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Optimization of antifouling coatings incorporating butenolide, a potent antifouling agent via field and laboratory tests

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ABSTRACT

Rosin-based antifouling paint with the incorporation of butenolide, a promising antifoulant, possesses the potential to deter the settlement of marine organisms on submerged surfaces. With the purpose to extend the antifouling duration, this research investigated the respective contribution of paint ingredients, including butenolide concentrations (5%, 10% and 15%), pigment choices (TiO_2, Fe_2O_3, Cu_2O and ZnO) and binder compositions (acrylic copolymer to rosin at 1: 2.5, 1.5: 2 and 2.5: 1), to the field antifouling performance of butenolide. A raft trial was carried out at Yung Shue O, Hong Kong after the application of antifouling paints on PVC panels. Biofouling dynamics on panel surfaces, such as coverage percentage and biomass accumulation, were monitored until submersion for 6 months to allow for the assessment of antifouling efficiency. Field results showed that butenolide incorporation generally inhibited the settlement of fouling species on the coated panels as demonstrated by the decreased surface coverage and biomass weight. Coatings with 1: 2.5 paints containing 10% butenolide exhibited the best antifouling performance with only 34% of the surface covered by fouling organisms, which mainly consisted of algae and slime. The smallest biomass increase of the fouling community was also observed for 1: 2.5 coatings. An increased proportion of rosin in binder compositions yielded better antifouling performance following the order of 1: 2.5 > 1.5: 2 > 2.5: 1. Laboratory experiments were also conducted to examine the behavior of paint coatings in stirring artificial seawater. Butenolide addition decreased the film hardness and inhibited water uptake, but resulted in weight loss of paint coatings. Along with the gradual release of butenolide, the hardness of paint films increased gradually. Overall, a service life of 6 months, while eliminating the use of heavy metals, highlights the effectiveness of butenolide-incorporated paint formulation, especially 1: 2.5 paint, as an environmentally benign and fouling-resistant candidate for future antifouling application.

1. Introduction

In the marine environment, the undesirable colonization of anthropogenic surfaces by marine organisms, referred to as biofouling, has caused tremendous economic costs globally due to increased fuel consumption and accelerated surface corrosion [1]. In order to control biofouling, coating immersed surfaces with efficacious antifouling paints has been one of the most common measures to prevent the colonization of marine organisms [2]. During the slow erosion of paint into the seawater, the controlled release of biocides will form a protective film on the coated surface after nearby biofouling organisms are repelled or toxicated. Broad-spectrum antifouling biocides, such as tributyl tin (TBT), have been previously incorporated into marine paints and gained widespread application because of their remarkable antifouling performance. However, after decades of use, increasing reports have detected its accumulation in the marine environment and identified long-term impairment to non-target marine organisms due to the persistent nature and high toxicity of TBT [3]. The detrimental effects caused by TBT eventually drove the International Maritime Organization (IMO) to prohibit its use as an active substance in antifouling paint since January, 2003. As alternatives to organotin, diverse antifouling booster biocides have been introduced into paint, such as Diuron, Irgarol 1051, SeaNine 211, zinc pyrithione (ZnPT), copper pyrithione (CuPT) and chlorothalonil [2]. However, in light of their non-selective high toxicity against marine organisms and potential accumulation in seawater, they cannot be considered an ideal long-term solution to biofouling problems. Currently, there remains an urgent need to promote the development of environmentally-friendly as well as efficacious antifouling paint [4].

Of special interest is the recently patented butenolide, 5-octylfuran-

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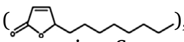
2(5H)-one (), a very promising antifouling compound derived from marine *Streptomyces,* which shows effective inhibition against the larval settlement of major fouling species, such as barnacles, bryozoans and tube-building polychaetes [5]. Compared with other antifouling biocides, the fast biodegradation (half-life: 13.0 h) together with the lowest toxicity against non-target organisms highlight the ecological safety of butenolide and add to its promising application in the antifouling industry [6–8]. After incorporated into paint, the fouling-resistant performance of butenolide has been shown in the field to protect coated surfaces for 3 months [5]. However, in the marine environment, a service life of 3 months is not durable enough to effectively inhibit biofouling accumulation on submerged surfaces. The requirements of frequent cleaning and repainting will inevitably increase expenses, especially considering the time required for dry-docking. Therefore, this study explored various compositions of butenolide paint formulations with purpose of understanding the respective influence of paint ingredients on the field performance of butenolide. Development of an optimized paint formulation was expected to increase the long-term antifouling efficiency of butenolide-incorporated antifouling paint while simultaneously protecting the marine environment from the undesired off-target impacts associated with traditional antifouling paints. Additionally, laboratory tests, including the measurement of leaching rate, erosion rate and water uptake, were also carried out to supplement the screening of the field test.

