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Ecofriendly Antifouling Marine Coatings

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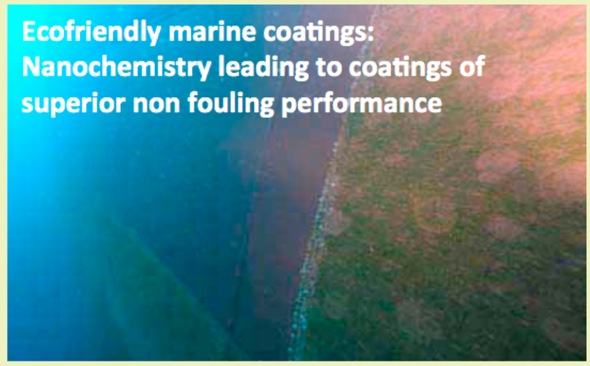
ABSTRACT: Foul release coatings were first used on vessels in the early 1990s, but despite early excitement about the technology, they have had a prolonged modest market share due to high cost and poorer performance when compared to biocidal marine coatings. Recently, these coatings are experiencing a renaissance. Accelerated progress based on nanochemistry has enabled the synthesis of ecofriendly coatings with improved foul release performance, and also antifouling properties. This study aims to provide an holistic overview of the research achievements that are driving the emerging commercially available nonbiocidal technologies for both large and small vessels.



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■ ANTIFOULING MARINE COATINGS

Biofouling. Once immersed in water, no matter whether saltwater or fresh water, within 1 h, an unprotected surface will be subjected to the settlement of fouling organisms.[1] The multistage biofouling process is induced by a layer of microfoulers (such as bacteria, diatoms and microalgae) that colonize the surface within a few minutes following immersion.[1] These attached microorganisms rapidly adsorb organic molecules on the surface, promoting the formation of a biofilm on which multicellular micro- and macrofoulers further strongly settle.[2]

Biofouling is involved in almost every process taking place in water, from water storage through underwater constructions and, of course, ship and boat hulls costing billions of dollars each year only in the sector of transportation.[3] Fuel consumption accounts for up to 60% of the operating costs of a ship, and because a ship without antifouling (AF) paint after 6 months would consume 40% more fuel due to additional hull drag from fouling,[3] AF paints are routinely used to prevent the settlement of marine organisms on the hulls of ships, as well as of smaller vessels independently of the construction material employed (steel, polymeric resin or wood).

Antifouling Paints. For almost 50 years, commercial AF paints used tributyltin (TBT), a broad-spectrum biocide introduced in the marine coatings industry in the late 1950s, formulated in copolymer paints with cuprous oxide.[4] Unfortunately, TBT is highly toxic for many aquatic organisms, well beyond the >4000 species responsible for biofouling, and its prolonged utilization has caused severe damage to aquatic life.[5]

In 2008, the international Convention[6] banning the use of TBT came into force. Industry reacted replacing TBT with surrogate organometal and organic biocides. Zinc pyrithione (zinc complex of 2-mercaptopyridine-1-oxide, ZnPT) and copper pyrithione (CuPT) added to Cu_2O-based biocidal coatings became the main booster biocides. It should be noted that the amount of copper within antifouling paints before and after the TBT ban increased only slightly, because Cu_2O was (and still is) the main biocide used in antifouling paints. Indeed, Cu contamination in coastal marine environments due to copper-containing AF coatings on ship hulls was already a global issue at the end of the 1990s,[7] with elevated levels of Cu being recorded in many coastal areas including ports in the United Kingdom with dissolved copper levels as high as 20 μg/L (20 ppb).[8] Copper concentrations that exceed 3.1 ppb (the U.S. federal standard) affect various life stages of marine organisms including mussels, oysters, scallops, sea urchins and crustaceans.[9]

In 2009, biocidal coatings represented 95% of the global market volume.[10] Four years later, CuPT was the main biocide employed, with over 50% of the market share,[11] even though CuPT is not approved for use by the U.S. Environmental Protection Agency due to high toxicity toward nontarget aquatic organisms.[12] In the United States, therefore, ZnPT formulated with Cu_2O is used in place of CuPT, even though ZnPT and Cu have strong synergistic effects, partly due to the formation of CuPT. This potentially creates increased ecological risk, which means that single biocide toxicity assessments may underestimate the effects of these biocides when in combination.[13]

Today's AF coatings typically provide protection over extended periods, maintaining the surface relatively smooth

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and fouling free up to 90 months.[1] The main biocide-containing antifouling paints on the market are self-polishing copolymer paints (SPC), in which copper is typically formulated at levels between 40 and 75% by weight. The mechanism of action of these paints is based on a chemical reaction between water and the coating (a slowly hydrolyzed methacrylate polymer). The coating polishes as the vessel moves through the water exposing new layers of biocide-containing material at the surface to prevent fouling. However, if the vessel is static for extended periods of time a leach layer will build up on the surface of the paint sealing the copper biocide in to the paint film and preventing further release to the water course.

