New Strategy to Prevent Adhesion of Biofouling to Coatings

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1. Introduction

Marine microorganisms’ adhesion on submerged surfaces forms the so-called biofilms. Later on fouling organisms, from seaweeds, algae to hard foulers (Barnacles, mussels, etc.), will attach over time (macrofouling). Nowadays the most effective antifouling strategy to combat this marine biofouling employs coatings which act by a controllable biocide releasing mechanism¹. But the continued releasing of toxic agents to the marine environment, led to serious side effects on ecosystems, and rigid international regulations have been issued (EU Regulation, 2012), which can compromise permission to use biocides currently in use. Non-toxic technologies are therefore sought.

The most recent coatings’ technology focus on foul-release mechanisms, provided by low surface energy materials such as silicone based coatings, which leads to minimal adhesive smooth surfaces (non-stick properties). However, and in order to remove the weak attached organisms these coatings with typically 5 to 10 years lifetime are only effective for fast moving vessels (> 15 knot)². This paper aims to present non-releasing coating systems by providing newly developed isocyanate functional biocides suitable to be tethered to the most effective marine coatings.

2. Experimental

Commercial biocides, Irgarol and Econea have been selected to be functionalised. Briefly, the functionalization process involves biocides reaction with a diisocyanate reagent³. This process was recently fully described in a patent application (PT N° 108096, 12 Dec. 2014).

Binding of functional biocides with a conventional polyol (Desmophen 651 MPA/X, HEMPEL A/S) was performed to prove the effective biocide immobilisation. The reaction progress was evaluated by Fourier transform infrared spectroscopy (Nicolet Magna FTIR 550 Spectrometer).

Immobilisations of the functional biocides were performed on a commercial silicone based marine coating (Reference 87500, Hempel A/S). The obtained antifouling coatings were used to coat PVC prototypes (10x10x6 cm) for field tests in Atlantic sea, Portugal (22 ± 1°C, salinity: 35.2-36.7, pH = 8.3), performed in accordance with ASTM D6990 and D3623-78a.

3. Results and Discussion

Conversions of 95 ± 5 % were obtained for the functional biocides. FTIR spectra (Fig. I) confirmed that

![Fig. 1 FTIR spectra of Econea and Irgarol biocides and their functional counterparts.](image-url)
the structure was not modified and that the isocyanate functional group (band range: 2327-2144 cm\(^{-1}\)) was successfully attached to the expected bridging point of biocide structure.

Representative FTIR analysis of the binding reaction between the functional biocides (3 wt. %) into a conventional polyol component evidenced the disappearance of the isocyanate functionality, after 24 hours of reaction, confirming functional biocide binding effectiveness (Fig. 2).

Field sea immersion tests on silicone based coated prototypes (Fig. 3) evidenced that after 23 weeks of seawater exposure the coating with immobilised biocides didn’t evidenced biofouling, in fact it can be seen that around the prototypes there is a considerable colonization, including the growing of algae. On the other hand, for the coating control (Fig. 3, right), this is, silicone coating without fixed biocides, it can be seen some hard fouling adhesion, which can suggest a weaker antifouling performance when compared with the biocidal coatings.

4. Conclusions

A newly functionalisation process was found to be effective for biocides fixation in polymeric matrixes. Immobilised biocides in silicone based coatings revealed promising antifouling effect after 23 weeks of seawater exposure. Tests are on progress to assess coatings antifouling behaviour for longer immersion periods (a year) and to evaluate synergetic effects through the immobilisation of different biocides in a same polymeric matrix.

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References