NON-RELEASING BIOCIDAL COATINGS: A NEW ECO-FRIENDLY STRATEGY TO PREVENT MARINE BIOFOULING

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ABSTRACT

Marine biofouling accumulation on ships' hulls is a major environmental and economic issue. It is not only associated to hulls deterioration, but can also lead to drag friction increases up to 40% and subsequent power penalties of up to 86% at cruising speed. Hitherto, antifouling marine coatings, which act by a controlled-release mechanism of biocidal substances, are the most effective strategy to combat this bio-attack. However, and in order to protect the environment rigid international regulations have been issued due to the toxic biocides side effects on ecosystems. As a result, a new generation of non-toxic strategies emerged, but their effectiveness is still limited to a range of organisms and/or conditions (mostly non-stationary conditions). New alternatives are needed to widening its antifouling action. In compliance with this aim, this work provides a newly eco-friendly strategy through the development of non-releasing biocidal coating systems. Those systems were obtained by tethering functional biocides (Econea and/or Irgarol), produced by a recent developed process (PT Nº 108096), in silicone based marine paints. The immobilisation of biocides on those silicone based systems, starting from contents as low as 0.56+0.01 wt.% can infer paint antifouling properties changes which require further optimisation. Atlantic seawater immersion tests at static conditions, on coated prototypes with the developed biocidal coating systems evidenced promising antifouling effects up to 6 months. Longer immersion periods (a year) tests are still on progress. An environmental compatibility study performed accordingly with the European standard protocols, mainly to evaluate paint releasing impact, evidences that the developed non releasing biocidal coatings present low environmental impact.

Keywords: antifouling coating, ecotoxicity, immobilised biocides, field prototype validation

1. INTRODUCTION

Marine biofouling, a spontaneous unwanted colonization by a biodiversity of marine organisms on surfaces in contact with seawater, is a major economic and environmental concern for marine industry. It affects the performance of both stationary and non-stationary marine structures, e.g. from oil and wind-turbine platforms, pipelines, fishing nets to ships and vessels, by promoting substrate deterioration or substantial loss in equipment efficiency, thus, follow-on costly maintenance and retrofitting consequences. The shipping industry in particular, is the most affected. For instance, the settlement of aquatic organisms on ships' hull, leads to the modification of the surface roughness, increasing the skin frictional drag between the surface and the seawater, thus affecting its hydrodynamic performance. Studies reported that biofouling can lead to drag friction increases on ships up to 40% (Dahlbäck, 2010) and subsequent power penalties of up to 86% at cruising speed (Callow, 2011). Hence, more energy is required to propel the vessel through the seawater, which is provided by extra fuel consumption. It was also reported that just 10 μm increase in average hull roughness can lead to increments in fuel consumption ranging from 0.3 to 1.0% (Champ, 2000). Being aware that fuel consumption is the biggest cost fraction in ships' operation, which accounts with up to 50% of the total vessel operating costs, this is a significant economic penalty in marine transportation. The Clean Shipping Coalition estimated that for a typical sailing interval (about 50 months) the impact in the efficiency of the world's fleet can be reduced by 15-20%, owing to the deterioration in hull and propeller performance (MEPC 63/4/8, 2011). On the other hand, such fuel consumption increasing, results in a subsequent augment of Greenhouse gas (GHG) emissions (Banerjee, 2011). The International Maritime Organization estimated that CO2 emissions associated with fuel consumption from international shipping could more than double by 2030 under extreme scenarios (IMO, 2009). In addition to the aforementioned drawbacks, this biofouling attachment on ships' hull is also responsible for the introduction of invasive species (or non-native species) into different ecosystems, overpopulating and acting as predators to local species. These effects justifies why in the last decade so many efforts have been done to mitigate such marine biofouling. The main strategy followed by the marine industry to mitigate or control this biofouling relies on the use of biocidal coatings, which act by a chemical control mechanism, this is, coatings able to emit toxic substances (biocides) into the immediate surrounding area of the contaminated surface, thus killing potential fouling organisms before they can attach. The most revolutionary coatings generation emerged with the use of tributyltin (TBT) and/or derivatives in coatings formulation. However, its ecotoxicity and cumulative effect proved to be harmful to the marine ecosystem (Alzieu, 2000 and Antizar-Ladislao, 2008). As a result, the use of TBT and derivatives was totally banned by the International Maritime Organization (IMO) and the European Union (EU) under the International Convention on the Control of Harmful Anti-fouling Systems on Ships through the Regulation 782/2003. Since then, efforts have been done to provide alternative and less toxic antifouling systems, most of them still based on a biocidal releasing strategy, usually a combination of copper oxide with a booster biocide (co-biocide) (Guardiola, 2012 and chambers, 2006). But even if these alternatives revealed to be less harmful due to their lower ecotoxicity or higher degradability, after the TBT generation, all the used biocidal substance have been put under strict regulation. Some of them are currently under scrutiny (BPD EU Regulation, 2012) (Guardiola, 2012, Rodríguez, 2011 and Marcheselli, 2010), and more restriction are expected in a near future. Reason why this strategy is becoming less acceptable, and because the applied biocides still revealed to be somehow harmful to the marine environment (Sheikh, 2009, Thomas, 2010, and Ezeonyejiaku, 2011). New strategies, which can combine more efficiency against biofouling and non-toxic properties for the aquatic systems, are sought. This desire gives rise to a new generation of antifouling coatings, based on non-toxic and/or non-biocide-release strategies (Nurioglu, 2015). The majority of those strategies rely on the development of new polymers structures in order to create or improve properties such as: hydrophilicity, amphilicity and/ or surface topography. But and despite the potential of the new antifouling strategies, most of them are still under optimization or proof-of-concept. And the few on the field are still limit to some specific conditions or evidence technical limitations (Banerjee, 2011 and Lejars, 2012). For example the foul-release silicone based coatings, characterised by possessing non-stick surfaces, are only totally effective for fast moving vessels (> 15 knot) (Stevens, 2001). Therefore, marine biofouling is still causing headaches on shipping business, a potential alternative for its control and/or prevention is still an urgent need.

