward developing effective environmentally benign and economically viable AF alternatives were undertaken worldwide.[8] Numerous alternative solutions were discovered and reported including algal extracts that inhibit bacterial settlement and natural products as biocides.[9] Foul-release (FR) coatings made of nanostructured and hydrophilic–hydrophobic surfaces, too, are heavily investigated, especially because they provide a nontoxic alternative to biocidal AF coatings.[10] In this context, sol–gel derived functional coatings based on amorphous silicas, already commercialized for many practical applications,[11] are emerging as suitable alternative FR marine coatings.

Formulated to cure at room temperature, the silica-based sol–gel coatings strongly bind to the metal (or polymeric) vessel surfaces via covalent bonds. Compared both with polysiloxanes and with organic polymers such as PEGs, sol–gel derived coatings are more robust, yet they are easily organically functionalized resulting in hybrid organic–inorganic structures that conjugate the chemical and physical stability of glass along with the versatility of organic polymers and organic molecules.[12]

In the following, we summarize the main achievements with sol–gel antifouling and foul-release coatings and provide arguments to justify our conclusion that the sol–gel coating technology is now a mature platform for the development of environmentally friendly AF and FR formulations for marine coatings.

2. Toward Amphiphilic Surfaces

Studying the mechanism of microfouling (and thus not of barnacle attachment) in 1968, Baier first showed that the least favorable surface energy for bioadhesion is around 23 mN m^{-1}.[13] In more detail, the Baier curve of adhesion strength vs surface energy (Figure 1) has a region from 20 to 25 mN m^{-1} where minimal bioadhesion is due to the formation of weak boundary layers between the surface and the (protein) adhesives of fouling organisms.

Hydrophobic surfaces, with surface energies near the Baier's minimum, reduce the ability of fouling organisms to adhere to the vessel, while the movement of the vessel results in removal of weakly bonded foulers by shear stress. Hence, high-activity vessels such as ferries, traveling at high-speed, today often employ hydrophobic poly(dimethylsiloxane) or fluoropolymer surfaces with low surface energy. These nonbiocidal antifouling (AF) or fouling-release (FR) coating paints are of obvious environmental relevance.

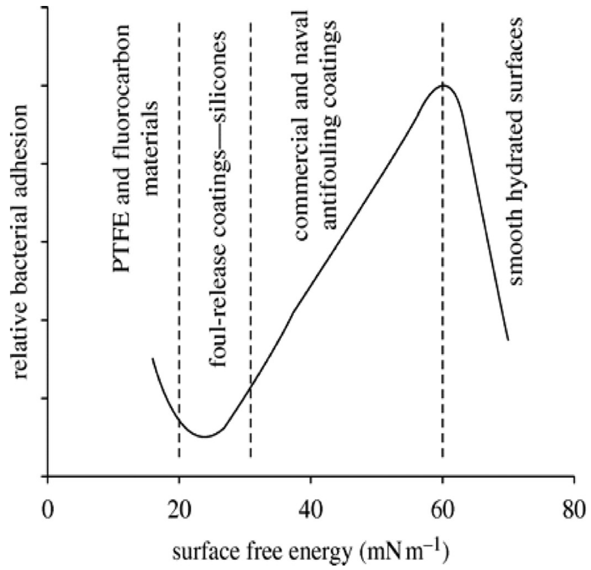


FIGURE 1. The Baier curve. Reproduced from ref 1 with kind permission.

Biofouling, however, is a complex biochemical phenomenon. For example, diatoms bind through hydrophilic proteins, while barnacles bind through hydrophobic adhesive proteins (Figure 2). Hence, also hydrophilic coatings are of interest in AF design because they reduce bioadhesion and weaken protein adsorption.

In general, therefore, effective new AF or FR coatings need to combine within adjacent heterogeneous nanoscale regions the low surface energy effect of hydrophobicity and the resistance to protein adsorption characteristic of hydrophilicity.[1] In brief, new generation nonbiocidal coatings should optimally provide an amphiphilic surface, with both hydrophilic and hydrophobic areas (Figure 2).