A typical SPC paint applied in Europe or in Asia is comprised of zinc acrylate (35%) and CuPT (10%). The polymer has good heat and pH stability and low water stability, continuously leaching Cu^+ and CuPT to minimize fouling for the entire lifetime of the paint.

Less Toxic AF Paints. Prior to the TBT ban, a number of less toxic organic biocides had been in use in industry, from SeaNine 211 and Econea through recently developed Selektope. SeaNine (4,5-dichloro-2-*n*-octyl-4-isothiazoline-3-one), a fungicide that effectively prevents fungi growth with rapid biodegradability, poses high risk to dismantle the biotic community through rapid bioaccumulation in nontarget benthic organisms.[14]

Econea is the noncorrosive fluorinated pyrrole tralopyril currently used in several antifouling paints, especially for recreational boats. The substance is effective toward hard foulers. However, it is not capable to prevent the growth of slime and other marine plants requiring the concomitant use of metal biocides such as ZnPT (zinc omadine) or CuPT.[15]

Finally, Selektope or medetomidine is a biodegradable molecule that prevents barnacles settling on the hulls of ships and boats without causing damage either to barnacles or to other animals or plants (one gram of Selektope can replace 500 g of copper).[16] Other biocidal organic pesticides and herbicides such as diuron and Irgarol 1051, which clearly damage marine organisms and the marine environment,[17] were also used in commercial AF paints. But paints containing one of these two biocides are not currently used, as these two biocides were banned in several countries.[18]

Foul Release Coatings. The main alternative to AF paints slowly releasing toxins into water are fouling release (FR) coatings. Free from biocides, these coatings provide a nontoxic alternative to biocidal antifouling paints.[19] Serendipitously discovered in 1975 by Milne, a research chemist at one large coatings supplier, and then extensively researched in the UK (at Newcastle University),[20] the biofouling release properties of elastomeric polydimethylsiloxane (PDMSE) led to the first generation FR coatings (Silastic T2).

The first comprehensive review on tin-free (FR and organic biocides) coatings for the prevention of marine biofouling was published by Yebra and co-workers in 2004.[21] The study emphasized that, once again, there was a lack of knowledge of their environmental effects. Ten years later, researchers in The Netherlands trying to identify the environmental impact of antifouling coatings based on data available from literature, concluded that such impact was "significant" and not yet fully understood.[22]

Comprehensive studies on the progress of marine AF technologies followed,[23] including a thorough survey of the first approaches to environmentally effective AF systems in 2006,[24] accompanied in 2010 by a review on nontoxic coatings in which Brennan and co-workers were concluding that "at this point, no single technology has been demonstrated universally effective at either antifouling or fouling-release".[25]

The aim of this study is not to provide another comprehensive review of the existing ecofriendly AF/FR technologies, but rather to articulate a critical insight into an important domain of sustainability-driven chemical research in which nanochemistry has been (and is being) used to develop a green technology in urgent demand.

Are nonbiocidal nonfouling coatings an effective technology to replace traditional biocidal strategies? Is it realistic to foresee replacement of biocidal paints with green technology?

NANOCHEMISTRY PERSPECTIVE

Nanochemistry is the utilization of synthetic chemistry to make nanoscale building blocks of different size and shape, composition and surface structure that can be useful in their own right or in a self-assembled structure.[26] The development of second-generation FR coatings is one of the most successful examples of contemporary chemical research using nanochemistry to solve a serious environmental issue of global dimension.

