FP7-OCEAN-2013

Grant Agreement Number 614034

SEAFRONT

Synergistic Fouling Control Technologies

Deliverable D3.21: Performance assessment of Selektope-functionalized coating (electrostatic attachment)

Delivery date: January 2017

Table of contents

1 Introduction

Deliverable 3.12 has been completed, providing a performance assessment of antifouling coatings which were formulated to contain the electrostatically attached non-lethal biocide Selektope.

2 Partners involved

Newcastle University – School of Chemistry,, I-Tech, Solvay, Newcastle University – School of Marine Science and Technology, AkzoNobel

3 Description of technology delivered

To 'electrostatically' bind Selektope molecules into a coating, Selektope underwent an acid-base reaction with the *bis*-phosphonate fluoropolymer to afford the Selektope-polymer salt as a viscous liquid (see D3.7 for more information on electrostatic attachment of Selektope). The Selektope-polymer salt was shipped to AkzoNobel where it was then formulated into 'grey' PDMS and a commercial fouling release product referred to here as 'Fouling Release A' at different weight percentages (Table 1) by James Ferguson.

Table 1: Summary of formulations of grey PDMS and Fouling Release A with Selektope-PFPE salt.

Code	Details
IP-006	Grey PDMS, non-functional
IP-007	Grey PDMS with 2.5% Selektope-PFPE
IP-008	Grey PDMS with 5.0% Selektope-PFPE
IP-009	Fouling Release A
IP-010	Fouling Release A with 2.5% Selektope-PFPE

These coatings were applied to either metal plates (in field studies) or glass microscope slides (laboratory studies) following manufacturer instructions.

3.1 Field studies in Singapore

Formulations IP-006-010 were applied onto a 6 x 6 latin square and submerged in Singapore starting on 03/09/2015. The board was then removed after 10 weeks and visually examined, revealing a build-up of macrofouling upon all samples (Figure 1a). The Time-weighted Hydrodynamic fouling rating for all formulations was determined by standard methods (Figure 1b,c) to provide a measure of extent of fouling.

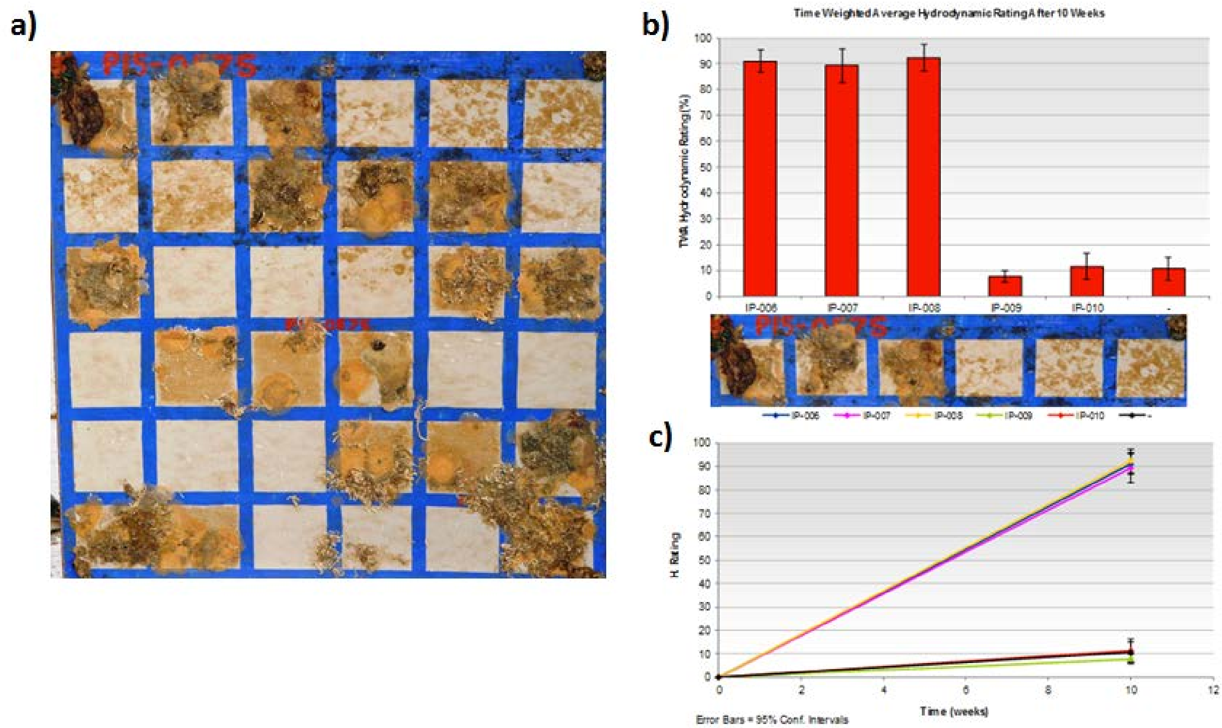

Figure 1: 6 x 6 Latin square board after 10 weeks immersion in Singapore (a); time-weighted average ~~hydrodynamic~~ fouling rating for each coating at 10 weeks (b); hydrodynamic (H) rating as a function of time (c).