First generation commercial AF/FR coatings were based on thick (500 μm), low-surface-energy, low-modulus silicone coatings to minimize adhesion of fouling organisms. Intersleek 700, for example, is the trade name of a commercial silicone-based, low-modulus FR system for large ships invented in 1975[14] whose second-generation commercial version (Intersleek 900, introduced in 2006) makes use of a fluoropolymer-modified silicone with improved FR characteristics against micro- and macrofouling organisms.[15] Due to the amphiphilic surface nature and to the block copolymer structure, the fluoropolymer-modified silicone composition of IS900 provides a chemical "mosaic" that is absent in the silicone-based IS700 version.

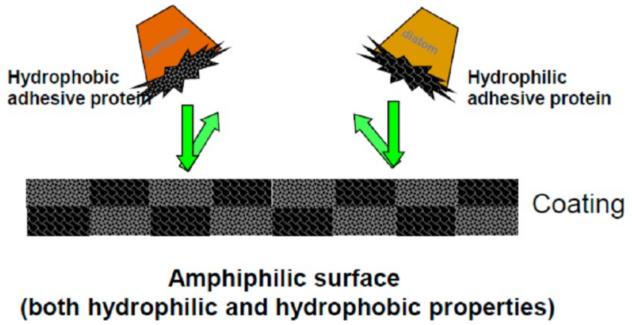


FIGURE 2. An amphiphilic surface such as that provided by second generation silicone coatings is better suited to prevent fouling compared to traditional silicones. Reproduced from ref 1 with kind permission.

Similarly, a methoxy-terminated poly(ethylene glycol) conjugated to the adhesive amino acid L-3,4-dihydroxyphenylalanine (DOPA, a mimic of mussel adhesive proteins selected on the basis of its resistance to protein and mammalian cell fouling) shows superior foul-release performance over a standard silicone coating (the poly(dimethylsiloxane) elastomer Silastic T2) in diatom assays and approximately equivalent performance to T2 in algal zoospore assays.[16]

The approach to developing nontoxic sol–gel coatings similarly relies on the functionalization of the coated surface via doped or undoped ORMOSIL (organically modified silica) nanosol precursors, as detailed in the following.

3. Antifouling and Foul-Release Sol–Gel Coatings

Organic functionalization of the precursor silanes, for example, with alkyl or fluoroalkyl groups generally results in low-energy, smooth (see below) organically modified silica (ORMOSIL)[17] surfaces that can act as ideally suited FR coatings. In another approach to developing environmentally benign sol–gel AF coatings, nontoxic chemical or biological species with antifouling properties are encapsulated in the inner porosity of the silica xerogel from which the biocidal species (or biocidal precursors) are slowly released and prevent fouling.

3.1. Nonbiocidal Sol–Gel Coatings. In the former approach to developing nontoxic sol–gel coatings, the antifouling and foul-release properties are due to functionalization of the coated surface with the hydrophobic ORMOSIL coating. The first successful example was an ORMOSIL hybrid xerogel made of a combination of *n*-octyltriethoxysilane (C8) and tetraethoxysilane (TEOS) in 1:1 molar ratio prehydrolyzed in aqueous isopropyl alcohol (eq 1, unbalanced, in which R is the *n*-octyl group):[18]

$$\mathrm{Si(OEt)_4 + RSi(OEt)_3 + H_2O \overset{PrOH}{\rightarrow} [R\text{-}SiO_nH_m(OEt)_q]_p + EtOH} \quad (1)$$

Actually, the hydrolytic polycondensation reaction never results in the formation of pure silica oxides, and it is

FIGURE 3. The boat whose fiberglass hull was coated with the 1:1 C8/TEOS sol–gel paint after its pulling from the Irondequoit Bay (NY) waters (left) and following mild polishing (right). Reproduced with kind permission of Dr. M. R. Detty.

precisely the fact that $m \neq 0$ and that a large number of unreacted silanol groups exist at the material's surface that gives rise to the large chemical diversity of silica amorphous xerogel applications.[19]

This water-based transparent paint (AquaFast) is simply and efficiently applied at ambient temperature, requiring no pretreatment coat for bonding to different substrata. The painted surfaces are uniform, uncracked, and topographically smooth, which makes them suitable AF or FR coatings. The submerged, durable, and smooth surface is resistant to the glycoprotein that fouling organisms secrete, making it difficult for them to adhere strongly to the surface.