This work aims to contribute to this aim, by providing a novel non-release biocidal strategy, based on the chemical linkage of biocide agents, through covalent bonds, in polymeric coatings structure. The proof-of concept is mainly provided by field tests in Atlantic sea of coated prototypes using silicone based marine paints, and an environmental compatibility study.

2. METHODS

2.1 BIOCIDES IMMOBILIZATION IN POLYMERIC MATRICES

For the biocides immobilization in a polymeric matrix a newly developed method was used (Silva, 2015). It comprises a prior functionalization of compatible biocides (Silva, 2014) with isocyanate functionality, in order to becoming those biocides able to be chemically immobilised in a polymeric paint system, this is with suitable bifunctional coating components.

Two different commercial biocides were used, the Irgarol 1071 from Ciba Specialty chemicals, and Econea from Janssen PMP. Briefly, the functionalization process starts with the biocides dissolution in a suitable solvent (15-30 wt.%), butyl and ethyl acetate p.a. from Sigma-Aldrich for Irgarol and Econea, respectively. The obtained solutions are further added dropwise (7-10 hours) into a three necked round bottom flask containing an aromatic diisocyanate (4,4 diphenyl diisocyanate-MDI) at 40 ± 5 ºC under mechanical agitation (300-400 rpm) and inert atmosphere. After mixture the reaction proceeds at stoichiometric conditions, in terms of NCO functionality of the diisocyanate and the NH functionality of the biocides, for about 1-2 hours, maintaining the above described conditions. The reaction mixture is then left to cool to room temperature, promoting the product precipitation. The product is finally filtrated and further dried in a Butchi R-210/215 rotovapor for solvent removal.

The obtained solid products, named as Irgarol-NCO and Econea-NCO, are further used as biocide additives for the coating formulation base (polymeric matrix).