These results suggest that the incorporation of Selektope into grey PDMS (Figure 1a, IP-007, IP-008) does not improve its antifouling performance relative to grey PDMS (IP-006) which displays a near-identical hydrodynamic rating. Likewise, the addition of Selektope into Fouling Release A (IP-010) appears not to improve its antifouling performance relative to the pure coating. These results also suggest that incorporation does not decrease the antifouling performance of these compounds.

3.2 Field Studies in Hartlepool, UK

Formulations IP-006-010 were applied onto a 6 x 6 latin square and submerged in Hartlepool Marina, UK, starting on 06/10/2015. The board was then removed after 6 weeks and visually examined, revealing a build-up of macrofouling upon all samples (Figure 2a). The Time-weighted ~~Hydrodynamic~~fouling rating for all formulations was determined by standard methods (Figure 2 b,c).

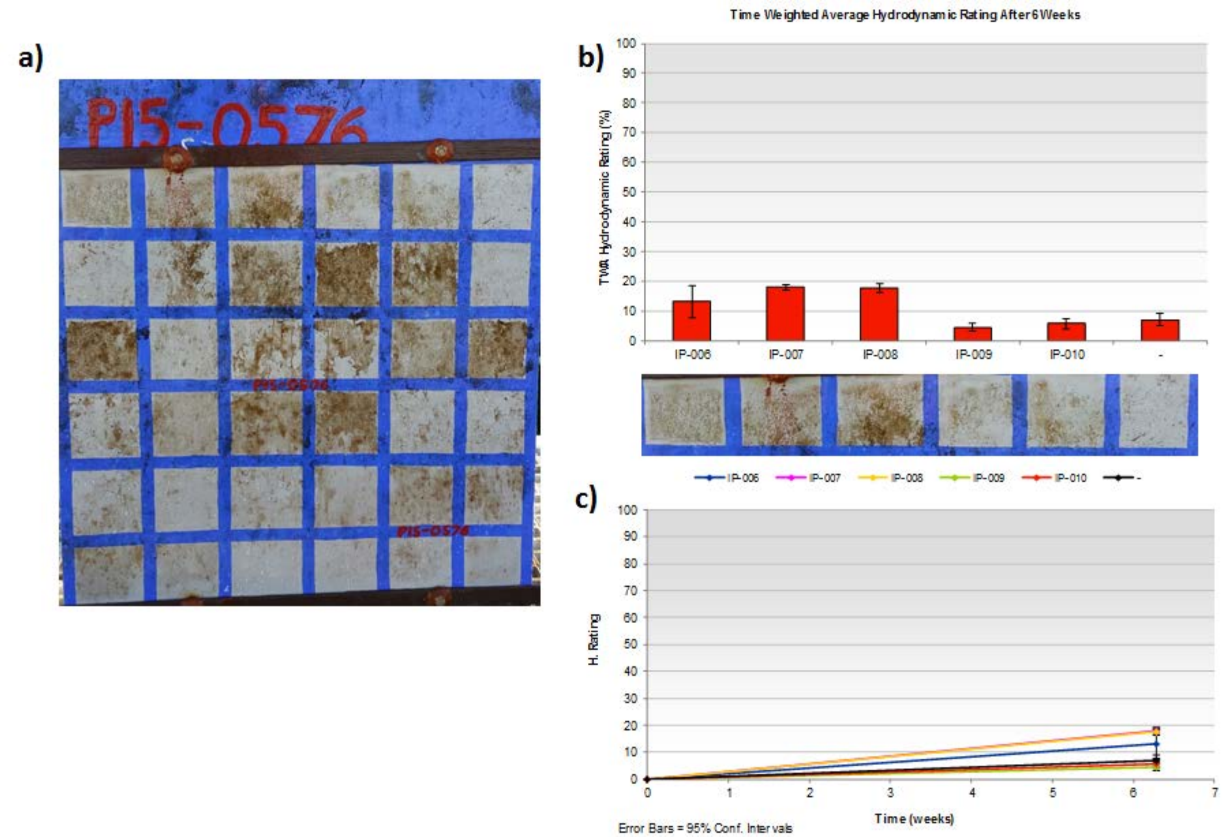

Figure 2: 6 x 6 Latin square board after 6 weeks immersion in Hartlepool, UK (a), time-weighted average ~~hydrodynamic~~fouling rating for each coating at 6 weeks (b); H-rating as a function of time.