For example, the 1:1 C8/TEOS colorless coating was applied by paint brush to the boat shown in Figure 3 on May 20, 2006. After the 20 μm thick coating had cured for 48 h at ambient temperature, the boat was placed in fresh water for the summer season. The boat was used on weekends and was in harbor the remainder of the time.

Figure 3 shows that when the boat was pulled from the water on September 1, 2006, the light coating of algae and diatoms could be easily removed with brush (and towel). No strong acids or other chemical agents were required. During the winter months, the boat was stored on land under ambient conditions.

The AF/FR performance was maintained during the 2007–2009 boating seasons. The coating was reapplied in the fourth year (2010) and continues to give similar performance (now through the 2013 boating season). For comparison, in the case of recreational boats, traditional biocidal paints are typically renewed every 12–18 months, depending on the boat's use. Since 2006, the 1:1 C8/TEOS xerogel has been applied to over 100 boats in Lake Ontario with similar success rates on most boats. While the removal of algae has been continually successful, the removal of diatom stains has shown some variability with mooring sites.

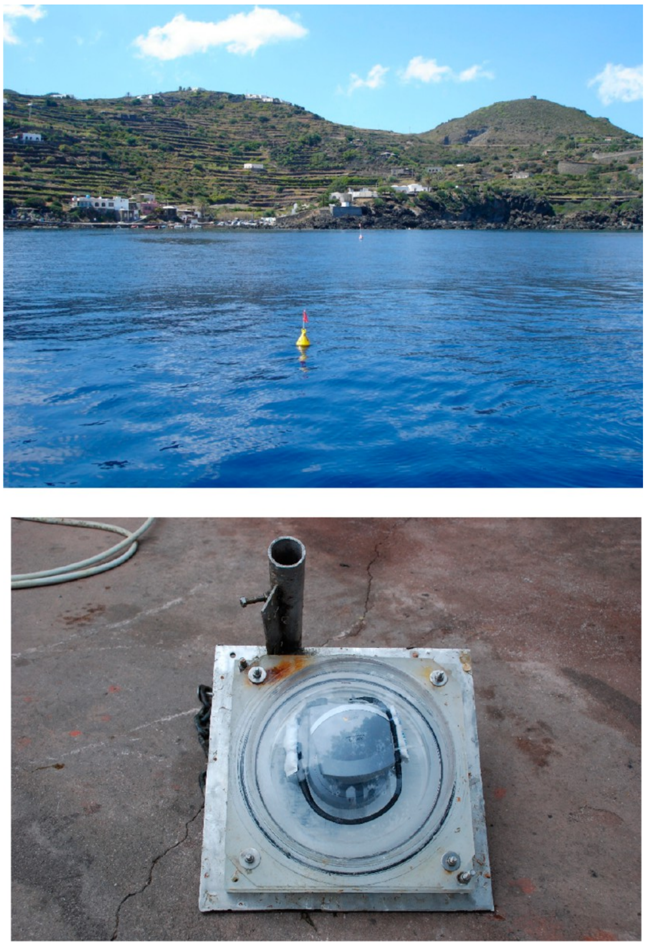


FIGURE 4. The AquaFast paint is successfully employed to protect from fouling the polycarbonate transparent hemisphere protecting the underwater camera monitoring the Cala Gadir archeological site in the Pantelleria's sea. Reproduced from with kind permission of Dr. P. Selvaggio.

The same sol–gel paint has also been used to minimize biofouling on the transparent polycarbonate surface protecting the camera of the monitoring system of an underwater archeological site in the sea of Italy's island Pantelleria (Figure 4).[20] The polycarbonate dome painted and reimmersed in 2007 so far has been mildly cleaned with a towel from minor algal biofouling only once, after 3 years since application of the sol–gel paint. When no protective coating was applied, the polycarbonate dome was rapidly colonized by algae and other organisms. Indeed, this was the case before the sol–gel paint application, when every 40 days a diver was required to pull the system from the 27 m deep sea bottom to clean the dome by removing the fouling organisms, prior to its reinstallation underwater.

Compared with silicone-based AF/FR systems, the xerogel ORMOSIL coatings have tunable surface energies and are thinner (1–10 μm), with much higher elastic modulus. Despite the very low thickness, however, the sol–gel glassy coating has superior wear and chemical resistance. The mechanism of foul release, too, is different.