2. Material and methods

2.1. Chemicals

Butenolide with a purity > 99% was synthesized by Medicilon, Inc. (Shanghai, China). Chemicals for the measurement of butenolide concentrations were of high performance liquid chromatography (HPLC)-grade. The other chemical agents used in this study were of analytical grade.

2.2. Paint formulations and production

In order to figure out the respective influence of paint ingredients on the field performance, different paints were formulated by varying butenolide concentrations, pigment types and binders' ratio (Table 1). Butenolide served as the antifouling agent. To examine the concentration-dependent effect, different amounts of butenolide (5%, 10% and 15% by weight) were, respectively, added to the paint formulations. The pigments, including titanium oxide (TiO_2), cuprous oxide (Cu_2O), ferric oxide (Fe_2O_3) and zinc oxide (ZnO) with distinct solubility (highly insoluble: TiO_2, Fe_2O_3; sparingly soluble: Cu_2O, ZnO), were added to the paint formulations, respectively, to study their possible effect on the paint performance. Insoluble acrylic copolymer and soluble rosin were used as the binder. Different binder compositions, which might affect the leaching of antifoulant and erosion of paint film, were also formulated, respectively, with acrylic copolymer and rosin ratio as 1: 2.5, 1.5: 2 and 2.5: 1. PVC panels without paint coating and paint formulations without antifouling compounds were used as negative controls. In addition, two commercial antifouling paints (White: Seajet 038 alusafe; Red: Seajet Seagrandprix 2000) were purchased from Chugoku Marine Paints and also used as positive controls for field test.

All the ingredients, including binders, antifoulants, pigments as well as the extender ($CaCO_3$) and additive (bentonite), were first dispersed efficiently at 1500 rpm for 30 min and then minced twice through a laboratory scale ball mill (150 mL jar) to achieve a fine particle size of around 20 μm. Three coats of each paint formulation were applied onto sandblasted and degreased polyvinyl chloride (PVC) panels (200 mm × 150 mm) using brushes and allowed to dry for 24 h between each application. Each paint formulation contained three replicate panels (n = 3) and the total dry film thickness was measured to be 80–100 μm. No more than 48 h elapsed before the panels were immersed into seawater for the field or laboratory tests.

2.3. Field performance

To field-test the antifouling efficacy of butenolide, three panels for each paint were hung to the floating rafts of a fish farm at Yung Shue O, Hong Kong (114°21′E, 22°24′N) where the rafts are heavily fouled. The panels remained constantly immersed 50 cm deep in the seawater during the observation period lasting from December 2013 to June 2014, when the fouling challenge is most serious with bryozoans, tubeworms and barnacles flourishing. Because the fish farm is entirely floated on the seawater offshore, the immersed depth of panels was not affected by tide waves. The fouling species and extent of fouling were checked and photographed every week. The coverage percentage of submerged panels by fouling species were then quantified with the help of the image processing package Adobe Photoshop 7.0 (Adobe Systems, San Jose, CA) through pixel analysis without consideration of the 1 cm edge around the panels. Additionally, the fouling organisms were stripped from each panel and weighed upon termination of the raft trial to assess the biomass accumulation. The antifouling efficacy of each paint formulation was assessed according to the French Standard (NFT 34-552 September 1996) and previous research [9], which takes into account both the coverage percentage and fouling species. An efficiency parameter N was calculated as:

$$N = \Sigma I \times G$$

where I represents the fouling intensity as indicated by the surface coverage and G represents the fouling severity as indicated by the fouling species.

2.4. Laboratory test

In order to gain a deeper understanding of paint behavior in the seawater, the panels of each paint (n = 3) were immersed into 7 L artificial seawater (Table 2, pH 8.1) for 30 days of observation. The

Table 1
Ingredients of different paint formulations.

Components (g)		0%	5%	10%	15%	Ti −	Ti +	Fe −	Fe +	Cu −	Cu +	Zn −	Zn +	1: 2.5	1.5: 2	2.5: 1
Binder	Acrylic copolymer	15	15	15	15	15	15	15	15	15	15	15	15	10	15	25
	Rosin	20	20	20	20	20	20	20	20	20	20	20	20	25	20	10
Pigment	TiO_2	20	20	20	20	20	20							20	20	20
	Fe_2O_3							20	20							
	Cu_2O									20	20					
	ZnO											20	20			
Antifoulant	Butenolide	0	4	8	12	0	8	0	8	0	8	0	8	8	8	8
Extender	$CaCO_3$	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Additive	Bentonite	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Solvent	Xylene (mL)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100