Research Progress of Nanomaterials in the Prevention of Biological Fouling on Ships

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Abstract. Marine fouling is one of the causes of Marine corrosion, which causes material corrosion to sailing vessels and a variety of Marine structures, but also has a great increase on the daily maintenance cost and energy consumption. In this paper, the formation process, mechanism and harm of biological fouling are briefly introduced, and then the application research progress of nanomaterials in preventing Marine biological fouling of ships in recent years is comprehensively discussed. We found that the research mainly focused on the application of nano-oxide materials in Marine biological fouling prevention, and adding anti-fouling agents of nano or modified nanomaterials in the preparation of materials to enhance the properties of materials, which could provide support for further exploration of nanomaterials in biological fouling.

Keywords: Marine fouling organism; Corrosion; Composite nano-coating; Modified nanomaterials; Preparation and application

1. Introduction

It has been many years of exploration to reduce Marine fouling. In 2008, organotin self-polishing coatings were banned completely because of high Marine pollution. And the research of coating materials mainly oriented to environmental protection has been widely concerned by scholars. Structure determines the nature of the nanomaterial with its own unique nanoscale tiny structures. This kind of materials has the special performance (such as nanoparticles, high specific surface area, quantum size effect, etc.). Nanotechnology in different areas (such as: building materials, clothing, etc.) has also received extensive attention. On the surface of the ship coatings of related study, scholars are also working on it combined with the traditional Marine coatings nanomaterials or replaced, in order to paint in the antimicrobial properties, corrosion resistance, aging resistance and other performance effectively improved.

2. Hazard of Marine Fouling by Living Organisms

In the ocean, Marine organisms, plants and microorganisms will attach to the surface of ship bottom and cause fouling \[1\]. The manifestation of fouling bottom is relatively intuitive. Scholars generally use visual inspection to evaluate the state of the bottom from three aspects: the type of the bottom, the size of microorganisms and the area of the bottom \[2\]. Through the study on the form of fouling bottom, Wang Mingchen \[3\] et al. established a three-dimensional model of the hull, and analyzed the influence of different forms of ship fouling bottom on the resistance performance of the ship. Chen Yonghong \[4\] et al. showed that micro-fouling organisms increased the friction resistance of the hull by 1%~2%. Soft
fouling organisms increase the friction resistance of the hull by 10%; Hard fouling organisms increase the friction resistance of the hull by 40%. Yao Xuelei [5] et al. showed that the increasing sailing resistance of ships increases with the rising level of roughness and speed, accounting for nearly 30% of the total resistance at most. The effect of the dirty bottom is greater than the roughness, which can account for about 50% of the total resistance. Demirel and Yigit [6] et al. used CFD software to conduct CFD simulation, and explored the influence of ship antifouling painting and fouling attachment on ship friction resistance. Kiosidou, Evangelia [7] et al. carried out towing tests on a 3mm thick plate and extrapolated the test results to the size of the ship with the method of extrapolation, so as to explore the influence of the roughness of the ship on the ship resistance. Generally, a new ship has an average surface roughness of 125μm. A study conducted by the British Ship Research Institute on the relationship between hull surface roughness and frictional resistance of operating ships shows that after 3 years of operation, the ship speed decreases due to the increase of hull roughness. In order to maintain the ship speed, the shaft power must be increased by about 15% [8].

When the performance of Marine diesel engine is determined, the fuel consumption of diesel engine is mainly determined by the resistance of the hull and the speed of the ship. In the ship-machine-propeller propulsion system of a ship, the increase of hull resistance will affect the propeller propeller efficiency, and lead to the increase of the output power of the main engine of the ship, resulting in a significant increase in the fuel consumption of the vessel [9]. Chen Aiguo [10] et al. studied the influence of hull surface roughness on ship resistance and fuel consumption by measuring the real ship roughness resistance of different types of ships. Road [11] study on ship's main engine, propeller and shaft transmission device, such as the normal operation of equipment and near sea state conditions under the premise of different period of ship host will fuel consumption of the difference is mainly caused by the change of the hull resistance. Tillig F [12] and Baldi F [13] et al. established a general ship energy system model, analyzed the interaction mechanism between ship speed, fuel consumption and energy efficiency, and applied it to ship energy consumption assessment and operation characteristics analysis. Xiong Yichao [14] for overcoming the effective power of the hull resistance and host power output ratio [15] measure of energy use efficiency, and vessel operating efficiency index EEOI formula to measure the size of the ship main engine efficiency and get the corresponding target ship propulsion efficiency, the simulation analysis under different speed, hull surface rough sailing conditions, float state of structure to promote energy efficiency and operating efficiency of the system, the results show that the target ship at low speed when the integral EEOI value is low, the roughness rating for the influence of the energy efficiency is relatively small. At a higher speed, the overall EEOI value of the target ship increases significantly compared with that at a lower speed. In this case, the influence of the roughness level on the ship's propulsion efficiency is more obvious. The larger the roughness value, the lower the ship's propulsion efficiency.