In the case of Silastic T2, IS700, and IS900, low modulus materials (all with an elastic modulus of 1 MPa) typically applied as thick coatings (typically between 150 and 500 μm), foulers are released by a peeling mechanism involving interfacial slippage with failure at the bioadhesive surface interface. On the other hand, the release of fouling from the much harder (elastic modulus 10^2–10^4 MPa) and thinner silica-based xerogel coatings, which cannot undergo similar deformation, is dependent upon shear.

The fouling characteristics of a series of ORMOSIL surfaces modified with fluorocarbon, aminopropyl, and hydrocarbon groups were examined toward adhesion of bovine serum albumin (BSA), settlement of barnacle larval cyprids, and attachment and release of the diatom *Navicula perminuta*.[21] The fluorocarbon, aminopropyl, and hydrocarbon groups provided a range of surface chemistries and surface energies (γ_S from ~19 to >53 mN m^{-1}), with the fluorinated surfaces showing the lowest surface energies.

The adhesion of BSA to all the xerogel surfaces of this study was weaker than adhesion to a poly(dimethylsiloxane) standard. Furthermore, adhesion of BSA to the xerogels mimicked the Baier curve with adhesion being stronger to surfaces with lower and higher values of γ_S. Barnacle cyprids showed the strongest adhesion to surfaces with higher surface energies, while diatoms showed the strongest adhesion to surfaces of lower surface energy.

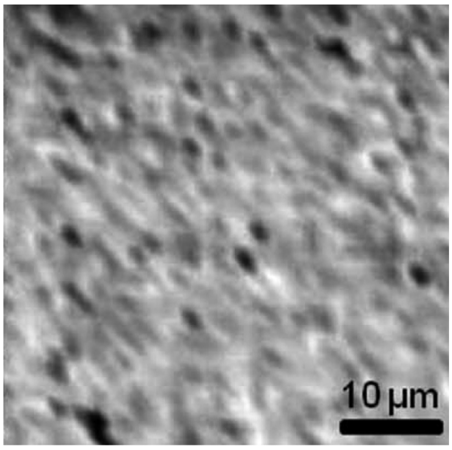


FIGURE 5. Imaging reflectance IR microscopy comparing the fluorocarbon and the hydrocarbon regions in the 1:14:35:5 C18/TDF/C8/TEOS xerogel. Darker regions represent higher C–F and lower C–H intensity, while lighter regions represent lower C–F and higher C–H. Reproduced from ref 23 with kind permission. Copyright 2012 Taylor & Francis.

The xerogel surfaces, furthermore, have very low roughness values on the order of 10^{-9}–10^{-10} m, which is several orders of magnitude lower than the roughness of the IS700 and IS900 coatings (6×10^{-5} m). Reduced roughness is more significant than surface energy in determining the strength of adhesion of diatoms to these surfaces. We remind the reader that surface energy, elastic modulus, and roughness are the three main surface properties determining the settlement and the ease of removal of fouling.[21] The elastic modulus, in particular, influences the fracture mechanism of fouling organisms.

The original formulation (1:1 C8/TEOS) was further improved by incorporating topographical features and chemical inhomogeneities in the resulting xerogel by exploiting the versatility of the sol–gel process. First, a thin (55 μm thickness), hard xerogel incorporating C18/C8/TEOS in 1:49:50 molar ratios (C18 = *n*-octadecyltrimethoxysilane, C8 = *n*-octyltriethoxysilane) was found to give comparable results to a standard 500 μm thick silicone T2 coating.[22] Then, new xerogel formulations incorporating C18, TDF (tridecafluoro-1,1,2,2-tetrahydrooctyl-triethoxysilane), C8, and TEOS in 1:4:45:50 and 1:14:35:50 molar ratios, with values of γ_S within the Baier zone of minimal bioadhesion (21.3–23.1 mN m^{-1}), showed even better performance compared with the improved C18/C8/TEOS formulation, with respect to the release of juvenile barnacles and *Ulva* sporelings.[23]

