ActiGuard®: Novel technology to improve long-term performance of silicone-based Fouling Defence coatings

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Summary

A new and unique fusion of biocide and hydrogel technologies into ActiGuard® offers unprecedented control of biocide-release from silicone coatings, as well as efficient utilisation of the biocide content. ActiGuard® not only provides a biocide-activated hydrogel at the surface of the coatings, it also controls the release of biocide in an unprecedented manner. The biocide release-rate for ActiGuard® follows the increase in temperature, but it does not change with speed. Since fouling pressure increases with increasing temperature, but decreases with speed, these features ensure efficient utilisation of biocide. Considering together, the limited amount of biocide utilised, and the significant impact ActiGuard® has on antifouling performance, this technology breaks ground to a new era of unprecedented fuel-efficiency from environmentally friendly Fouling Defence coatings.

Introduction

Fouling Release

Silicone-binders for Fouling Control coatings were first invented in 1972 [Swain 1998]. However, not until the middle 1980's were the mechanisms behind unveiled [Swain 1998]. The Baier curve depicted in Figure 1 shows the relative adhesion of marine bacteria as a function of surface tension. Baier explains the superior properties of silicone surfaces against fouling by its high hydrophobicity coming from the very low surface-tension. However, as seen in Figure 1, the surface tension of polyfluorinated materials is even lower, which is not reflected in the relative adhesion of marine bacteria to these substrates.

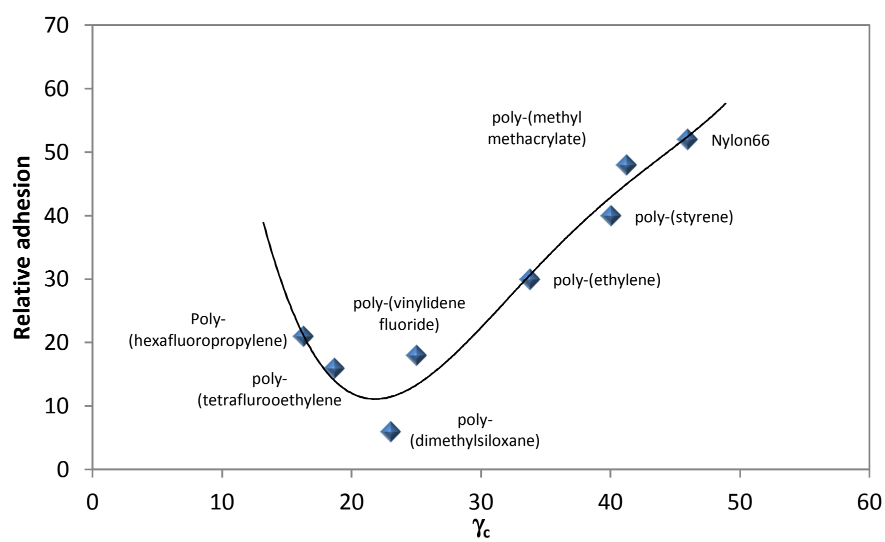

Figure 1: The 'Baier curve': Relative adhesion as a function of surface tension. Data from Brady and Singer [2000]

Brady and Singer [2000] explain the superior performance of silicone compared to fluorinated polymers by the elasticity. Silicones are inherently flexible, and as seen in Figure 2, the combined surface tension and flexibility proposed by Brady and Singer nicely predicts the relative adhesion of marine bacteria.

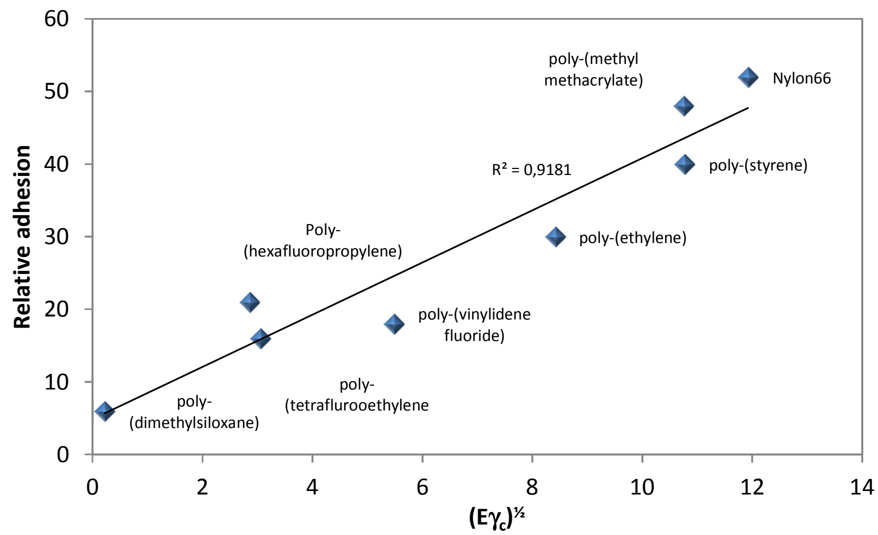

Figure 2: Relative adhesion as a function of squareroot of the product of the substrates elasticity and surface tension. Data from Brady and Singer [2000]