For fouling to occur, the surface must have favorable characteristics for organisms to adhere. The glues that hold the organisms to the surface must compete with water for binding to the surface. In the 1960s, Baier discovered that, at least for microfoulers, there is a zone of minimal bioadhesion at a critical surface tension of 22−24 mN/m dubbed by Baier the "theta surface".[27]

The least favorable surface energy for bioadhesion is around 23 mN m^{-1}, with a region from 20 to 25 mN m^{-1} in the curve of adhesion strength vs surface energy (Figure 1) where minimal bioadhesion is due to the formation of weak boundary layers between the surface and the adhesive proteins of fouling organisms.[28]

Surfaces with energies near the Baier's minimum, reduce the ability of fouling organism to adhere to the surface because the thermodynamic cost for water to rewet the surface at this value of surface energy is minimized, while the movement of the

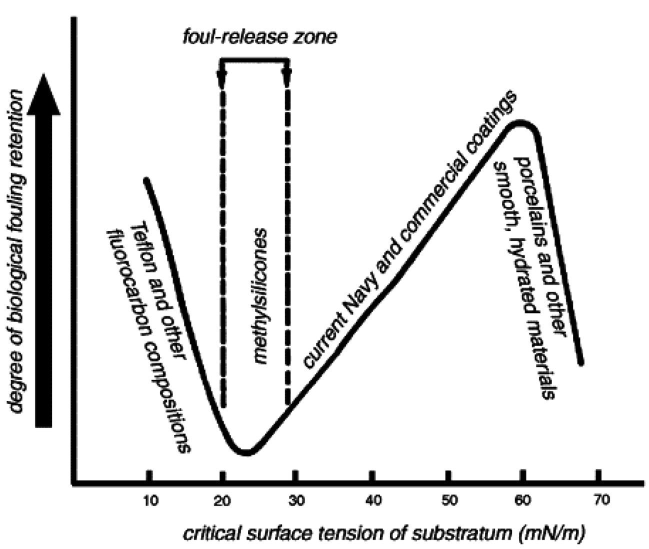

Figure 1. Relative amount of biofouling versus critical surface tension of the substrate. [Reproduced from ref 27, with kind permission.]

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surface results in removal of weakly bonded foulers by shear stress acting on the low-modulus FR coating. First generation commercial AF/FR coatings were based on thick (200−500 μm), low-surface-energy, low-modulus silicone coatings to minimize adhesion of fouling organisms.

Biofouling, however, is a complex biochemical phenomenon. For example, diatoms bind through hydrophilic proteins, whereas barnacles through hydrophobic adhesive proteins. Hence, new AF/FR coatings 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 optimally aim to provide an amphiphilic surface, with both hydrophilic and hydrophobic areas.

Silicone-based Coatings. Built in 2013 in South Korea, the hull of the longest ship in the world (Figure 2) is protected

Figure 2. 488 m hull of the *Prelude* floated out of the dry dock in Geoje, South Korea, where it was built. The hull was coated with 40 000 L of fluorosilicone foul release paint. [Image courtesy of Seokyong Lee/Royal Dutch Shell.]

from biofouling by a fluorinated silicone coating formed after curing of 40 000 L of paint Intersleek 900.[29] Furthermore, besides enhanced AF/FR properties, the frictional drag of surfaces coated with these smooth fluorinated polymer is reduced with relevant benefits in terms of reduced fuel consumption.[30]

Introduced to the market in 2006, this second generation FR coating Intersleek 900 makes use of a fluoropolymer-modified silicone with improved FR characteristics against micro- and macrofouling organisms due to the above-mentioned amphiphilic surface nature and to the block copolymer structure,[31] which provide a mosaic chemical structure absent in the previous PDMSE-based commercial paint. As of 2014, over 350 large ships were already protected from biofouling with Intersleek 900.[32]

Twenty years before, in 1993, the first PDMSE-based coating had been applied to a full vessel in Florida. At the first dry docking of the ship in 1995, the only fouling on the vessel's hull was slime.[33] Consisting of about 10 types of diatoms, the unicellular organisms comprising the slime film, however, strongly adhere on the FR coating (remaining attached to the coating even on vessels at speeds > 50 knots), thereby contributing to increased drag. In early 2012, a major shipping company (Maersk) switched back to biocidal copper-based antifoulings after having used first generation FR paints based on PDMSE.[34] In detail, the company had set the target for 2007 that 60 container vessels should use environmentally friendly biocide-free antifouling paint based on silicone FR technology. The application, however, stopped with 58 vessels due to the development of the slime layer and fast decrease in efficiency of vessels with silicone-based paint.[35]