The latter C18/TDF/C8/TEOS and C18/C8/TEOS xerogel coatings were thus compared with commercial nonbiocidal coatings IS700, IS900, and Silastic T2 elastomers with respect to AF and FR characteristics.[24] The commercial silicone coatings are better in minimizing biofouling, but the xerogel coatings provide improved performance with respect to

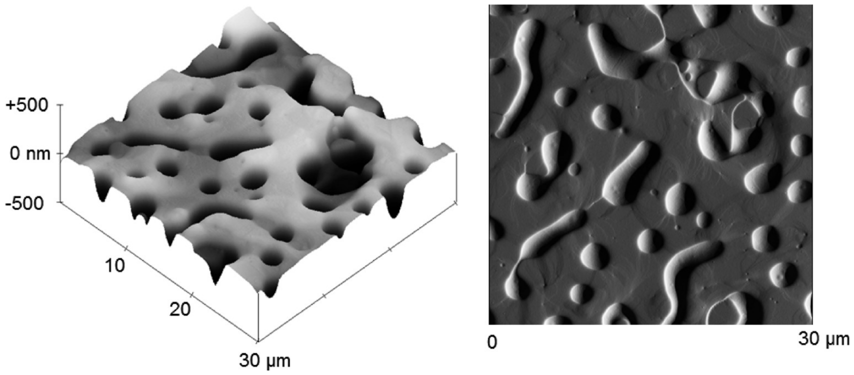
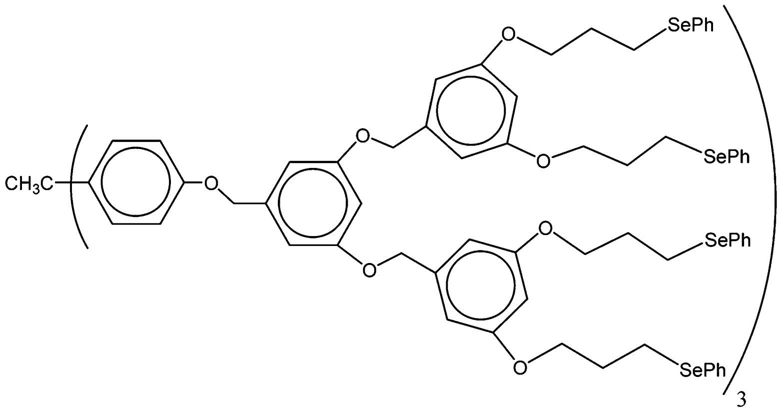
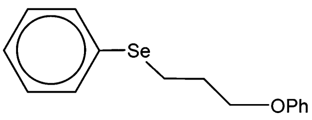


FIGURE 6. AFM height image of 0.5 mol % PEG in 50:50 TDF/TEOS xerogel (left) and AFM image of the 0.5 mol % PEG in 50:50 TDF/TEOS xerogel in amplitude mode (right).



PhSe-12



PhSe-1

FIGURE 7. The organoselenide PhSe-12 (left) shows catalytic activity more than 900-fold greater than monoselenide PhSe-1 (right) for the oxidation of halide salts in the presence of hydrogen peroxide.

microalgal release relative to IS700 and IS900 coatings, as well as the T2 silicone standard.

The chemical "mosaic" presented by the C18/C8/TEOS and the two C18/TDF/C8/TEOS xerogels contributes to the increased fraction of reattached barnacles removed via shear. The latter xerogels, indeed, show islands of harder and softer material, which also appear as chemical inhomogeneities in hydrocarbon and fluorocarbon content. Indeed, while the original C8/TEOS xerogel is topographically smooth and chemically homogeneous, both the C18/C8/TEOS and C18/TDF/C8/TEOS xerogels show a network of nanoscale pores and regions of higher and lower hydrocarbon content in the surface (Figure 5).[23]

Modification of the original C8/TEOS xerogel can be further extended by replacing C8 with TDF (perfluorinating six of the eight carbon atoms) and adding small amounts of poly(ethylene glycol) (PEG). Figure 6 shows AFM images in height and amplitude mode of a xerogel surface consisting of 0.5 mol % PEG (MW = 3200) in an equimolar sol of TDF and TEOS. Features on the order of 10–15 μm are readily discerned and, in amplitude mode, features of different modulus.[25]

With respect to FR behavior, the PEG-containing coatings out-performed the C8/TEOS coatings and were comparable to the T2 silicone standard with respect to the removal of juvenile barnacles.[26] The critical removal stress (CRS) for the 1 mol % PEG/TDF/TEOS xerogel was 0.21 ± 0.02 mN mm^{-2} and 80% (12/15) of barnacles pushed were removed completely. In comparison, CRS for the Silastic T2 coating was 0.15 ± 0.02 mN mm^{-2} and 71% (10/14) of barnacles pushed were removed completely.