Commercial Fouling Release technologies

The very first patent on fouling release coatings was based on biocide-free silicone rubber [Krøyer 1973]. Later it was found that adding non-reactive hydrophobic siloxane-oils such as poly dimethyl siloxane and polyphenylmethyl siloxane to the siloxane binder system improves the Fouling Release properties [e.g. Truby 2000]. However, these versions were still insufficient in staying fouling-free [Yebra and Catalá 2011] During the middle of the zeroes, and beginning of this decade, several new launches of commercial fouling release coatings were seen [Lejars 2012]. Of these Hempel's Hempasil X3, International paint's, Intersleek 900, and Jotun's Sea-lion repulse included new materials to improve performance [Lejars 2012]. However, whereas intersleek 900 and intersleek 1100 contain fluoropolymers in order to obtain an amphiphilic surface that aids the Fouling Release properties, and Jotun's Sealion repulse contains nanosprings to repel and release fouling organisms, Hempel's Hempasil X3 includes hydrogel precursors for the formation of an extremely hydrophilic hydrogel on the outermost surface of the coating. This is inspired by state-of-the-art biomedical research, and even though it may seem contradictive that the very same technology that was introduced due to highly hydrophobic properties would benefit from introduction of a hydrophilic hydrogel to its surface, the technology provides state-of-art non-fouling properties (Yebra and Catalá 2011). The reason has been explained by Baier [2006] by the expansion of the Baier curve to also cover hydrophilic surfaces. The data reported by Baier in [2006] is illustrated in Figure 3 below.

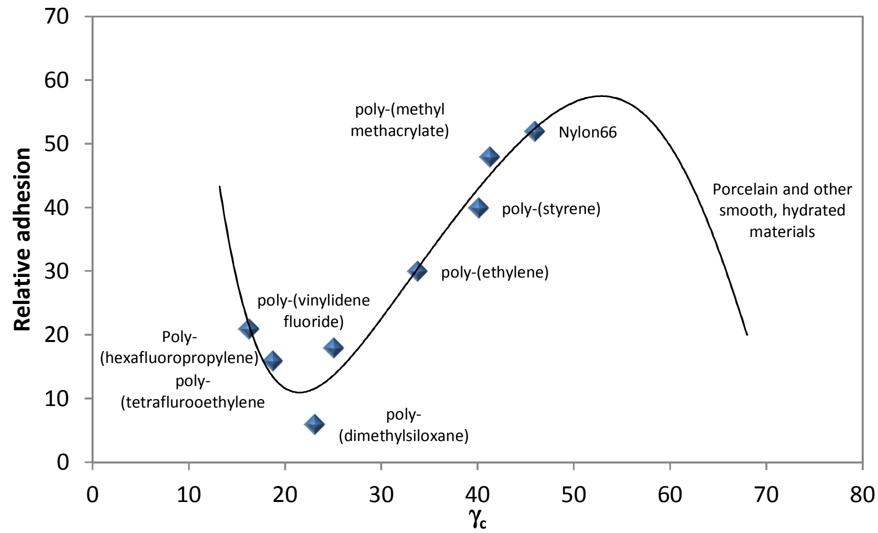

Figure 3: Relative adhesion as a function of critical surface tension. Modified from Baier [2006]

Since water has a surface tension of 72 dynes/cm, the hydrogel induced on the surface of Hempasil X3 therefore belongs to the highly hydrophilic part of Baier's curve. It was concluded by Baier (cf. Figure 3) that hydrophilic surfaces also poses non-fouling properties (so-called zeta-surfaces).

