



NOTE

Development of Environmental Friendly Antifouling Coatings

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Received: 13 November 2013;

Accepted: 16 December 2013;

Published online: 23 June 2014;

AJC-15395

Marine structures such as platforms, jetties and ship hulls are subject to diverse and severe biofouling. This article introduces briefly the process and damage in respect of marine biofouling. The use of antifouling coatings for protection from the marine environment has a long history. By considering the historical and current approaches to antifouling systems, this paper presents the use of modern approaches to the design of an environmentally acceptable, broad spectrum antifouling system for a large ship's hull.

Keywords: Marine biofouling, Antifouling coatings, Environmental friendly.

The fouling process consists of four general stages: polysaccharides, proteins, proteoglycans and inorganic compounds in the ocean accumulate on the surface and give rise to the so-called conditioning film¹. This process is essentially governed by Brownian motion, electrostatic interaction and van der Waals forces. Rapidly developing bacteria and single-cell diatoms settle on this modified surface. Then protozoa and rotifers adhere and form a microbial biofilm².

Biofouling causes severe problems to governments and industry with severe economic consequences particularly on vessels. It increases the hydrodynamic drag, fuel consumption and docking time^{3,4} leading to considerable economic losses for centuries. It could significantly accelerate the metal corrosion rate because the oxygen supplying situation changes to form oxygen concentration difference battery⁵. Marine fouling organisms attached on the aquaculture box decrease the flow of the water exchange capacity and reduce illumination necessary for biological growth resulting in morbidity and mortality of fishing⁶.

Recently, biofouling has also been indicated as the major mechanism for transfer of invasive species which might result in bioinvasion. Bioinvasion, poses threats to human, animal, plant life, economic and cultural activities and the aquatic environment itself. It has been recognized by the International Maritime Organization (IMO) leading to the adoption of the resolution in July, 2011, for the control and management of biofouling on ships to minimize the transfer of invasive aquatic species⁷⁻¹⁰.

To fight against biofouling, various copper and tributyltin (TBT) based coating have been widely used. Tributyltin self-polishing copolymer (TBT-SPC) coating known as marine antifouling special weapons have been the most successful solution in combating biofouling on ships. Unfortunately, these formulations have seriously affected marine ecosystems and imposed a complete prohibition since 2008¹¹. Cuprous oxide antifouling coating is still dominant in antifouling coatings. However, this coating easily causes coagulation, sedimentation and pollution, so finally will be prohibited¹². With the improvement of marine environmental protection consciousness, the environmental friendly antifouling coatings become the hot spot.

In order to master marine antifouling coating technology, development and progress on the marine antifouling coatings will be summarized in this review.

Tin free self-polishing copolymer antifouling coating: The tin free self-polishing copolymer (TF-SPC) coating uses both hydrolysis and erosion to control the antifouling activity. Organic metal Cu and Zn forms covalent bond with resin. The resin doesn't dissolve in water, but the covalent bond could be hydrolyzed to hydrophilic groups by metal ions. Hydrolysis reaction continuously carries out and antifouling agent also constantly released. This controlled dissolution on the surface of the coating could last a longer lifetime¹³. The TF-SPC coating containing biocidal groups connects with biocidal function groups on the side chain. Biocidal groups are released in the process of hydrolysis enhancing the antifouling performance of the antifouling coating.

Low surface energy antifouling coating: Marine fouling organisms secrete mucus so as to wet the surface and then attach on the polymer coating surface by chemical bonding, electrostatic interaction, mechanical interlock and diffusion¹⁴. According to $W_a = r_s + r_{Lv} \times r_{sL}$ (W_a : adhesion work, r_s : solid surface energy under vacuum conditions, r_{Lv} : surface energy under liquid gas balance conditions, r_{sL} : Solid-liquid interface free energy), adhesion would reduce with the loss of the free energy¹⁵. The surface energy of low surface energy antifouling coating is low so that it is difficult for marine fouling organisms to attach on the surface^{16,17}. At present, the relatively mature research is organosilicon and organicfluoride low surface energy antifouling coating. The main component of organosilicon low surface energy antifouling coating is organosiloxane which has strong hydrophobic, low surface energy, stable structure and smooth surface. While the main component of organicfluoride low surface energy antifouling coating is organicfluorine polymer which could improve the surface tension and reduce the adhesion of fouling organisms. Organic silicon-fluorine composite compounds are the future development trend of low surface energy coating.