Data shows that the main cause of safety risks and reducing the use time of offshore equipment are the attachment of Marine organisms to it. Such organisms are not only attached to them, but also grow on them continuously. When they are attached to the surface of the ship, the speed of the ship will decrease and the flexibility of turning will be weakened, which leads to a significant increase in safety risks [16].

In addition to increasing the ship's navigation resistance, which leads to the increase of fuel consumption and safety risks, the corrosion of Marine organisms will also have a serious impact on all kinds of equipment and ship navigation in the ocean. For example, marine biological fouling will reduce the strength of cross-sea Bridges, submarine pipelines and coastal structures [17-18], and even reduce the accuracy of marine monitoring equipment, leading to distortion of marine monitoring data [19]. Marine fouling can also reduce the service life of marine equipment [20].

In addition, the contamination of Marine organisms will also pose a threat to the local ecosystem. Due to the long distance transportation characteristics of ships, attached microorganisms will be transported to other places along with the voyage of ships, which will impact the local ecological balance and lead to the risk of alien species invasion [21]. Studies clearly show that the direct economic losses caused by marine pollution are as high as US $440 billion every year [22-23].
3. Research Status of Nanomaterials in Biological Fouling Prevention of Ships

As early as 2008, Song Xudong et al. clarified the definition of nanomaterials and proposed that nanomaterials should be used in the research direction of ship coatings. Wu Xing [24] expounds the biological fouling prevention coating agent release type, namely organic tin, although have good antifouling effect, but because of its containing tributyltin (TBT), paint Marine pollution serious and has been disabled at home and abroad, put forward an environment-friendly antifouling coating, described and nanometal contact antibacterial activity, antibacterial properties of silver nanoparticles, which can be widely applied in the field of Marine biological pollution prevention MAO [25] the field comprehensive classification such as toxic antifouling materials were summarized. The application of nanomaterials as antifouling coatings is an important direction for ship antifouling, but attention should still be paid to the nontoxicity, antibacterial and corrosion resistance of antifouling coatings in practical application.

Because of its broad spectrum antibacterial properties, bacteria cannot produce drug resistance and other advantages, nano-silver particles have a good application prospect in the biological damage prevention of ships. In the study of Li Moqing [26], it was found that with the increase of nano-silver concentration, the rougher the surface of activated sludge became, and the microbial community decreased. Nano-silver could effectively inhibit microbial proliferation, destroy membrane integrity and cause cell death, and affect the structure of microbial community. Cui Jixing [27] et al. proposed to use nano-silver as the main antibacterial component to produce a new type of long-acting nano-silver powder coating, which has been proved by experiments to have good antibacterial performance and durability. Xu Yue [28] et al. studied a new non-toxic and degradable low surface energy antifouling coating material, and explored the antifouling mechanism. Millie Kong and Huixian Wu [29] et al. studied the adhesion and inhibition of Marine bacterial biofilms by using the emerging nano-silver technology. By analyzing the antibacterial ability of nano-silver with different particle sizes, they designed and prepared two kinds of composite particle materials, namely SiO2-loaded nano-silver and SiO2-coated nano-silver, and concluded that 50nm nano-silver had a strong antibacterial effect. Both of the two materials showed good laboratory effects in inhibiting biofilm formation. In the direction of oxide materials, scholars at home and abroad focus on applying this kind of material to anti-fouling and anti-corrosive coatings for ships. Through continuous experiments on antifouling agents and coupling agents of nano and modified nanomaterials, various properties of the materials are improved.