These results suggest that the ~~incorportation~~incorporation of Selektope into grey PDMS (Figure 2b, IP-007, IP-008) does not improve its antifouling performance relative to grey PDMS (IP-006). Likewise, the addition of Selektope into Fouling Release A (IP-010) appears not to improve its antifouling performance relative to the pure coating (IP-009). Note that less fouling is observed in this field trial in comparison to the Singapore field trial, a difference which arises because of the significantly stronger fouling challenge present in the warmer waters of Singapore. Taken together, the results of the field trials in UK and Singapore do not suggest that the addition of Selektope to PDMS or Fouling Release A affords any statistically significant improvement in performance against slime or animal fouling. These results also suggest that incorporation does not decrease the antifouling performance of these compounds.

3.3 Slime farm

Samples on glass microscope slides were immersed for 53 days at the Dove Marine Lab (Newcastle, UK) in a pool with a flow through seawater system taking water from the sea then filtering it through sand to allow in the pool only the species forming microbial slime layers. Slides were removed at 13 and 53 days and their percentage slime coverage determined by imaging software. Results are presented in Figure 3.

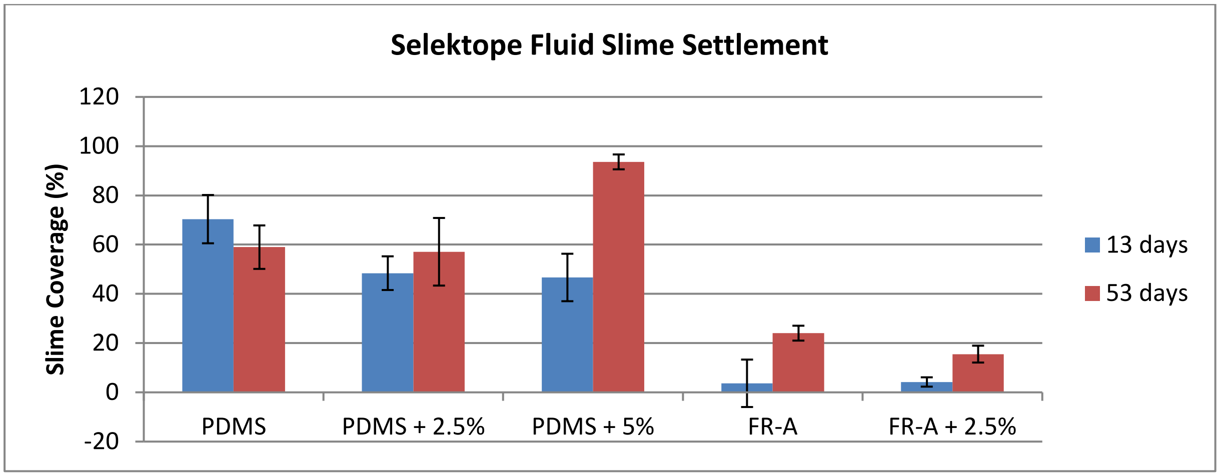

Figure 3: Slime coverage of glass microscope slides coated with IP006-010 after 13 and 53 days in Dove marine laboratory 'slime farm'.

These results suggest that addition of Selektope to PDMS actually improves slightly its antibiofilm~~ouling~~ performance over 13 days, but at 53 days the sample with 2.5% Selektope performs no worse that pure PDMS, and the sample with 5% Selektope performs worse. Addition of Selektope to Fouling Release A does not affect significantly performance at 13 days, but there ~~is probably~~appears to be a slight improvement at 53 days.

The effects of shear flow upon slime removal were then investigated (Figure 4), revealing that the addition of Selektope into either PDMS or Fouling Release A makes little difference to the ease of removal of fouling.