The isocyanate functionality of the biocides was confirmed by Fourier transform infrared spectroscopy (FTIR). The FTIR analyses were performed on biocides supported in KBr discs in a frequency range between 500–4000 cm−1, and recorded on a Nicolet Magna FTIR 550 spectrometer. The NCO free content was obtained by a standard adapted procedure from the standard ASTM D2572.

2.2 ENVIRONMENTAL COMPATIBILITY STUDY

The main mechanism of action of the majority of the commercial antifouling marine paints is based on the releasing of the biocidal agents into the surface (e.g. hull) surrounding, reason why and due to their associated ecotoxicity, a rigid environmental compatibility study is imperative. Particularly, for the new approach of this work, the risk of any biocide releasing to the marine environmental should not exist, since the biocidal action is provided by contact as a result of the chemical biocide immobilization in the paints´ matrix. On the other hand, there is always, and in an extreme scenario of external wear (e.g. cleaning operations) on coated surfaces, the possibility of paint releasing, thus a toxic product would be released into the environmental. Therefore, it is important to perform an accurate evaluation of the environmental risks associated to the developed systems, including the functional biocides.

An environmental study was therefore performed, which included an accurate ecotoxicity assessment by following standard included in the EU hazard assessment of substances and European Eco-label. In order to obtain the leaching from the paints to be analysed, two methodologies were followed:

(a) Stirring test

A stirring test procedure was adapted from published methods (Bergmann, 2009) which follow the standard OECD 313, 2007. This test aims to assess the leaching behaviour of the obtained coating formulations, in order to guarantee that the immobilized biocides remained attached to the polymeric paint matrix along time. Briefly, it comprises the immersion of coated acrylic prototypes (3.5x6 cm) in simulated seawater (750 mL) under continuous stirring (60 rpm) and for a period of 45 days. The pH is controlled in order to remain around 8.5 in a temperature ranging from 18 to 25 ºC. The obtained leaching waters are further analysing in terms of toxicity (tests described in subsections 2.2 c and d).

(b) Washability test

The washability test was performed according to ISO 11998:2006 “Paints and varnishes: Determination of wet-scrub resistance and cleanability of coatings”. This method is used in order to test the paints’ resistance to wear caused by repetitive cleaning operations and penetration of soiling agents. After each test, it is possible to collect the leaching obtained and evaluate its toxicity. The use of this tribological experiment allow to accelerate the painted panel degradation, thus wear particles containing biocides from the topmost part of the paint release to the aquatic environment and toxicity tests can be performed.

The tests were performed for each painted panel in the equipment Braive Instruments for a scrub rate of 50 000 cycles with a speed of 37 cycles per minute, using standard sea water (ASTM D1141) as lubricant. Two loads of 254 g and 918 g where applied on each brush used for accelerating the wear on the exposed surfaces. The washability tester has a closed circuit, which allows the circulation of the artificial seawater. The seawater is pumped and spread along the sample, with a brush, which scrubs at the speed mentioned above (37 cycles per minute). The resulting leaching is returned to the electrolyte container, being collected at the end of the tests.

(c) Drag friction tests

The drag friction test (Tulcidas, 2015) consisted of placing static coated cylinders in a small (Ø210 mm) and large (Ø220 mm) rotative recipients containing standard sea water (prepared according to ASTM D1141), working at different speeds (200 rpm, 500 rpm, 1000 rpm and 1500 rpm). The testing samples (substrates) consisted of hollow PVC (Polyvinyl chloride) cylinders of Ø200 x 200 mm. The hollowness reduces the weight of the samples. The selection of PVC material, reduce the absorption of humidity and facilitate the painting and machining. The cylinder was coated with silicone based with 0.56% Econea. Each container has its own lid to avoid the loss of water due to the rotating movement. For the toxicity assessment, the leaching was collected from the container, after testing the big and small gap configurations at different rotational speeds. Before collecting the leaching, each cylinder rotated for approximately 26 hours (25 hours and 42 minutes) at 200 rpm.