Commercialized in 2008, a related biocide-free technology uses an hydrogel silicone that provides nonstick properties preventing fouling of the hull of vessels going at speeds above 8 knots.[36] In detail, the Hempasil X3 paint forms a PDMSE coating along with a hydrogel microlayer at the water interface of the coating, which forms a water-absorbent polymeric network over the hull.[37] As a result, fouling organisms perceive the hull more as a liquid rather than a solid surface. This minimizes algae and slime fouling while the silicone backbone retains the self-cleaning properties, namely the release mechanisms and drag reduction ensured by conventional silicone-based coatings, leading to enhanced antifouling performance when compared to conventional AF technologies,[38] with a reduction in a vessel's fuel consumption in the 4−8% range within the first year, depending on the type of ship.[39]

Finally, the PDMSE matrix serves as reservoir for hydrogel precursors that self-regenerate the hydrogel surface layer in case that it is damaged through mechanical abrasion (a known weakness of conventional elastomeric coatings).[40]

Painted with the silicone hydrogel coating, the hull of the 380 m long *TI Asia Ultra* oil tanker remained free from fouling for >13 months (Figure 3), saving each day 12 tons of bunker fuel (at that time priced at $800 per ton).[37]

Figure 3. Ship's hull after 25 months of navigation at 13 knots average speed with 60% activity. The patch covered with silicone hydrogel is clean, whereas the hull coated with SPC copper-based paint is fouled by algae and slime. [Reproduced from ref 37, with kind permission.]

Sol−Gel Coatings. Describing in detail the emerging strategies for the development of environmentally friendly AF/FR systems based on biocidal and nonbiocidal hybrid xerogel coatings obtained via the sol−gel process, we were recently concluding that the technology is "a mature platform for the development of new marine coatings for both the prevention of biofouling as well as to enhance the hydrodynamic properties of boat and ship hulls".[41]

The first successful example was an ORMOSIL hybrid nanosol obtained by hydrolytic polycondensation of *n*-octyltriethoxysilane (C8) and tetraethoxysilane (TEOS) in

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Figure 4. Bayliner 27′ boat pulled from water after 4 months (coated on July 1, and retrieved on November 7, 2005). There is a small white area wiped clean with a finger. After sitting in the sun 1 day, the alga is sloughing off to give a clean surface. No friction or washing required. [Images from Prof. M. R. Detty.]

1:1 molar ratio in aqueous isopropyl alcohol.[42] Trade named AquaFast, the water-based coating of low critical surface energy (γ_S = 21.5 mN m^{-1}) provided reduced settlement of algae and barnacles applied to several recreational boats.

Figure 4, for example, shows that the modest alga biofouling layer formed after 4 months in water on the fiberglass hull of recreational boat coated with a 20 μm thick AquaFast layer (cured for 48 h at ambient temperature), self-removes after exposure to the sun 1 day. No friction or washing with acids was required. In fresh water, for three different fiberglass hulls (not primed), the coating was effective for two seasons (May 1 to October 1). In the third season, algae and diatoms became more difficult to remove.

Besides containing no biocides, the colorless and transparent coating can be applied via roller, brush or spraying to all sort of surfaces, including cameras[43] at ambient temperature, requiring no pretreatment coat for bonding to different substrata. The painted surfaces are uniform, uncracked and smooth.

Although the removal of algae using AquaFast has been continually successful, the removal of diatom stains was less successful. Here the versatility of the sol−gel nanochemistry approach to tune not only the hydrophilic−lipophilic balance (HLB) of the coating but also its roughness becomes evident. Along with (i) surface energy, the (ii) elastic modulus and (iii) the surface roughness are the main surface properties determining the settlement and the ease of removal of fouling.

In brief, the sol−gel process affords low-energy smooth FR coatings comprised of thin organically modified silica layer,[44] in which each of the three parameters above can be tuned for optimal performance.[45] It is indeed enough to add a 1 mol % of long-chain C18 alkyl-modified silane (*n*-octadecyltrimethoxysilane, C18) to the original AquaFast formulation to create a coating surface topographically and chemically inhomogeneous.[46]

The xerogel coatings are thinner (10−60 μm) and have much higher elastic modulus compared to silicone-based AF/FR systems which are typically applied as thick (between 150 and 500 μm) coatings. Despite low thickness, however, the sol−gel glassy coatings have superior wear- and chemical resistance.

For instance, application of a 5 μm thick coating of the recently developed xerogel CORE Coat 010 is enough to effectively protect from fouling production equipment of offshore oil extraction platforms thanks to excellent repellent properties (smooth hydrophobic surface, with a surface energy of 20 mN/m)[47] accessing superior wear- and chemical resistance and heat conductivity.