The actual working mechanism of the hydrogel in Hempasil X3 is three-fold. The hydrated layer of the hydrogel-polymers utilised in 3rd generation Fouling Release coatings can be considered similar to the co-existence of water and ice at low temperature [Yebra and Catalá 2011]. Water trapped in this layer exhibits a gradient from liquid water to more gel-like, trapped water. This gradient presents the biofouling organisms encountering the hydrogel-layer with a surface unlike other surfaces in the marine environment. Those fouling organisms, actively exploring the surface, do not recognise the surface of a hydrogel [Rosenhahn 2012], and the opportunistic foulers that do not exhibit exploratory behaviour, cannot displace the water-molecules bound in the hydrogel-layer with their glue. As a third level of protection, the silicone-based matrix underneath the hydrogel layer offers very low surface energy for the fouling organisms to anchor their glue, and as outlined above, silicone is well known for its Fouling Release characteristics. These three effects combined offer a potent means to protect against biofouling organisms.

Biocide in Fouling Release coatings

Biocide release from Fouling Release coatings has, until recently, not been possible due to:

- Only low amounts of biocides can be used to maintain surface smoothness and low surface energy
- A very rapid release of biocides from the silicone matrix, which is not optimal for controlled release purposes

The below figure shows the effect of adding biocides into commercial Fouling Release coatings, it is evident that the biocides do not improve the performance compared to a biocide-free hydrogel-based Fouling Release coating.

Figure 4: comparison of biocide-free and biocide containing commercial Fouling Release coatings. Left: Hempasil X3 after 8 months immersion in Singapore. Middle: Hempasil 77500 with biocide after 7 months in Singapore. Right: Fluoropolymer Foul Release coating with biocide after 7 months in Singapore.

With the introduction of the ActiGuard ® technology, it has become possible to exploit biocides in silicone-based coatings and thereby further prolong the fouling-free period of these types of coatings. HEMPAGUARD® X5 and HEMPAGUARD® X7 are the first coatings to exploit ActiGuard® as a defence mechanism against biofouling. The results are unprecedented long term fuel savings.

ActiGuard®-technology

Actiguard® works by forming a biocide-activated hydrogel on the surface of the Fouling Defence coating. The hydrogel effectively traps the biocide during diffusion out of the film thereby increasing the surface concentration of the biocide and prolonging the retention time of biocide in the coating matrix and on the surface. This means that a lower amount of biocide is needed to effectively prevent the settlement of biofouling animals. The working mechanism of ActigGuard® is schematically illustrated in Figure 5 below.

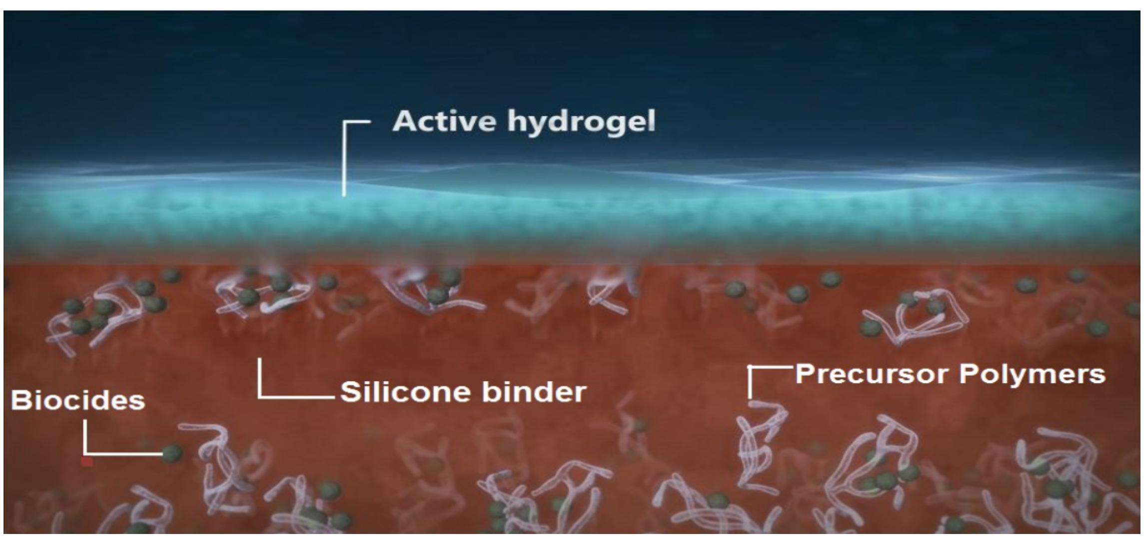

Figure 5: schematic illustration of ActiGuard®.

The figure shows that the apparent concentration of biocide in the hydrogel surface of the coating is higher for Actiguard® than for a conventional Fouling Release coating containing biocides. This is because the biocide is trapped in the hydrogel on the way out of the coating. In addition to very effectively utilise a minimal amount of biocide, it also means that the biocide concentration can be kept at a level where the silicone coating retains it silicone properties.

