REPORT

Studies on nano-additive for the substitution of hazardous chemical substances in antifouling coatings for the protection of ship hulls

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Abstract: Adhesion and growth of biofouling organisms have severe influence on the reliability, service life and environmental adaptability of marine ships. Based on the bactericidal capacity of cuprous oxide and photochemical effect of nano-additive, environment-friendly and efficient marine antifouling paints were prepared in this study. The evaluation of the antifouling paints was carried out by the laboratory method using bacteria and phytoplanktonic microorganisms as target organisms, as well as measurements with panels in shallow submergence in natural seawater. Results showed good agreement of all the tests, indicating the remarkable antifouling performance of the paints. To our knowledge, this was one of the first systematic studies on effects of nano-additive for the substitution of hazardous chemical substances in antifouling coatings for the protection of ship hulls by measurements on bacterial inhibition, algal adhesion and growth of large organisms.

Keywords: Biofouling; antifouling coating; nano-additive; photochemical effect.

INTRODUCTION

Marine animals, plants and microorganisms generally adhere to surface of ship hulls serving in the marine environment, which is termed as biofouling. It is estimated that resistance of the ship covered with 5% surface area of marine biofouling organisms is equivalent to twice of that with clean surface, which costs 10% increase of the fuel consumption. Additionally, biofouling directly threatens to the reliability, service life and environmental adaptability of marine ships, resulting in huge economic losses (Woods Hole Oceanographic Institution (WHOI), 1952). Despite of the advent of novel technologies, more environmentally friendly antifouling technologies involving antifouling coatings, seawater electrolysis, heavy metal electrolysis, water filtration and conductive coatings, synthetic biocide-based antifouling paints are still regarded as the most efficient solution for the protection of ship hulls against marine biofouling (Yebra, *et al*., 2004). In order to prevent the adhesion and growth of antifouling organisms, toxic substances such as copper, arsenic, lead, mercury and tin compounds have been used for antifouling paints for a long period of time. Although marine fouling organisms can be reduced or eliminated, the release of hazardous substances also causes serious problems to the environment and human health. As tin-based antifouling paints have been banned by the International Maritime Organization (IMO) worldwide in 2003, copper-based antifouling paint is currently dominated on the national market. However, some problems also arise with such antifouling paints: copper ions prone to aggregate and settle during storage and transportation process, leading to the instability of cuprous release rate; copper in the antifouling paints used individually has no effect on diatoms and other algae, which should be integrated with other auxiliary toxic agents (Kenneth Schiff, *et al*., 2004), while the resultant composite toxicity is almost equal to tin-based compounds; also a large number of cuprous accumulation in the harbor may reduce the activity of the enzyme inside marine organisms, causing the increase of biological mortality; even copper ions at low concentration may have influence on the health of animals and plants through the enrichment affect of food chain, causing damage to the ecological balance (Kallio, Alajoki, 2006). For example, the copper-based antifouling paint increases the paramoebae prevalence on netting of sea cages, and induces a higher AGD prevalence of reared Atlantic salmon within these cages (Douglas-Helders, *et al*., 2006). Therefore, research and development of low toxicity and effective marine antifouling paints is imperative.

Nanotechnology is deemed to have the potential to bring about fundamental changes in products and processing technology and a number of research studies have been focused on the potential benefit of nanotechnology with regard to environmental issues. Nano-materials are usually designed to substitute for hazardous substances in antifouling paints caused by a physical property: nano-structured surfaces prevent biofilm formation and

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bacterial adhesion as well as the attachment of larger organisms in view of reduction of adhesion. However, recent research indicates that nanoparticle, e.g. CuO, ZnO and TiO_2, owes their self-toxicity to growth inhibition of algae (Villem Aruoja, *et al*., 2009, Hund-Rinke *et al*., 2006, Baveye *et al*., 2008).

In this work, in view of the problems of traditional antifouling coatings, nano-material with photochemical effect was utilized for antifouling paints to reduce the copper content and substitute hazardous chemical substances, so as to provide a possibility for the development of stable, efficient and environment-friendly antifouling paints. Additionally, evaluation of the antifouling performance was carried out by laboratory method and test with panels in shallow submergence.