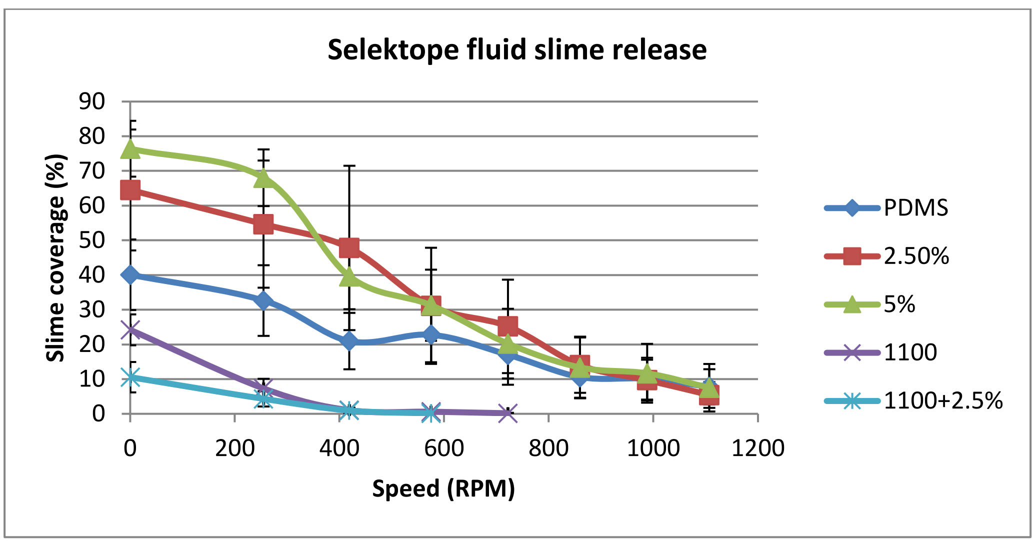

Figure 4. Slime coverage as a function of shear water speed (water speed represented by the pump impeller speed in RPM).

3.4 Barnacle nauplii activity/mobility assays of coating leachate

Coatings were leached for 48 and 77 days and the leachate collected. The activity and mobility of barnacle nauplii in these leachates were assessed after 24, 48 and 72 h. The activity was determined by counting the proportion of nauplii which displayed any movement, whereas the mobility was measured by counting only the proportion which were actively swimming (Figure 5).

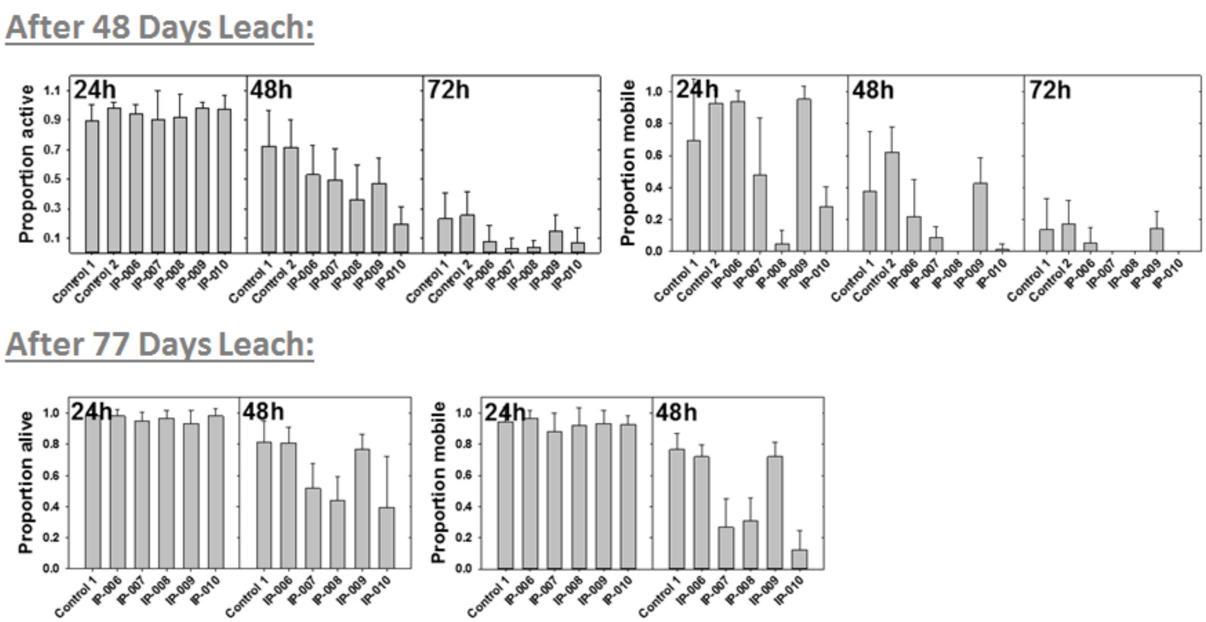

Figure 5: Proportion of active and motile nauplii at 24h, 48 h and 72 h time points in leachate obtained at 48 and 77 days.