The mechanism of foul release, too, is different. The elastic modulus crucially influences the fracture mechanism of the fouling organisms. In the case of silicone low modulus materials (all with an elastic modulus of 1 MPa), foulers are released by a peeling mechanism involving interfacial slippage with failure at the bioadhesive surface interface. In turn, the release of fouling from the much harder (elastic modulus 10^2−10^4 MPa) and thinner silica-based xerogel coatings that cannot undergo similar deformation is dependent upon shear.

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. By increasing the surface inhomogeneity on the nanoscale (as it happens with AquaFast Pro) it becomes possible to enhance the antifouling behavior toward hard foulers such as barnacles and diatoms.

In June 2013, a large U.S. vessel (*H. Lee White*) was coated with four 10′ × 10′ patches of AquaFast Pro, the second generation xerogel coating obtained by addition of small percentage of C18 moieties to the original AquaFast formulation for enhanced removal of hard foulers barnacles and diatoms. After one year of navigation in freshwater in the region of the Great Lakes in Northern America, the hull was in ideal conditions, and showed largely reduced fouling relative to untreated hull.

Biocidal Foul Release Coatings. Biocidal technologies can be coupled to new FR coatings technology affording the benefits of both. Hempel, for example, in 2013 commercialized a paint (Hempaguard), which offers both outstanding resistance to fouling during idle periods (up to 120 days) and significant protection against fouling to vessels operating with long service intervals (up to 90 months), which has been the main limitation for first generation FR coatings.

Developed by Yebra and co-workers,[48] the technology uses microencapsulation of the biocide (Sea-Nine, for example) making it compatible with the silicone-hydrogel Hempasil matrix composition introduced by the same company in 2008, which retains its mechanical integrity and smoothness (and FR properties).

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A microencapsulated biocide is added to the original formulation which will be slowly released, ensuring effective antifouling action with far reduced aquatic contamination. The company claims that the new paint releases 95% less biocide than traditional AF paints, with considerable extension of the effective lifetime in the film;[49] while the integration of the AF and FR properties in a single paint makes it applicable to vessels planned to cruise at slow or fast speed almost independently of the level of activity.

Prior to the introduction of the above innovation, the integration of biocides into PDMSE matrices had not been possible because only low amounts of biocides could be used in a silicone coating in order to maintain surface smoothness (due to high level of immiscibility with the matrix composition), and the biocides were rapidly released from the silicone matrix (due to high water solubility).

Photocatalytic Coatings. In the mid 1990s, Morris and Walsh in the U.S. discovered that colloidal ZnO (microparticles of size between 0.10 and 0.50 mm) sensitized with an insoluble photosensitizer (organic dyes such as bianthrone, azulene, terthiophene and hypericin, among others) are able to absorb visible light and effectively catalyze the production of peroxides when in contact with water and dissolved oxygen.[50]

Equipment submerged in natural waters at depths of more than one meter receives significant amounts of light energy only in the blue-green region of the electromagnetic spectrum at around 500 nm. Thanks to the photosensitizer the ZnO pigments, that normally reflect visible light, now absorb visible light with wavelengths between 400 and 700 nm, and, when contacted by water and oxygen, cause the photosynthesis of effective concentrations of hydrogen peroxide.

Hydrogen peroxide is an eminently clean antifoulant that has long been investigated as alternative to common, toxic biocides,[51] as it makes the hull inhospitable to the settling larvae of fouling organisms thanks to fast decomposition into water and oxygen (eq 1) via a free radical intermediate that actively prevents attachment of hard foulants:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(aq) \quad (1)$$

Today, a small U.S. company (ePaint) manufactures some 10 000 gallons per year of photocatalytic AF paints in which the ZnO-based photoactive pigments are formulated with 5 wt % active biocides ZnPT and SeaNine 211 to repel hard-shell organisms (barnacles, zebra mussels and diatoms) through formation of a thin H_2O_2 layer around the hull; and slime and other marine plants thanks to the boosting action of the biocides added in lower amount when compared to Cu_2O typically present in antifouling paints in 40−75 wt %.[52] However, ZnO nanoparticles (widely used in commercial products like sunscreens, coatings and paints) are not only toxic to aquatic biota but were recently found to be toxic on marine algae,[53] due to both the release of zinc ions and to the nanosize of nanoparticles leading to peculiar surface interactions with the cell walls.[54] Hence, a thorough environmental assessment of this technology will take into account the release profile of ZnO incorporated in this paint and its environmental fate.