Biocide content

ActiGuard® needs only a very limited amount of biocide to work effeciently during prolonged immersion. Figure 6 shows the average biocide content pr. square centimetre coating for two ActiGuard®-systems (HEMPAGUARD X5 and X7) compared to a conventional silyl acrylate antifouling coating. It is evident from the figure that the biocide content in a typical ActiGuard®-formulation is almost negligible compared to that, in a conventional antifouling coating.

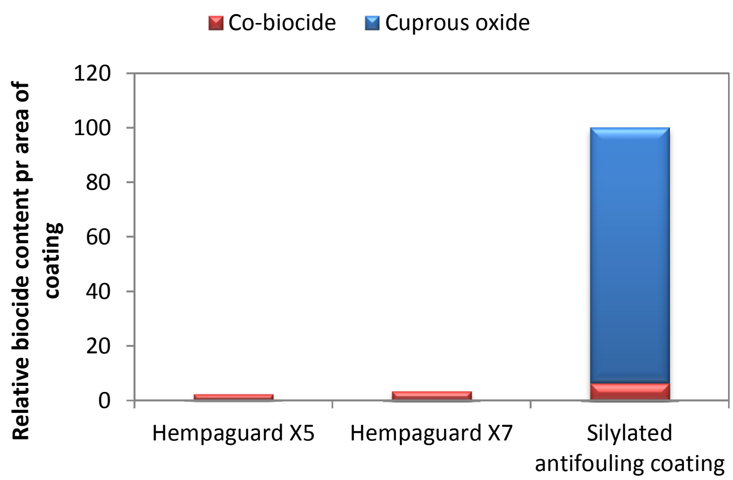

Figure 6: Average biocide release over the life-time of the coatings for HEMPAGUARD® X5 and X7 compared to a conventional silylacrylate antifouling coating. The calculation is based on conventional specifications (150 µm DFT for HEMPAGUARD® and 280 µm for the antifouling system).

Biocide release

The biocide release rate from ActiGuard® can be described by the following mathematical formula derived from Fick's laws of diffusion:

$$RR = \frac{A\,Dc_s}{l_s}$$

RR is the biocide release-rate from the surface of the coating, A the area, D the diffusion coefficient of the biocide, c_s *the concentration of biocide at the pigment front, and* l_s *the thickness of the diffusion layer.*

The validity of this model is seen in Figure 7, where the amount of remaining biocide in an ActiGuard® -system is compared to that predicted of the model. It is seen that the practical observations are in very good alignment with the model. This means that the mechanism responsible for the control of the release-rate is the diffusion of biocide through the coating matrix (as opposed to the rate of dissolution of the biocide at the pigment-front for self-polishing antifouling coatings [Kiil et al. 2001]).

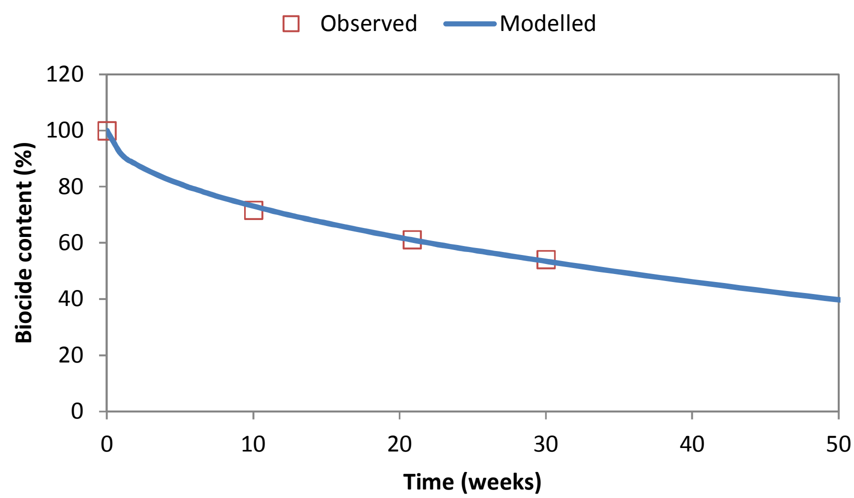

Figure 7: Model of biocide content over time in a dynamically immersed HEMPAGUARD® coating.