Biological antifouling coating: Marine organisms such as dolphins, seacrab, sponge, algae and coral survive in the sea for ages but not stick fouling organisms because they could secrete chemicals inhibiting fouling organisms and the surface morphology would avoid the adhesion of fouling organisms on the surface^{18,19}. Accordingly researchers prepare compounds having similarly functional groups which is the antifoulant of coating composition²⁰. It is hard for marine organisms to close and adsorb on the ship surface when it is covered with dense fibrous fluff because of the block of fiber fluff layer. And furthermore marine organisms refuse to stay and grow on a completely unstable substrate in that fibrous fluff keeps swinging with the current. According to the principle, scientists develop flocking antifouling coating. Some researchers prepare a series of lotus leaf biosimulation coating by investigating blade surface microstructure and hydrophobicity.

Conductive antifouling coating: Using conductive polymer coating on the hull and marine structures as anode and the bottom of ship contacting with sea as cathode, hypochlorous acid ions generated by seawater electrolysis would kill the larvae of fouling organisms or stop it attaching. It would not pollute the environment because hypochlorous acid ions concentration generated by seawater electrolysis in the sea is lower than it in the water. The researchers find that the antifouling coating consisting of graphite as conductive filler and polyurethane as film forming matter shows good antifouling performance after 500 days' exposure to marine environment²¹.

Fluorescent antifouling coating: Fluorescent antifouling coating was the recent years' novel antifouling technology. Due to the ocean photophobic organisms such as barnacle larvae tend to be far away from marine structures coating the phosphor compounds. Domestic scholars add titanium dioxide as a fluorescent material to antifouling coating system. The results show that marine organisms obviously reduced with the increase of titanium dioxide content²².

Conclusion

A wealth of alternatives have been initially investigated for various marine applications to replace the use of tributyl tin. This brief survey on the current trends on the marine antifouling coating suggest that antifouling technology is moving toward efficient, non-toxic, environmental friendly.

REFERENCES

1. M.E. Callow and R.L. Fletcher, *Int. Biodeter. Biodegrad.*, **34**, 333 (1994).
2. A.S. Clare, D. Rittschof, D.J. Gerhart and J.S. Maki, *Invertebr. Reprod. Dev.*, **22**, 67 (1992).
3. J. Bellas, *Aquat. Toxicol.*, **83**, 52 (2007).
4. J. Bellas, *Aquat. Toxicol.*, **88**, 308 (2008).
5. P. Venkatesan, N. Palaniswamy and K. Rajagopal, *Prog. Org. Coat.*, **56**, 8 (2006).
6. R. De Nys and J. Guenther, in eds.: C. Hellio and D. Yebra, *The Impact and Control of Biofouling in Marine Finfish Aquaculture*, Advances in Marine AF Coatings and Technologies, Woodhead Publishing, Cambridge, UK, pp. 177-221 (2009).
7. MEPC Resolution 207 (62), Adopted by Marine Environment Protection Committee, International Maritime Organisation, London, MEPC 62/24/Add.1 (Annex 26) (2011).
8. J. Bellas, *Sci. Total Environ.*, **367**, 573 (2006).
9. O. Floerl, G.J. Inglis, K. Dey and A. Smith, *J. Appl. Ecol.*, **46**, 37 (2009).
10. C.M.R. Farrapeira, D.O. Tenório and F.D. Amaral, *Mar. Pollut. Bull.*, **62**, 832 (2011).
11. D.M. Yebra, S. Kiil, K. Dam-Johansen and C. Weinell, *Prog. Org. Coat.*, **53**, 256 (2005).
12. M. Pérez, G. Blustein, M. García, B. del Amo and M. Stupak, *Prog. Org. Coat.*, **55**, 311 (2006).
13. M. Sugihara, JP Patent 2002194293 (2002).
14. M. Hirao, H. Sugimoto and H. Ohno, *J. Electrochem. Soc.*, **147**, 4168 (2000).
15. J.-M. Lévêque, J.-L. Luche, C. Pétrier, R. Roux and W. Bonrath, *Green Chem.*, **4**, 357 (2002).
16. Y. Li, Y.H. Gao, X.S. Li, J.Y. Yang and G.H. Que, *Colloids Surf. B*, **75**, 550 (2010).
17. A.A. Al-Juhni and B.-Z. Newby, *Prog. Org. Coat.*, **56**, 135 (2006).
18. J. Guezennec, J.M. Herry, A. Kouzayha, E. Bachere, M.W. Mittelman and M.N. Bellon Fontaine, *Int. Biodeter. Biodegrad.*, **66**, 1 (2012).
19. N. Bellotti, B. del Amo and R. Romagnoli, *Prog. Org. Coat.*, **74**, 411 (2012).
20. W.W. Cong and L.M. Yu, *Asian J. Chem.*, **23**, 687 (2011).
21. H.J. Ruy and L.W. Ting, *J. Coat. Technol. Res.*, **7**, 111 (2012).
22. Y.H. Qi and Z.P. Zhang, *Chin. Surf. Eng.*, **23**, 74 (2010).