3.2. Biocidal Sol–Gel Coatings. The idea to encapsulate bioactive species in the cages of sol–gel silica dates back to the early 2000s when organochalcogen catalysts capable of mediating the reaction between ambient hydrogen peroxide and the halide salts found in seawater were encapsulated in xerogel coatings. In particular, dendrimeric organoselenide and organotelluride derivatives that mimic the activity of haloperoxidases are preferentially encapsulated because they

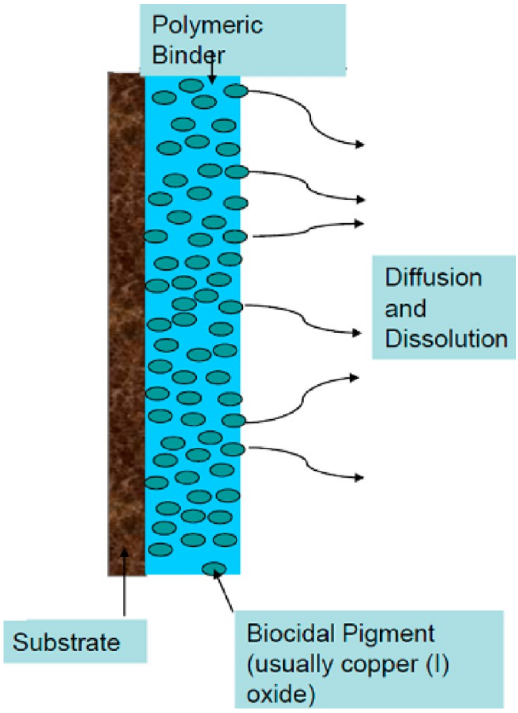


FIGURE 8. Antifouling paints contain a biocide, usually CuO, in a polymeric binder that is slowly released from the paint surface to surrounding waters preventing fouling on the boat's hull. Reproduced from ref 1 with kind permission.

lead to enhanced catalytic activity through cooperative effects (for example, the organoselenide PhSe-12 shows catalytic activity more than 900-fold greater than monoselenide PhSe-1 for the oxidation of halide salts in the presence of hydrogen peroxide, Figure 7).[27]

In detail, near the surface (0–25 m), ocean water contains $(1-2) \times 10^{-7}$ M (0.1–0.2 μM) hydrogen peroxide, originating from the photochemical decomposition of organic matter and from rainwater that interacts with lightning to produce hydrogen peroxide in the rain drops. The concentration of H_2O_2 in harbors can be even higher near the surface when mixing of the surface waters with deeper waters is reduced. Several different kinds of bacteria also produce hydrogen peroxide on a submerged surface. Local peroxide concentrations can be as high as 50 μM.

In the presence of the xerogel-sequestered catalyst, the reaction of H_2O_2 with the halide ions (0.5 M in chloride, 1 mM in bromide, and 1 μM in iodide in seawater) is accelerated producing a monolayer of H_2O_2/HOX on the xerogel surface, namely, a mixture of hydrogen peroxide and hypohalous acid around the boat's hull, which creates a surface inhospitable to settlement of marine organisms.

The sol–gel coatings are very porous and permit ready contact between the dendrimeric derivative and seawater, yet leaching of dendrimeric derivative from the sol–gel matrices does not occur,[28] thereby increasing the activity and lifetime of the coating and reducing the risk of

