

Biofouling Control Coatings Utilizing VOC-free Biodegradable Chitothane and Nanotubes Containing Non-toxic Natural Product Repellents

Ronald R. Price* and Jonathan Matias**

* Glen Muir Technologies Inc, Stevensville, MD, glenmuirtek@gmail.com

** Poseidon Ocean Sciences, New York, NY, matias@poseidon.com

nature. Many marine species such as shrimp and crabs

ABSTRACT

Control of biological fouling is a complex problem if non-toxic means are employed, as biofilms consist of a broad range of species and thus require a range of control strategies. Currently the standard for control of biofouling in the marine and aquaculture industries consists of the use of copper based biocides. A novel new approach combines the idea of ablative coatings in conjunction with encapsulated synthetic analogs of natural fouling-repellent compounds. We report the application of a polysaccharide-based coating that is crosslinked with a water soluble diisocyanate which will ablate on fouling and two novel compounds found to control a wide range of marine and fresh water fouling organisms.

Keywords: biofouling, chitothane, nanotubes, non-toxic

1 Introduction

A range of industries from commercial shipping to power generation and aquaculture facilities depend on an efficient and cost effective means to control biofouling. Uncontrolled fouling on marine surfaces increases fuel use which results in higher direct operating costs in addition to producing increased emissions from marine fuels. In power generation facilities, fouling requires additional maintenance which increases the costs of power generation that results in higher rates for electricity. In aquaculture, the failure to control fouling results in the rapid deterioration of netting, holding tanks and water circulation equipment and also increases disease and parasitism of the species being cultured.

Current approaches consist of the use of polymer based coatings that contain copper as an oxide or more commonly as a copper thiocyanate. Some coatings utilize non-metallic biocides such as Sea Nine 211 or other herbicide compounds that are highly toxic to marine species. Due to increased regulation of metallic and toxic biocides it has become necessary to look for low-toxicity or non-toxic means for the control of biofouling. To optimize biofouling control using non- or low-toxicity materials, it is necessary to craft a total system that is not only biomimetic but is capable of being utilized in a commercial setting at a reasonable cost [1].

Chitosan is the second most abundant natural polymer in

utilize protective shells made of chitin, thus, as a marine-based polymer, many species of fouling organisms produce enzymes that break down chitin into sugars that can then be directly utilized as food.

Treatment of the naturally occurring chitin with hydrochloric acid and sodium hydroxide will modify it to form chitosan which is soluble in a 5% acetic acid solution. By crosslinking the chitosan with modified diisocyanates it is possible to form chitothane coatings. These coatings exhibit a range of degradation rates depending on the degree of crosslinking and thus serve as a replacement for the self-polishing coatings that were developed for tributyltin and copper containing paints.

Designed to ablate only when subjected to chitinase enzymes produced by marine fouling organisms, these coatings exhibit their best performance when challenged by fouling species that produce natural chitin degrading enzymes. Thus the greatest self-polishing rate occurs in an environment where fouling pressure is high. The coating does not readily degrade when fouling pressure is low which can extend the lifetime of the coating under some conditions.

Many currently available commercial biocides and natural repellent compounds unfortunately degrade the performance of the base polymer systems in paints when included at the high rates necessary to achieve a long working life. This poses a problem for the formulator who must utilize large amounts of biocide to obtain a long-lasting, effective coating. To solve this problem both microcapsule-based formulations and nanostructured biocide delivery systems have been developed; however, the utilization of large microcapsules results in increased surface roughness and thus increases drag. On the other hand, nanostructured tubules based on halloysite clay form coatings that are easily sprayable yet result in minimal surface roughness. In addition, as 1:1 aluminosilicate clays, they pose no environmental risk to the aquatic environment or to workers who apply or remove such coatings.

To control fouling it is necessary to find compounds that can disrupt the ability of bacteria and other marine species to colonize a surface. By disrupting their means of interspecies communication and their ability to sense the surface they wish to colonize, the fouling cycle may be disrupted, thereby resulting in a fouling free surface. Two compounds capable of acting in such a manner have been developed:

MR-08 is effective against a range of fouling species, and analogs of 2-FNPK[2] are also capable of acting not only as a repellent for marine species but also as an anti-bacterial control against many common bacteria including e-coli.

By combining an ablate-on-fouling coating with a delivery system that acts as a depot to protect the coating from degradation of physical properties such as adhesive strength and scratch resistance, it becomes possible to load the coating with active agent to high levels while still maintaining the physical properties of the coating. This is due to the ability of the halloysite nanotubes to form a composite with the chitohane polymer, thereby increasing abrasion resistance. In addition to providing protection for the delivery system, the chitosan protects the active agent(s) from early degradation by the chemistry of the coating itself or the external environment, thus extending the performance of the active agents. The utilization of natural products that are non-toxic also reduces the build up of resistance in target species which is often induced by toxic agents and thus should result in a longer useful lifetime for the coating.

2 Materials and Methods

Chitosan (Sigma-Aldrich); the polyisocyanate was synthesized in our lab; MR-08 (Poseidon Ocean Sciences); and 2-FNPK (Naval Research Laboratory) were utilized in the production of the coating.

Chitosan was solubilized in a 5% acetic acid solution in deionized water. Chitosan was added at a rate of 3%-5% by weight and was subjected to a high shear mixing environment for 30 min. after which it was filtered through a 300 thread count pillow case to remove any remaining shell or other contaminates from the chitosan solution.