The toxicity of the leaching obtained from stirring, washability and drag friction tests the methods were performed according with the following standards:

A) Luminescent bacteria Vibrio Fisheri test (ISO 11348)

Vibrio Fischeri is a luminescent bacterium found globally in the marine environment. This bacterium is bioluminescent, robust, nonpathogenic and easy to breed, which makes it an ideal organism for laboratorial use. Vibrio Fischeri uses riboflavin-5-phosphate to react with oxygen to produce water and cold light emitted with a wavelength of 490 nm. The emission of luminescence is directly proportional to the metabolic activity, thus any inhibition of the enzymatic activity causes a corresponding decrease in the bioluminescence.

In this test, the decrease of bioluminescence of a culture of liquid-dried luminescent bacteria of the strain Vibrio Fischeri NRRL-B-11177A was measured after 15 and 30 minutes of exposure to the biocide release from paints, using the DR Lange LUMIstox 300 photometer, at 15 ± 1ºC. For obtaining the final testing samples a series of dilutions (1/2; 1/4; 1/8; 1/16; 1/32) were prepared from the leaching products of each paint obtained after stirring, drag friction and washability tests. The pH of the leaching was between 6 and 8.5. A 2 wt.% solution of sodium chloride (NaCl) in deionized water was used as dilution medium. The bioluminescence of the bacteria was also tested in parallel with 22.6 mg/L of a reference substance (potassium dichromate, K2Cr2O7) diluted in 2 wt.% NaCl solution. During each test, the validation of the bacteria action with the reference substance is measured, confirming that the value of EC50 (Effective Concentration able to cause some defined toxic effect to 50% of the test organisms) should be between 2.35 and 4.65 %.

B) Algae growth inhibition test OECD 201

This test was executed using MARINE ALGALTOXKITTM, which contains all the material necessary to perform growth inhibition tests with the marine diatom Phaeodactylum Tricornutum. This type of diatom is among the most common type of phytoplankton.

The species of alga Phaeodactylum Tricornutum, were incubated with the testing leaching samples, for 72 hours, in disposable cells of 10 cm path-length. Algal growth or inhibition was registered every 24 hours, measuring the optical density (OD) at 670 nm in the spectrophotometer Jenway 6300, equipped with a holder of 10 cm cells. Having obtained the optical density, it was possible to calculate the EL50, which is the concentration of the test substance that causes a decrease of 50% in the growth of the algae.

2.3 ANTIFOULING ASSESSEMENT: FIELD PROTOTYPE AND TRIAL TESTS

Immobilisations of the functional biocides were performed on commercial silicone (Ref.87500, Hempel A/S) based marine paints (gently provided by HEMPEL A/S). The obtained antifouling paints were used to coat 10x10x6 cm polyvinyl chloride prototypes for field tests in Atlantic sea at static conditions (22 ± 1 ºC, pH = 8.3, salinity of 35.2-36.7), which were performed in accordance with ASTM D6990 and D3623-78a standards.

The selection of a silicone coating system relies on the fact that 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). Therefore, in order to combine and find synergistic effects, the developed functional biocides were immobilised in this kind of silicone based systems.

In addition to the prototype test, the best obtained formulation was used to coat a ship for a trial test of a year. This ship was provided by ENP SA (Estaleiros Navais de Peniche, Portugal), which also performed its coating and supervision together with HEMPEL SA.

3. RESULTS AND DISCUSSION

Econea and Irgarol biocides have been functionalised in order to acquire the immobilization ability in polymeric matrices. The functionalisation effectiveness can be confirmed from the obtained FTIR spectra's (Figure 1), where a isocyanate functionality is detected in the typical biocides structures by the appearance of the isocyanate characteristic peak, ranging from 2327 cm-1 and 2144 cm-1 (Silverstein, 2005). In the case of Econea-NCO spectra, a broader NCO characteristic peak was obtained which is due to the overlapping with the band attributed to the structural nitrile (CN) functional group of the Econea biocide.

NCO contents of 11 ± 2 wt.% and 9 ± 2 wt.% were obtained for the Irgarol-NCO and Econea-NCO, respectively. Deviations on the NCO content are associated to the presence of impurities and moisture, which is impossible to remove completely during the preparation procedure.