MATERIALS AND METHODS

Preparation of antifouling coating

Copolymer of vinyl chloride and vinyl isobutyl ether MP25 (BASF) was used for film forming of antifouling paints, anatase titanium dioxide and zinc oxide were used as nano-additives, and other raw materials were commercial. According to the formulation shown in table 1, dispersing agent, nano-additives were added to the solvent. Then the dispersed slurry obtained with all components as well as chlorinated polyether resin solution were mixed and ground sufficiently to obtain the desired painting.

Table 1: List of the reagents for antifouling paint preparation

Reagent	Mass concentration. %
Nano-additive (TiO_2 & ZnO)	5~20
Cupprous oxide	10~30
Copolymer of vinyl chloride and vinyl isobutyl ether MP25	20~30
Rosin	3~5
Solvents and additives	20~40
Other pigments and fillers	5~10

Anti-microbial activity test

Two bacteria, *Staphyloccocus aureus* and *Escherichia coli*, provided by microbiology laboratory of Ocean University of China, were used for anti-microbial effect test of the painting. Bacterial colony was separated and incubated in culture medium for more than 24h at certain temperature; afterwards the medium was diluted with physiological saline to 5‰ bacterial suspension.

Sterile culture medium was added to the culture dish, and 0.1ml 5‰ media with *Staphyloccocus aureus* or *Escherichia coli*, separately, were incubated and spread homogeneously. A group of painting samples and a blank one were set up in each dish with the help of sterile pipette. All the media samples were kept in an incubator at 37^oC for 24h. Then inhibition zone diameters were determined and averaged so as to make comparison of the antibacterial activity of the samples.

Settlement resistance test

Two phytoplanktonic microorganisms, diatom and spore were used as target organisms and two groups of tests were carried out to investigate their settlement to the coating. Firstly the prepared paints were coated on glass slides, dried for 48 hours. Then the coating samples and a blank slide were put into the 250ml glass flask, adding 200mL culture media for diatoms or spores, and then 2mL filtered diatoms or 10ml spores were incubated at room temperature for 4d, separately. Fluorescence microscopy was used to observe the settlement of the organisms and more than six counted numbers in vision area of coating were recorded and averaged.

Antifouling test in natural seawater

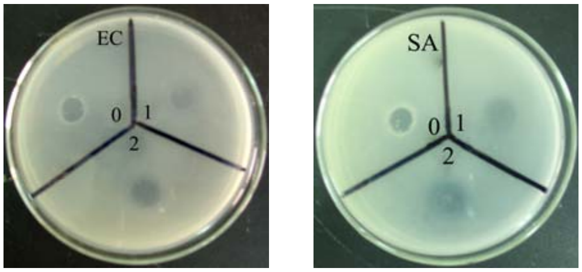
Escherichia coli (EC)

According to GB/T5370-2007, Q235 steel plates with dimension of 350mm×250mm×3mm, used for evaluation of the antifouling panels in shallow submergence were sandblasted prior to spraying anticorrosion and antifouling paints, with a film thickness of 100~150μm for the latter. The test location for shallow submergence was on a floating raft near Baisha Island in Zhoushan, East Sea of China. The settlement of organisms to the panels was periodically observed throughout a biological growing season.

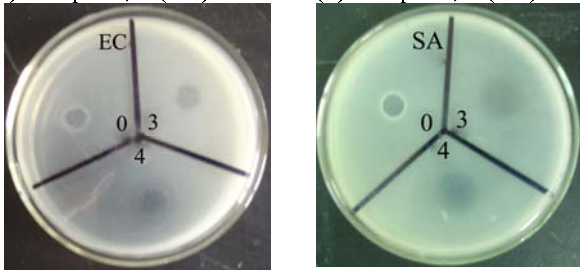
RESULTS

Fig. 1 shows the photographs of inhibition zone for the painting sample 1, 2, 3, 4 with *Staphyloccocus aureus (SA)* or *Escherichia coli (EC)* and the comparison of the diameters is shown in table 2. Wherein sample 1, 2, 3, 4 represented for a series of antifouling paints according to the formulation shown in table 1, with different concentration of components (herein sample 3, 4 contained higher concentration of copper ions than sample 1, 2). It was observed in fig. 1 and table 2 that the series of paints showed remarkable anti-microbial activity to the bacteria. The average diameter of inhibition zone for the blank sample with EC is 8.25mm while for the paint samples, 11.14mm~15.66mm, with a highest increasing rate of 90%. It was the same case for the comparison of paint sample with SA and the highest increasing rate was 78%.