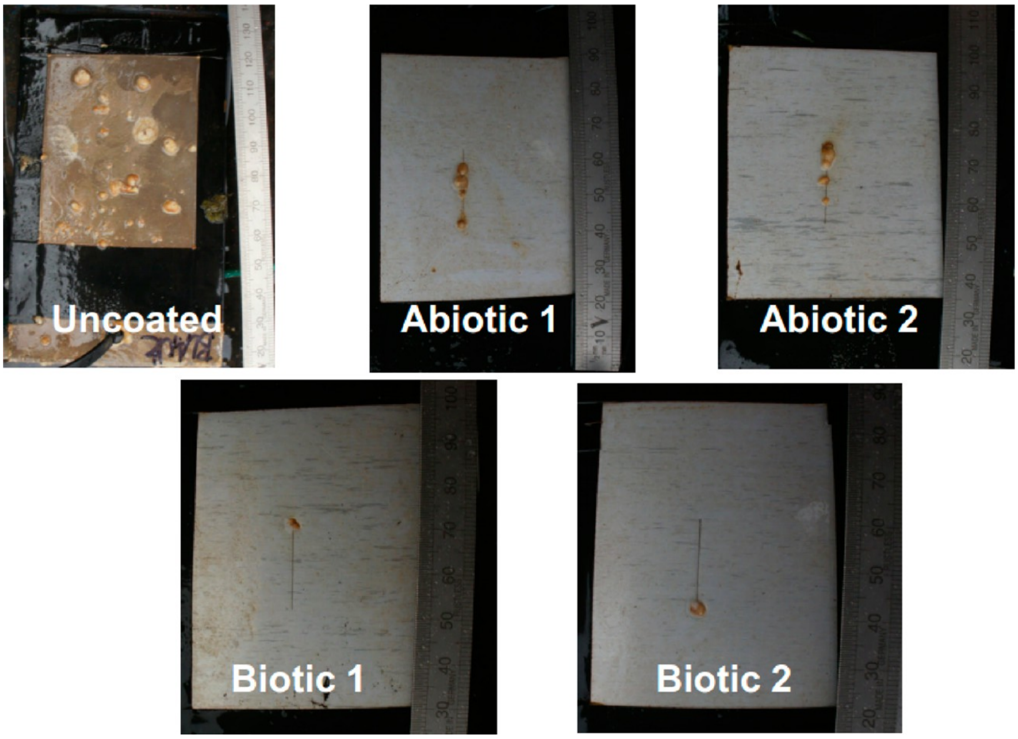


FIGURE 9. Reduction in biofouling around a 2 cm scratch in a 4 week immersion test at Whitby Harbor, UK. Reproduced from ref 33 with kind permission. Copyright 2008 Wiley-VCH.

contamination to the surrounding environment. This was shown,

for example, with xerogel films prepared from sols containing 1:1 aminopropyltriethoxysilane (APTES)/TEOS or 1:9 APTES/TEOS coatings doped with selenoxide or telluride catalyst, giving reduced settlement of cypris larvae of the barnacle *Balanus amphitrite* and larvae of the tubeworm *Hydroides elegans* in the presence of artificial seawater and hydrogen peroxide (5–100 μM) relative to glass controls.[29]

A similar approach based on the photocatalytic formation of H_2O_2 explains the mechanism of action of sol–gel TiO_2-based foul release coatings today commercialized with the ePaint trademark.[30] In this case, the 4% fraction of ultraviolet radiation of visible light in the water column induces the photocatalytic reaction at the coating's surface between water and dissolved oxygen to form hydrogen peroxide, which in its turn effectively deters biofouling from settling.

The sol–gel encapsulation of biological species including enzymes, bacteria and whole cells protects and stabilizes the entrapped dopant species opening the route to immobilized biologicals of prolonged activity and stability.[31] Using therefore a diffusion and dissolution mechanism similar to that of bound biocidal pigments (Figure 8), a sol–gel formulation doped with the nonpathogenic protecting bacterium *Paenibacillus polymyxa* was developed in 2008 by Akid and coworkers for the synergistic protection of metal surfaces from both biofouling and corrosion.[32]

A 6-month field trial conducted in a tidal estuarine environment using coated and uncoated Al sheets showed remarkable improvement in both corrosion and fouling resistance compared with an equivalent abiotic coating (Figure 9).[33]

Named "Biocoat", this approach is based on the slow release of vegetative cells in the marine environment that are formed by the encapsulated bacteria in response to immersion in seawater. Germination then occurs and vegetative cells are leached into water at the interface, where they prevent both fouling and corrosion. Again, the sol–gel coating, which is easily applied by spray coating, is thin (10 μm) and has the typical pronounced hardness of sol–gel silica coatings.