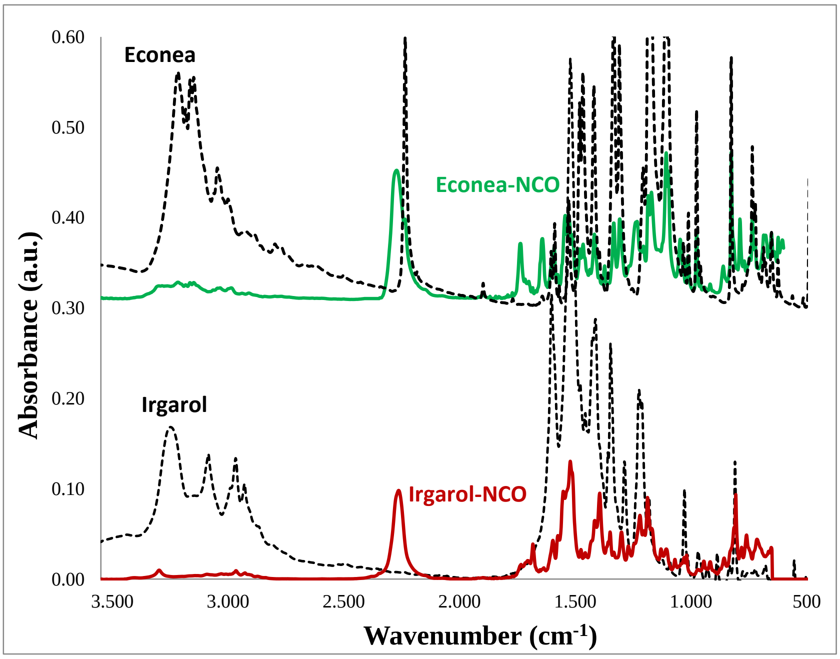

Figure 1: FTIR spectra of Econea and Irgarol biocides and their functionalised counterparts: Econea-NCO and Irgarol-NCO.

Silicone based paint formulations were prepared with the newly functionalised biocides (Table 1). In Figures 2 and 3, representative cured silicone based paint formulations containing immobilised single functional biocides are presented. From these figures it can be clearly observed that with the biocide content increasing, white crystals are formed on the coating surfaces, which are easily removed. Therefore, the silicone based system seems to not support biocides contents higher than 0.5 wt. % for formulations containing immobilised Econea. A similar effect was found for the formulation containing single immobilised Irgarol but for higher contents (5.0 wt.%). At lower contents such crystals can also be present, but the main paint properties remain unaffected, whereas for higher biocides contents a reduction on its smoothness and gloss is visibly observed. However, and as It can been depicted from Figure 4, the crystallisation equilibrium seems to be disturbed if instead of the immobilisation of single functional biocides in the silicone system, a combination of those biocides is included. Apparently, no crystallisation phenomenon is visible in a silicone based system with combined biocides, even for higher contents (SIL6), particularly if we compare with formulations with single Econea-NCO. This behaviour should be studied in more detail, but it goes beyond the main goal of this work. Nonetheless, it can be depicted from the results that most probably the different equilibrium conditions (e.g. solubility of single biocides and their mixture) for a combined system of functional biocides promotes an increasing in the total biocide content for the silicone system.

Table 1: Biocides content in the prepared paint silicone based formulations.

Paint formulations	Biocide content (wt. %)	
	Econea-NCO	Irgarol-NCO
Reference (SIL-R)	---	---
SIL1	0.57	---
SIL2	---	0.57
SIL3	2.57	---
SIL4	---	2.57
SIL5	---	5.00
SIL6	0.91	0.62

Figure 2: Coated PVC prototypes (10 x10 cm) with silicone based formulations, from left to right: 0 wt.% biocides (reference),containing 0.57 wt% and 2.57 wt. %of immobilised Econea-NCO.

Figure 3: Coated PVC prototypes (10 x10 cm) with silicone based formulations, containing from left to right: 0.57 wt.%, 2.57 wt% and 5.0 wt.% of immobilised Irgarol.