As was known with fluorescence microscopy observation (an example in fig. 2), the average number of settled diatoms in the settlement resistance test was 3 or less, with a slight difference between the coatings, while the average number was 781 for the blank sample within the same vision area. Very similar to the above result, the number of the spores adhering to the coatings varied little, 2 or less, but much lower compared to that of the blank sample, nearly 200. Therefore, it was suggested that the all the coatings had inhibited the settlement as well as the growth of diatoms and spores in the experimental conditions. Morphology of panels with antifouling paints, sample 1, 2, 3, 4 mentioned above, in shallow submergence for different exposure time was shown in fig. 3. In initial stage, stable. leached layer with apparent inhibition to marine organisms gradually emerged. The local area had undergone a growing season for algae, and the panels during this period were covered with small algae (75d). However, these algae had a very low adhesive force and a short growth cycle, which disappeared soon afterwards. About 100 d later, almost no fouling organism was visible on the experimental panels even after the growing season for barnacles, the main fouling organism in this sea area. Examples of panels with different painting based on formulation containing cuprous oxide but no nano-additive were also tested in the same condition for comparison, and the result was shown in fig. 4, which were covered with algae and barnacles representing failure of the antifouling paints. In terms of the color change of the panels during the exposure period, the color of the panels in initial stage was all bright red, indicating the presence of cuprous oxide. However, in the last stage, color of coating 3 #, 4 # changed little, suggesting a stable and slow release of cuprous ions; while coating 1#, 2#, with a lower concentration of copper ions turned to pale or white (color of nano-additive), revealing that the cuprous ions in the coating released completely, but the coating still maintained its antifouling effect. The possible explanation and discussions are as follows.



(a) Sample 1, 2 (EC) (b) Sample 1, 2 (SA)



(c) Sample 3, 4 (EC) (d) Sample 3, 4 (SA)

Fig. 1: Photographs of inhibition zone for painting sample 1, 2, 3, 4 with *Staphyloccocus aureus (SA)* or *Escherichia coli (EC)*

DISCUSSION

As is already known cuprous oxide serves as a common biocide in the reagents of the antifouling paints. Literature (Francesca *et al*., 2012) suggested that cuprous ions may be able to change membrane permeability, induced apoptosis and altered the activity of hydrolases. The copper-based coatings were designed to slowly release copper, in the dissolved and most toxic form, so as to retard growth and maintain a smooth underwater surface. Copper (I) was the principal biocidal component of most antifouling paints, mainly in the form of copper oxide (Cu_2O) or copper thiocyanate (CuCHNS). Besides, the settlement of the copper bound to organic material with high molecular weight in sediments and its dissolved and harmful form (Ranke, J., *et al*., 2000), in fact, the existence of cuprous resistant bacteria was well known (Marszalek, *et al*., 1979). and it had been shown that cages treated with cuprous oxide paint harbored four times more bacteria compared to nets treated with other antifouling paints or untreated nets (Dempsey, 1981). Novel compounds such as irgarol 1051 and diuron were used in antifouling paints normally in combination with copper. However, the ecological damage and environmental pollution caused by chemical biocides was obvious for their ecotoxicity or degradation difficulty in natural seawater (Gatidou, 2007).

Table 2: Comparison of inhibition zone diameters (mm)

Paint No. Bacteria	Blank	1	2	3	4
EC	8.25	13.03	15.66	11.14	13.23
SA	8.07	13.22	14.35	14.23	13.25

Anatase titanium dioxide had a remarkable photochemical performance, as was widely investigated and proved by scientists in many research fields (Jurgen, Joydeep, 2005). Most of fouling organisms, animals, plants and microorganisms, preferred to concentrate in the tidal zone or upper immerse zone of marine environment, where the sunlight was sufficient for their metabolic activities. And the antifouling coatings were also utilized in this area of the ship hulls accordingly.