Studies have found that titanium dioxide can produce superoxide free radicals, and its strong oxidation can lead to bactericidal effect [30-31]. The addition of nano titanium dioxide particles can enhance the antifouling and corrosion resistance of the coating, contributing to its hydrophilic, film forming and antibacterial properties [32-33]. In 2008, Li Shanwen [34] et al. proposed to combine bactericidal nano-TiO2 and small molecule silicone oil as antifouling active substances with low surface energy antifouling coatings to enhance the antifouling performance of the coatings. The addition of nano titanium dioxide can reduce the amount of biological attachment in polluted sea and enhance the antifouling effect. Sreejith Mohan [35] et al. developed a nano-structured ZrO-TiO2 film coating on AISI 304 stainless steel by using the alcohol-gel-impregnated coating technology, and simulated the effect of sea water on the corrosion resistance of steel. The corrosion resistance of stainless steel can be increased by 88.21% after coating increase. At the same time, the influence factors on the coating effect are also explored. In addition, nano silica has also been found to have good anti-aging properties [36]. According to the existing defects of nanomaterials in the anti-corrosion and anti-pollution of Marine facilities, Deng Sanxi prepared nano-SiO2 with small particle size by chemical precipitation method based on the currently commonly used nano-modification method, and prepared three different nano-SiO2 monomers by the precursor system of nano-SiO2 [37]. Yang Lingjuan reviewed the application of nano-silica or modified nano-silica and analyzed the properties of the following four coatings, namely: acrylate coatings, epoxy coatings, polyurethane coatings and acrylate polyurethane coatings [38]. Wang Zhenyu [39] et al. have studied the traditional antifouling coatings by adding nano silica concentrate slurry and nano zinc oxide concentrate solution. Through performance analysis and multiple tests, it can be proved that the traditional antifouling coatings can effectively improve a
number of properties of the epoxy/polyurethane paint system. Huang Jiao [40] proposed a preparation method of nano-modified organo-fluorosilicone Marine antifouling coating and characterized it. Nano-separates dispersants were selected to conduct experiments on the composite and dispersion effect characterization of nanopowders TiO2 and SiO2, and the antifouling broad-spectrum was expanded on the basis of non-toxic coating.

Nano-oxide materials synthesized by copper, zinc and their oxides also have a good development prospect in biological fouling prevention of ships: Lekshmi N. Manju, Ashraf P. Muhamed [41] et al. applied biological fouling prevention to aquaculture cages by coating combined with nano-zinc and silicon oxides and polyaniline. Robert J. Miller [42] et al. investigated the effects of nanometer and traditional copper-zinc antifouling coatings on Marine invertebrate communities by comparing traditional micronsized Cu and ZnO particles and two formulations containing Cu and ZnO nanoparticles. Lu Guijuan [43] et al. prepared a nano-zinc oxide composite titanium oxide Marine anticorrosive and antifouling coating, and conducted a comparative test with the traditional oxide layer to prove its better antifouling and anti-corrosion performance. YueXin careful study to the Marine environment and Marine corrosion of metal materials, in view of the nanometer ZnO has excellent antibacterial properties, this paper proposes a nano ZnO/epoxy resin composite Marine anticorrosive antifouling paint, choose E-44 bisphenol A type epoxy resin as a basic component coating, selection of titanate coupling agent modification of nanometer ZnO as additive, make the material has a very superior antibacterial biological fouling prevention performance [44]. S. Liang [45] et al. successfully prepared a novel PVDF membrane with anti-reversible fouling by wet phase separation method. Nano zinc oxide as an additive (accounting for 6.7%~26.7% of the mass of PVDF) is mixed into the membrane matrix, and the inner surface of the membrane hole is modified. The water flux recovery rate of the modified membrane is close to 100%, which can fully filter the seawater into the ship's internal ballast water system and protect the ship's internal equipment. K. Cheng [46] et al. modified PVDF ultrafiltration membrane by rapid one-step co-deposition of DA and DMAPs under the oxidation action of CuSO4/H2O2. The presence of copper ions and quaternary amine groups in the coating results in superior antibacterial properties, superior antibacterial activity, as well as excellent chemical and mechanical stability.

4. Conclusion

Complicated Marine environment, including a large number of biological species, for long-term in the Marine environment of ship structures, and all kinds of marine biological fouling caused the harm such as fuel consumption increase, infrastructure use cycle shorten, at present already has basic physical, chemical and biological methods to a certain extent reduce the biological fouling effect, but also bring the ocean pollution problems. This paper focuses on the nano materials of all kinds of application in the ship to prevent biological fouling and compared to similar, nano silver and various properties of the material such as all kinds of nanometer metal oxide has the trend of increase, but the current application of Marine facilities and the outer surface of the ship and modified nano coatings are still some problems such as economy, technology consistency, needs further research. In the future, further research on the application of nanomaterials should be carried out according to the actual environmental characteristics and sea conditions, and further excavation and development experiments should be carried out in potential materials in order to achieve better results.

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