Figure 4: Coated PVC prototypes (10 x10 cm) with silicone based formulations, containing combined functional biocides: 1.53 wt.% of immobilised Econea + Irgarol.

As a result of the above observations, only representative and not affected coating films were further analysed. Nonetheless, and since no additional paint property degradation was detected, all samples were tested at field conditions for proof of concept.

Toxicity assessment:

The obtained leaching waters, either from stirring and washability tests on representative biocidal formulations, were assessed in terms of its ecotoxicity by Vibrio Fisheri and Algae growth inhibition tests. In addition, similar ecotoxicity tests were performed on the commercial and functionalised biocides.

The obtained results from the toxicity tests performed on biocides and their functionalised counterparts can be found on the following table:

Table 2: Toxicity responses for the Vibrio Fisheri bacteria of pure and functionalized biocides

Vibrio Fisheri (ISO 11348)			
Sample	Sample type	EC50 (mg/L)	
		15 minutes	30 minutes
Econea	Commercial biocide	223.6	242.0
Econea-NCO	Functional biocide	196.2	199.6
Irgarol	Commercial biocide	109.5	116.2
Irgarol-NCO	Functional biocide	118.9	121.0

* EL50 is the concentration of the test substance, which results in a 50% reduction in its growth or growth rate relatively to its control.

From Table 2, it can be observed that all biocides showed low inhibition after 30 minutes for Vibrio Fisheri, since the EC50 values exceeded 100mg/L. The lowest toxicity was found in case of commercial Econea followed by functionalized Econea. The ecotoxicity of the functionalized Irgarol was slightly lower than Irgarol.

The toxicity response of leaching waters obtained from the stirring tests performed on the most promising developed paint formulations, were also evaluated. In Table 3, the toxicity responses for the Vibrio Fisheri bacteria of the analysed leaching waters for the different coated prototypes didn't get any inhibition, reason why all tested formulations can be considered as non-toxic. In case of marine algae growth inhibition, only two samples were evaluated. For both cases, SIL1 and SIL2, it was found that it is necessary very high concentrations of the samples in order to detect inhibition, being SIL2 not harmful and SIL1 nearly not harmful for the environment.

Table 3: Toxicity responses for the Vibrio Fisheri bacteria (ISO 11348) and marine Algae growth inhibition (OECD 201) of the leaching waters obtained from the 45 days stirring tests on coated prototypes

Prototype sample	Coating	Vibrio Fischeri Inhibition after 15 and 30 minutes of exposition		Algae growth inhibition
		15 minutes	30 minutes	EC50 (vol.%)
Reference (SIL-R)	Silicone reference paint	Non Inhibition	Non Inhibition	Not measured
SIL1	Silicone paint with 0.56 wt.% immobilised Econea-NCO	Non Inhibition	Non Inhibition	91.37
SIL2	Silicone paint with 0.57 wt.% immobilised Irgarol-NCO	Non Inhibition	Non Inhibition	102.30
SIL6	Silicone paint with 0.91 wt.% Econea-NCO + 0.62 wt.% Irgarol-NCO	Non Inhibition	Non Inhibition	Not measured

Antifouling assessment: field prototype tests

The marine silicone based coatings formulations (Table 1) have been immersed in Atlantic seawater at static conditions for 6 months (about 26 weeks). Representative exposed coated prototypes with single immobilised biocides are shown in Figure 4.