■ PERSPECTIVE AND CONCLUSIONS

Nonbiocidal, foul release coatings once confined to a niche market share of the global marine antifouling coatings, in a few years became the prime competitor for SPC antifouling using copper, zinc and other toxic biocides. The 2011 academic forecast that in the near future "it is likely that coatings to combat marine biofouling will be based on what are considered to be 'eco-friendly' biocides"[55] turned out to be erroneous. The current (2014) share of foul release coating applications on ship hulls approaches 10%, with all major AF marine coatings now including elastomeric foul release paints in their product portfolio. In 2009, this figure did not exceed 1%.

Relying on the versatile chemistry of silicon polymers (silicones and sol−gel derived silicas), research chemists have used the bottom-up approach of nanochemistry to devise and to reproducibly make nanotextured surfaces capable to prevent the adhesion of many species (fouling-resistant) as well as to release foulants (fouling-releasing), which are now used by some of the largest ships in the world, as well as by offshore platforms and recreational boats.

In brief, rapid progress in nanochemistry enabled the construction of surfaces comprising both hydrophobic and hydrophilic nanosized domains required for optimal foul release of organisms attaching via chemically different proteins; the buildup of an hydrogel nanolayer at the external surface of silicone which confuses the microfoulant organisms; the use of microencapsulated biocides coupled to FR surfaces, and the development of visible-light photocatalytic paints producing environmentally benign H_2O_2 as active antifouler.

Statistics on the volumes used and the value of antifouling paints are not readily available. Recently, the European Chemicals Agency validated[56] data of a 2009 report from industry's representatives, according to which the global market had a volume of 904 million liters in 2012, and a value of about €3.5 billion.[57] Recent market analysis forecast the global marine coatings market to more than double by 2018, growing at >11% annual growth rate over the period 2013−2018,[3] despite the ongoing severe crisis of global shipping (for example, German ship owners, with 1.600 container vessels, the largest stake in the container shipping trade worldwide, reduced the national merchant fleet by 200 vessels between 2012 and 2013),[58] as ship owners keep focusing on cost reduction to face historic high costs of oil-derived fuel.

Marine coatings manufacturers responded by developing AF/FR coatings that increase ship energy efficiency through improved ship's hydrodynamic performance. Two classes of new generation FR modified silicone coatings have actually emerged, namely fluorinated PDMSE (Intersleek 900) and hydrogel-modified silicone (Hempasil X3), including its latest version comprising microencapsulated biocide released at far lower amount (Hempaguard).

The second technology relies on sol−gel hybrid silica xerogels (AquaFast), which are mechanically, physically and chemically more stable and of longer duration when compared to organic polymers,[59] enabling, for instance, application to protect structures in contexts where most organic polymers fail, such as in the case of the xerogel coating (CORE Coat 010) developed by Danish Technological Institute to protect from biofouling offshore oil extraction platforms.

A last issue concerns the economic sustainability of the elastomeric coatings. For example, commercial paints based on fluoropolymer silicones formulated for racing yachts retail in the U.S., under various trade names, for \$110/L (not including the cost of application).[60] Applied onto large vessels that consume tens of thousands of U.S. dollars of fuel per day, the large return on the investment associated with the energy savings mentioned above largely justifies the higher capital expense to apply the new silicone-derived coatings on dry dock.

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For recreational boats, which account for 20% of the antifouling coatings market, this most often will not be the case.

In conclusion, modern chemical research based on nanochemistry has succeeded in providing several antifouling coatings for large and small vessels made of widely different materials (steel, aluminum, fiberglass, wood) that do not contain toxins, limit the extent of environmental damage produced by transportation of nonindigeneous species and consistently improve the hydrodynamic performance of large and small vessels ensuring significant fuel savings.

Progress will of course continue. Newly developed antifouling coatings will, for example, integrate the FR properties of advanced composite polymers with the antifouling action of microencapsulated hydrolytic enzymes capable of preventing settling (by degrading the adhesives of barnacles and algae without killing them[61] or by making entirely leach-proof the coatings using the ivermectin toxin used at 0.1% paint concentration[62]).

In conclusion, the achievements summarized in this account is one of the most relevant examples of how contemporary chemical research, reverting the public perception of chemistry as synonymous with "toxic",[63] is actually solving global environmental problems caused by older chemical technology.

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Notes

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