The blocked polyisocyanate is produced by heating deionized water to 78°C and saturating that solution with sodium metabisulfite then cooling that solution to 22°C and adding dropwise toluene diisocyanate at a 1:2 ratio to the sulfite solution. Once reacted (stirred for 1 hr.), acetone is added sufficient to precipitate the resulting blocked isocyanate from the water solution which is then filtered through No. 4 Wattman filter paper utilizing a buchner funnel. Once recovered it is again rinsed with fresh acetone and allowed to air dry.

The active agents (MR-08 and 2-FNPK) are incorporated into halloysite nanoclay that has been surface treated to facilitate the inclusion of the active agent(s). The treated clay is allowed to adsorb the chemical and then subjected to a 30mm/Hg vacuum which entraps the active agent. Following the entrapment the clay and active agent are then added to the chitosan solution at a rate between 30% and 50% by weight utilizing a high shear electric laboratory mixer. Following this step the blocked isocyanate is added at a rate of between 1% and 5% by weight of the chitosan in solution. The surfaces to be protected are then coated and allowed to air dry. As an alternative heat may be

applied to increase the reaction rate.

3 Results

Test panels were exposed either in the marine environment or in a laboratory fish tank that contained a wide variety of fouling species derived from the local marine environment. Following exposure for a period of months the panels were withdrawn for visual testing of the extent of fouling coverage.

After several months of exposure the panels were removed from the water and examined for fouling. MR-08 was tested in the Indian Ocean at Tuticorin, India [Fig. 2] and 2-FNPK was tested in our laboratory fouling tanks [Fig 3].

Neither compound was found to control marine algae or grasses but both offer excellent performance against both marine bacterial fouling and larger fouling species such as barnacles and bryozoans. The addition of 1% by weight zinc oxide to the 2s-FNPK coating eliminated algal fouling [Fig 3].

References

- [1] Novel Biodegradable Biofouling Control Coatings and Method of Formation, Ronald, R.Price, Eric R. Welsh, Linda Passaro, US Patent Application Publication US 2009/0162312.
- [2] Process for the Preparation of 21-Furyl-N-Pentylketone and Longer Chain Analogs., Linda Passaro US Patent Application Publication us 2006/0094888.

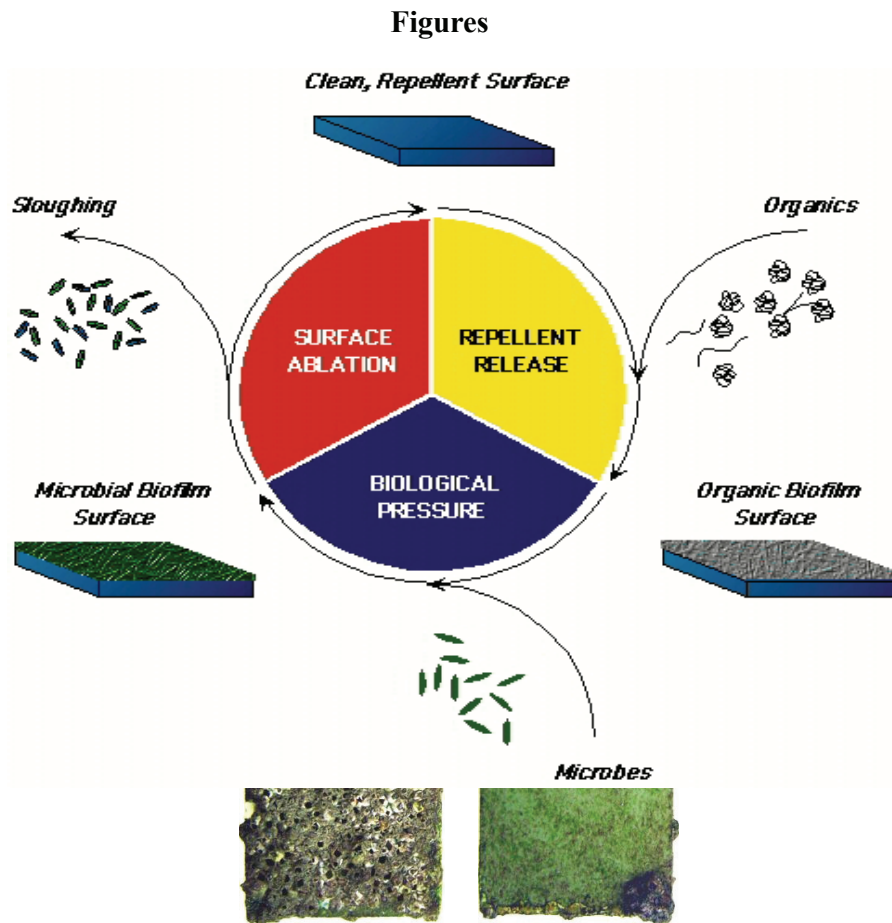


Figure 2: MR-08 panel left panel is control

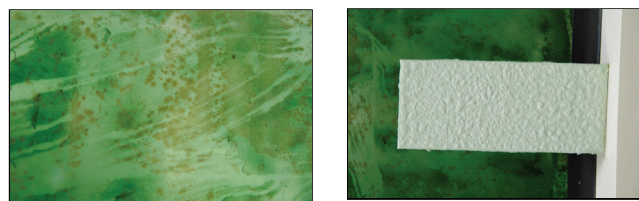


Figure 3: Analog of 2-FNPK (4 months) Right Panel MR-08 (5 months exposure).