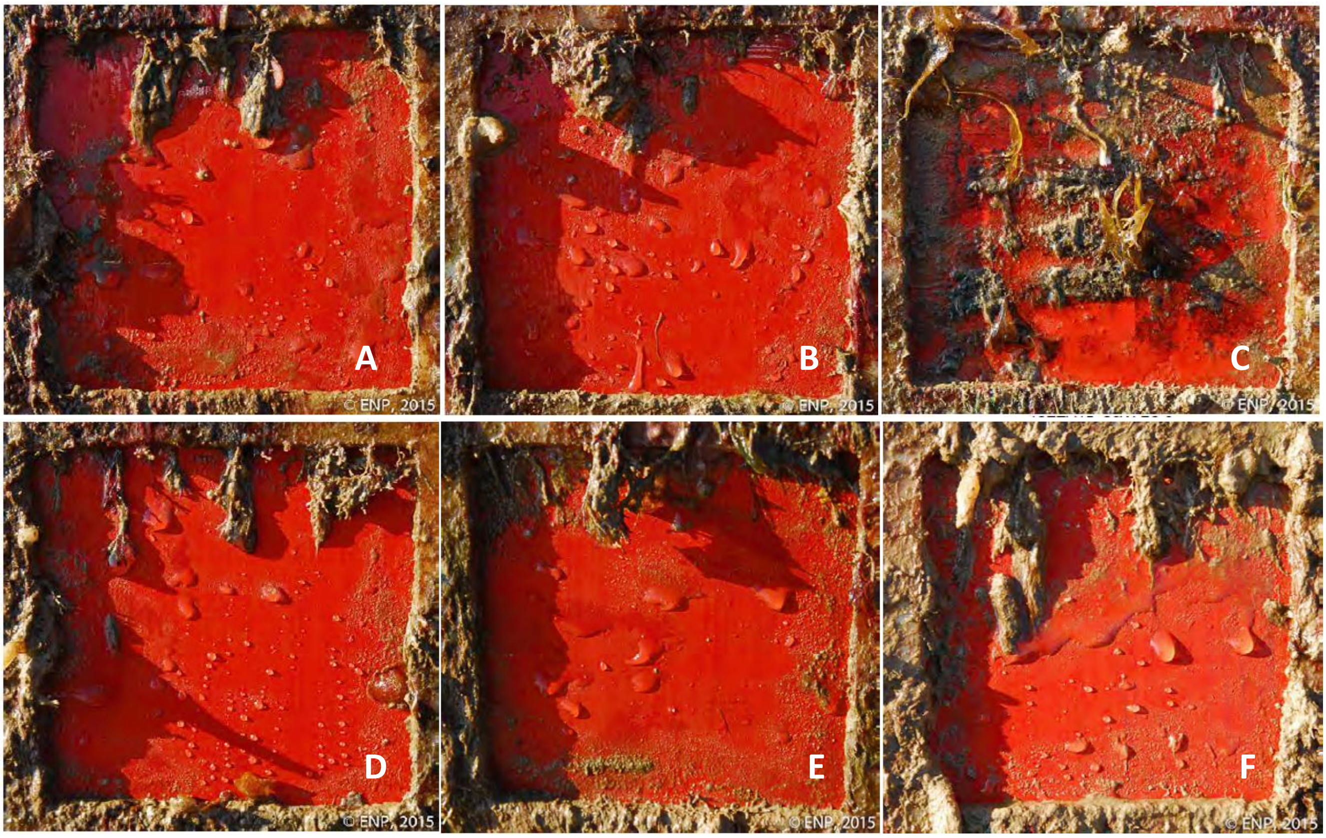

Figure 4: Coated PVC prototypes (10 x10 cm) with silicone based formulations, containing single immobilised biocides: (A) 0.57 %, (B) 2.57 wt. % and (C) 5 wt.% of immobilised Irgarol-NCO; (D) 0.57 wt.% and (E) 2.57 wt.% of immobilised Econea-NCO; and (F) the reference coating without biocides.

The exposed prototypes evidenced that on coatings with immobilised Irgarol-NCO (Figure 4, A to C) biofouling was not significant for the lower biocide contents (< 5wt.%). In fact, there is a considerable colonization around the prototypes, including the growing of algae. On the other hand, for higher contents (Prototype C with 5 wt.% of immobilised Irgarol-NCO) the prototype is highly fouled. This result was the expected one, since for this biocide content there was identified crystals (powder) formation during their curing, which promoted mainly a loss on the coating's smoothness and gloss. This coating's properties degradation promotes biofouling on the corresponding protected surface.