Several trends can be observed. The proportion of active nauplii decreases with time, with less activity observed at longer time points. Likewise, nauplii mobility also decreases with time. Most notably, there is less activity and mobility observed with those coatings which contain Selektope versus those which do not. This observation suggests that Selektope (which increases swimming activity in barnacle larvae) within the leachate has induced the nauplii to consume their energy reserves faster, leading to reduced survival / activity when counted after 24 hours.

3.5 Diatom settlement and removal assay

The standard SEAFRONT diatom settlement and removal assays were performed to determine the initial settlement of diatoms upon the surfaces and percentage removal after exposure to hydrodynamic shear stress (Figure 6).

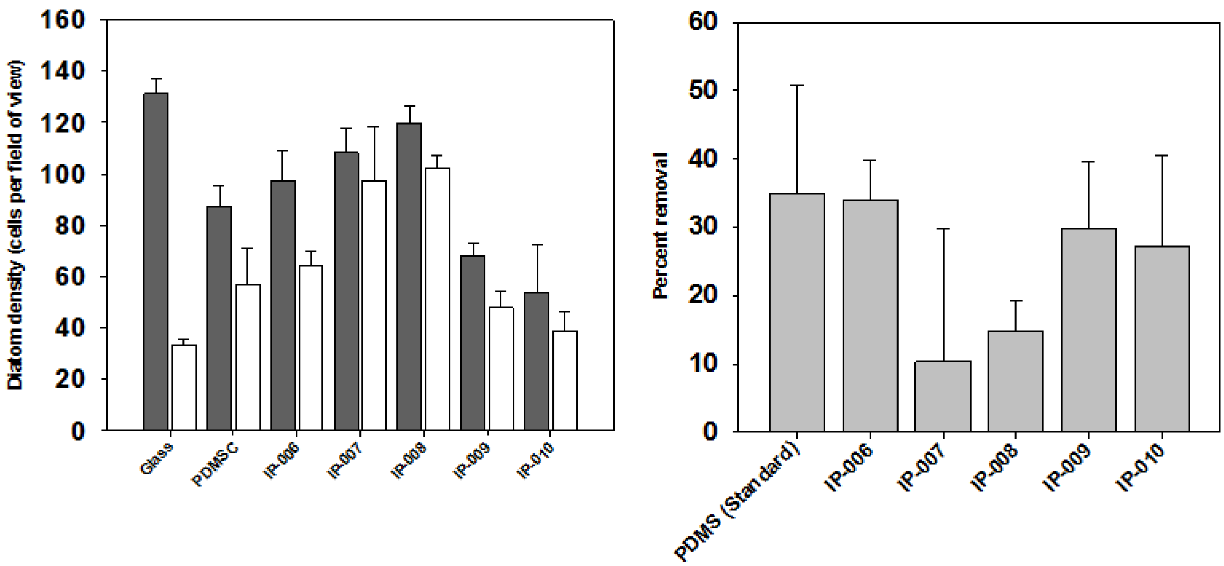

Figure 6: Density of diatom settlement before and after application of hydrodynamic shear (a), percentage of diatoms removed by application of hydrodynamic shear (b).

IP-006 performs as expected the same as the standard PDMS slides (Figure 6a). Adding Selektope (IP-007 and IP-008) seems to increase the adhesion of diatoms. In this assay there seems to be little effect of adding the Selektope to Fouling Release A (IP-009 is Fouling Release A and IP-010 is the Fouling Release A with the Selektope). There is no significant statistical difference. Similarly adding Selektope reduces the percentage release of diatoms (Figure 6b) from PDMS, and has little effect on Fouling Release A. These results suggest that addition of Selektope to PDMS decreases its fouling-release performance, and the addition of Selektope to Fouling Release A has little difference on its fouling-release properties.

4 Conclusions

In conclusion, the addition of Selektope to PDMS does not enhance the antifouling properties of this coating in field tests. Likewise, Fouling Release A also does not benefit significantly from the addition of Selektope. However, both coatings do not appear to have their antifouling performance in field tests impaired by the addition of Selektope. Results from diatom settlement assays suggest that addition of Selektope is detrimental to antifouling performance, a puzzling observation given the selectivity of Selektope towards barnacles.

These findings corroborate the conclusion drawn from the work on covalent attachment of Selektope to coating surfaces (see D3.13), namely that the Selektope needs to be untethered in order to maintain its activity against barnacle larvae.