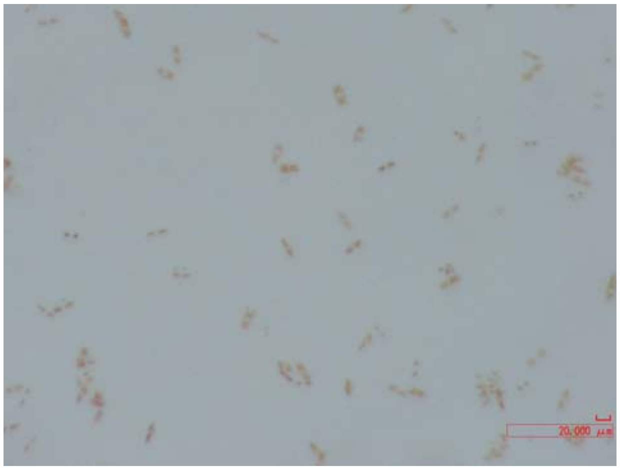
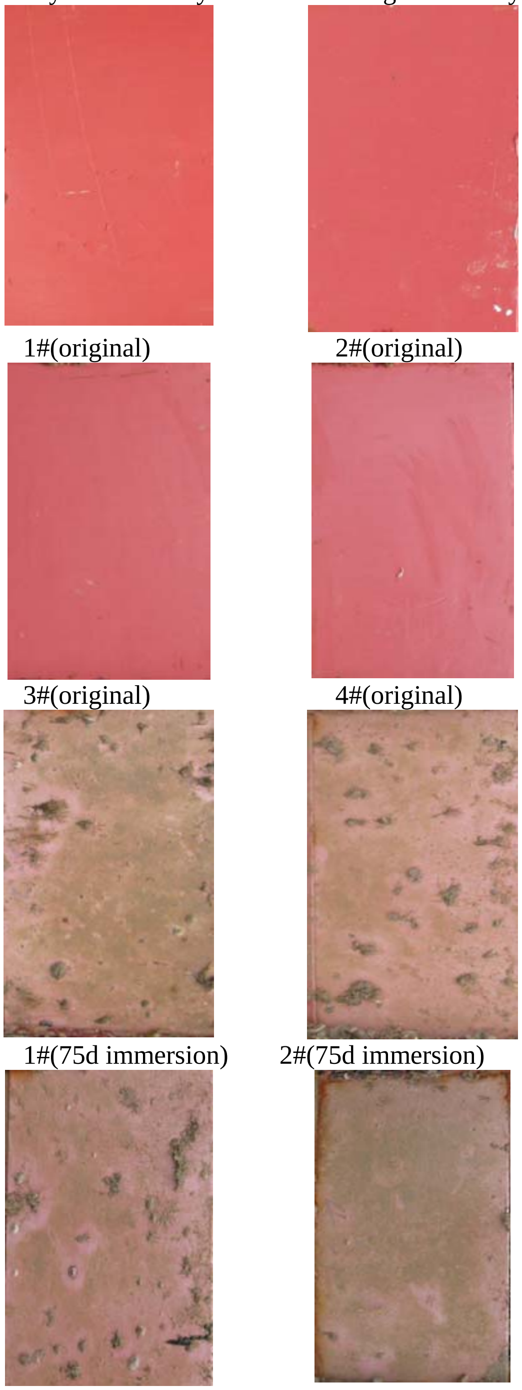


Fig. 2: Fluorescence microscopic photographs of attachment of diatoms to the glass slide

Hund-Rinke and Simon (2006) studied 25 nm and 100 nm TiO_2 particles in regard to their toxicity to the green algae *Desmodesmus subspicatus* and found the smaller particles to be more toxic. Further more, Villem Aruoja (2009) studied that nano TiO_2 appeared more toxic than the bulk form under test conditions. It was assured that TiO_2 nanoparticle aggregates reduced the light available to the entrapped algal cells and thus inhibited their growth. Baveye and Laba (2008) suggested that aggregation of TiO_2 nanoparticles may have toxicological implications, which may result in very dissimilar biological activity.