In the case of coated prototypes with single immobilised Econea-NCO (Figure 4, D and E), their behaviour is quite similar to the Irgarol based ones (A and B), the formed biofouling is not significant. In addition, a deeper observation of the coated prototypes with the antifouling coatings indicates that some unattached slime is also covering small prototypes areas. Taking in account this unattached slime, prototypes B and D suggest a better antifouling performance. Nonetheless, more time for the immersion test is required, in order to clearly identify differences on the biocidal coatings (A, B, D and E) antifouling behaviour.

For the coating control or reference (F), hard fouling adhesion was observed in a considerable prototype area, this can suggest a weaker antifouling performance when compared with those biocidal based coatings (A, B D and E).

In the case of the coating formulations containing a combination of immobilised biocides (Econea-NCO + Irgarol-NCO), its antifouling behaviour is clearly favourable relatively to the control (Figure 5). It also seems to be similar to the antifouling behaviour as the ones obtained for coated prototypes B and D (Figure 4) containing single immobilised biocides, 2.57 wt.% of Irgarol-NCO and 0.57 wt.% of Econea-NCO respectively. These results suggest that Econea-NCO is the most effective biocide for the tested conditions, but in order to be sure of any synergistic effect on its combination with Irgarol-NCO, it is necessary to proceed with the immersion tests for longer periods (a year). These tests are currently on-going and any synergistic effect resulting from the immobilisation of more than one biocide type in the polymeric matrices will be confirmed.

Figure 5: Coated PVC prototypes (10 x10 cm) with silicone based formulations, containing combined immobilised biocides: (A) 1.63 wt.% of immobilised Econea-NCO + Irgarol-NCO; and (B) the reference coating without biocides.

Toxicity tests after wear

At this point, and taking in account both the paint antifouling properties and the most potential environmental compatible biocide, it was decided to proceed with toxicity tests after paint wear carried out with test devices (drag friction tests and washability tests) that simulate the paint mechanical wear, before carrying out the ecotoxicity tests. The selected paint formulation was the SIL1 that it is a silicone based paint with 0.56 wt.% of immobilised Econea-NCO). The toxicity responses of leaching in artificial sea water (ASTM D1141), obtained from coated prototypes with the selected formulation, were assessed for the Vibrio Fisheri as can be seen in the next Table 4.

Table 4: Toxicity responses of leaching waters, obtained from Drag friction and washability tests of coated prototypes with Vibrio Fisheri (ISO 11348).

Prototype sample (coating)	Mechanical test where leaching was obtained from	EL50 (Vol. %)	
SIL1 (Silicone paint with 0.56 wt.% immobilised Econea)	Vibrio Fisheri bacteria (ISO 11348)		
	Drag friction tests,	15 min	30 min
		>50	48.5
	Washability test 10000 cycles	>50	> 50

* EL50 is the concentration of the test substance which results in a 50% reduction in its growth or growth rate relatively to its control.

Analysing the toxicity response of the selected paint formulation expressed by the EL50 parameter (Table 4), it is possible to conclude that the formulation SIL1 is not harmful for Vibrio Fisheri.

Antifouling assessment: trial test in an ENP (Estaleiros Navais de Peniche, Portugal) Ship

The optimised SIL1 formulation after optimisation provided by HEMPEL and containing 0.56 wt.% immobilised Econea is being assessed in an ENP ship. The trial test, including its final supervision is almost completed and soon the obtained antifouling assessment will be published (http://www.foulxspel-antifouling.com/).

Figure 6. Vessel “Mar Português” painted with a new silicone based non-leaching coating. Photos gently provided by ENP, SA.

5. CONCLUSIONS

The main conclusions of this paper, is that it seems possible to develop antifouling solutions by covalent bind or immobilize, including a really small quantity of biocides (0.56 wt.%). It has been analysed by means of toxicity analysis that the coating release is not harmful for the environment when testing with Vibrio Fisheri bacteria and practically not harmful when testing with marine algae. The paper present also the methodology for developing covalent bonded biocides in polymeric marine coatings and to evaluate its release at a laboratory level using different methods for obtaining the leaching products such as stirring, washability and drag friction tests in order to prior quantify the environmental impact. The selected paint formulation SIL1 is being successfully tested in an ENP ship.

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