4. Concluding Remarks

Nonbiocidal or nontoxic biocidal coatings are in high demand, and some AF/FR coatings showing good and even excellent performance have indeed been introduced. However, their high cost[34] has generally prevented their large scale employment in the heavily consolidated global marine coatings market (80% of the market owned by five companies).[35] In 2009, one year after the enforcement of the IMO ban on tributyl tin, traditional antifouling coatings using CuO formulated in copolymer paints represented 95% of the global market volume of antifouling coatings (worth $4.7 billion in 2012).[36] Biocidal TBT alternatives, such as pesticide, herbicide, and algaecide (for example, diuron and Irgarol 1051),[37] clearly damage marine organisms and the marine environment.

Sol–gel coatings are a promising alternative to traditional antifouling marine paints. From an economic viewpoint, the cost of the silanes used as precursors of sol–gel formulations today is around $1.5 per kg and continues to diminish. Ten years ago, this figure was 10 times higher, making the introduction of sol–gel technologies a costly and barely practiced alternative in many domains of the chemical enterprise.[38]

From an environmental viewpoint, in contrast to conventional paints using toxic biocides and abundant amounts of volatile organic compounds (VOCs) as solvents, water-based FR sol–gel paints do not contain harmful biocides and make limited use of VOCs mainly present as ethanol, isopropanol, or related small chain alcohols of limited toxicity. From a technical viewpoint too, low surface energy sol–gel paints are advantageous. Compared with thick and more expensive silicone-based AF/FR coatings, silica-based sol–gel coatings are 1 order of magnitude thinner, requiring less material, and are ideally suited to easily coat the surface of all rigid hull types (i.e., steel, wood, fiberglass, aluminum), with which the nanosol precursors form strong covalent bonds.

The nature and amount of marine organisms giving place to biofouling markedly varies depending whether the surface to be protected will be employed in fresh water or in moderate or high fouling marine environments. In this respect, one major advantage of the silane-based sol–gel approach to advanced functional materials lies indeed in the versatility of the sol–gel process.[38]

Akid rightly argues that to replace existing biocide-based antifouling technologies sol–gel AF/FR coatings will require low cure temperatures and prolonged stability.[8] Indeed, the nonbiocidal coatings described in this Account, along with others that are being developed in other research centers,[39] require minimal preparation, rapidly cure at ambient temperature, and show extended life span. For example, a successful nonbiocidal sol–gel coating (CORE Coat 010) efficiently reduces the accumulation of fouling layers on heat exchangers used in offshore oil drilling.[40] The coating is applied to a final thickness of only 5 μm and shows excellent heat conductivity.

Existing sol–gel paints perform already remarkably well. Yet, further improvements in these antifouling and foul-release coatings such as those described in this Account can be expected. For example, the hardness of ORMOSIL thin films (a crucially important parameter for the FR properties) can be varied by 1 order of magnitude by varying the alkylation degree of the ORMOSIL matrix;[41] while optimal sol–gel paints with the right hydrophilic–lipophilic balance (HLB) can be designed to protect the hulls of boats mainly used in specific marine, fluvial, or lake waters.

Indeed, the HLB of sol–gel xerogel silicas can be uniquely tuned to meet requirements of a specific application.[42] Similarly, the use of copolymers to produce sol–gel composites capable of affording the required amphiphilic surfaces is already being applied with success, such as in the case of the PEG-modified fluorinated ORMOSILs mentioned above. Sol–gel AF/FR coatings, we argue in conclusion, will soon be a large segment of the functional sol–gel coatings market,[43] while interdisciplinary research in which chemistry goes along with biology will continuously improve the performance of these alternative sustainable marine coatings.

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BIOGRAPHICAL INFORMATION

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Mario Pagliaro is a chemistry, solar energy and management scholar based at Italy's Research Council in Palermo. He has coauthored more than 100 papers and 16 books on the topics of his research, including highly cited volumes on glycerol, solar hydrogen, and silica sol–gels. Mario is also engaged in spreading new green chemistry and solar energy technologies in Québec and chairs the "SuNEC - Sun New Energy Conference" and the "FineCat - Symposium on Catalysis for Fine Chemicals", two international meetings held every year in Sicily since 2011.

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