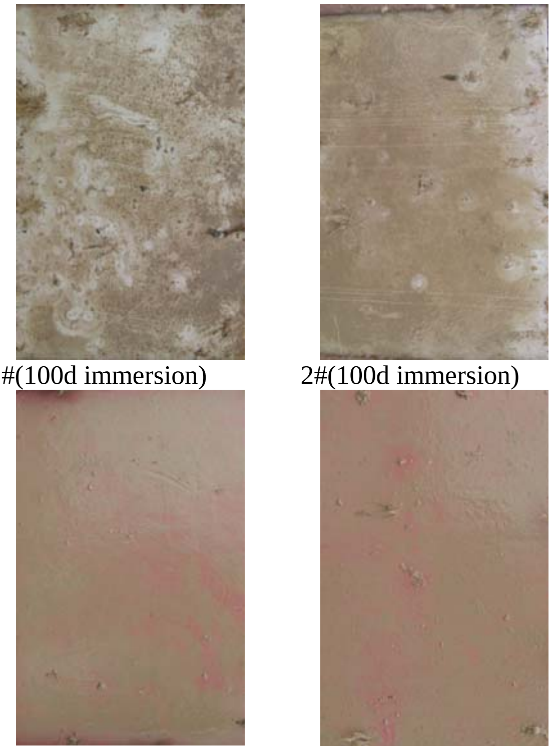


1#(original) 2#(original)

3#(original) 4#(original)

1#(75d immersion) 2#(75d immersion)

3#(75d immersion) 4#(75d immersion)



1#(100d immersion) 2#(100d immersion)

3#(100d immersion) 4#(100d immersion)

Fig. 3: Morphology of antifouling panels in shallow submergence for different exposure time

Another possible mechanism of toxicity of TiO_2 suspensions might involve generation of hydroxyl radicals by TiO_2 nanoparticles under visible light. In the presence of light, the photochemical effect of anatase nano-titanium dioxide from excitation of the light enabled a variety of redox reactions, resulting in a large number of hydroxyl radicals, excitation electrons and holes, which caused damage to the cell wall as well as morphological and functional change of the bacteria. The resultant hydroxyl radicals and reactive oxygen with strong oxidation capability were supposed to kill most microorganisms as well as to decompose organics to carbon dioxide and water or other inorganics easy to remove.

TiO_2 nanoparticles in combination with UV light (370 nm) had been shown to inactivate algae Anabaena, Microcystis, and Melosira (Kim *et al*., 2005) as well as to destroy the cell surface architecture of blue-green algae *Chroococcus sp*. (Hong *et al*., 2005). Toxicity of TiO_2 towards bacteria in the presence of light was also referred to photochemical reactive oxygen species (ROS) generation (Armelao *et al*., 2007).

In this work, the inhibition effect of the coating was systemically investigated involving the EC and SA, diatoms and spores, algae and barnacles, which separately represented for the bacteria, soft fouler and hard fouler emerging in chronological sequence during the colonization of the fouling organisms according to their nature. The series of paints showed good inhibitive performance for all the organisms, indicating a good antifouling effect.

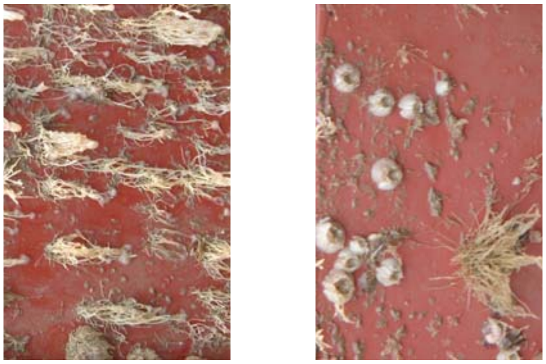


Fig. 4: Morphology of antifouling panels covered with algae and barnacles for comparison

In the prepared coating system, copolymer of vinyl chloride and vinyl isobutyl ether was an environmental-friendly alternative for chlorinated rubber considering of the release of carbon tetrachloride. Besides, it was also designed to strengthen the flexibility and adhesion of the whole coating film. Zinc oxide with a certain degree of solubility in seawater, as rosin, enabled to stimulate the exudation of copper ions so as to regulate the leaking rate. In general, the utilization of nano-additives to reduce the copper content and substitute for toxic antifouling reagents contributed to the development of stable., efficient and environment-friendly antifouling paints.

CONCLUSIONS

In this work, bactericidal capacity of cuprous oxide and photochemical effect of nano-additive were combined for the preparation of antifouling paints. The purpose for reduction of cuprous concentration was achieved with nano-additive substitution for other auxiliary toxic agents. Antifouling paints were prepared and proved to be efficient by experimental methods and tested in natural seawater, which provided a possibility for the development of stable, efficient and environment-friendly antifouling paints especially sui Tab. for the protection of tidal-zone ship hulls.

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