Biocide release from non-polishing film matrices have historically been used as antifouling coatings [Yebra 2004]. However, compared to these technologies, ActiGuard® keeps a high and stable biocide release-rate. Figure 8 shows the development in biocide release-rate from ActiGuard®. Also shown in the figure is the relative biocide release-rate of a conventional, non-polishing, antifouling coating containing an identical amount of biocide. It is seen that for ActiGuard®, the release-rate is kept higher and more stable than for other non-polishing coating types. The stable release-rate ensures efficient utilisation of the biocide, while keeping the hull free from fouling.

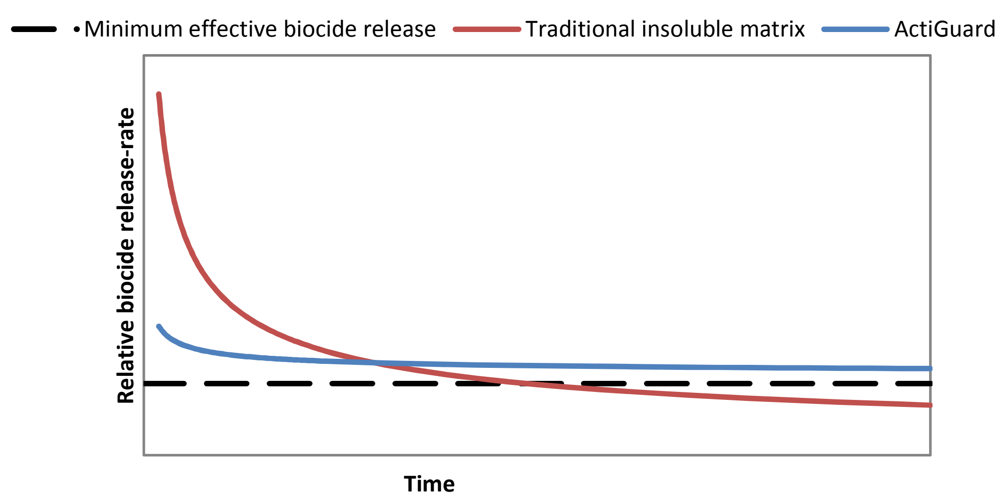

Figure 8: Comparison between the development in biocidal release-rate between ActiGuard®, and a conventional insoluble matrix antifouling coating. Both coatings contain a similar amount of biocide initially. A minimum effective biocide release-rate is indicated by a punctured line.

Biocide release-rate as a function of temperature

The release-rate of biocide from ActiGuard®-based Fouling Release coatings is rather stable as shown above. However the biocide release rate varies with temperature. Measurements at different temperatures have shown that the biocide release-rate's dependency on temperature follows the Arrhenius equation. Modified for coating parameters, the Arrhenius equation can be written as:

$$RR = A_0 \cdot e^{\frac{-E_a}{RT}}$$

RR is the release-rate of biocide, A_0 a constant, E_a the activation energy, R the gas constant and T the temperature in Kelvin.

Figure 9 shows a fit of biocide release-rate from ActiGuard® at different temperatures. Note that the fit is done on a semi-logarithmic scale (i.e. ln(P) fitted against 1/T). On this scale, the Arrhenius plot becomes linear, and the good linearity observed, proofs that change in biocide release-rate from ActiGuard® as a function of temperature follows the Arrhenius equation.

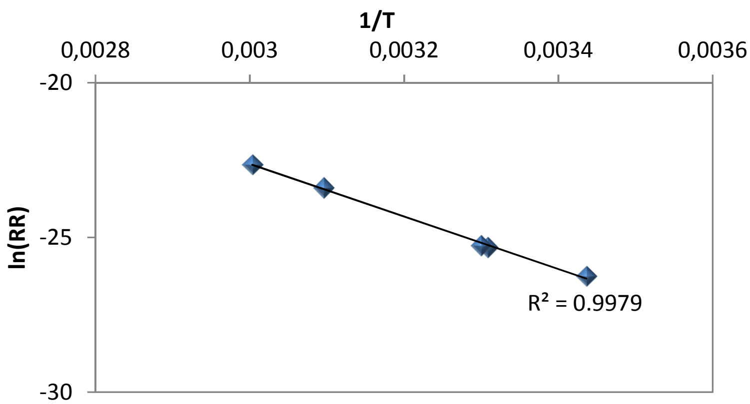

Figure 9: Observed release-rate data from ActiGuard® coatings at different temperatures. The data is fitted to an Arrhenius plot.

It is evident from Figure 9 that a change in temperature for a vessel protected from fouling by ActiGuard® will lead to a change in biocide release-rate. However, since fouling pressure also changes with temperature, the temperature dependency of ActiGuard® is an important factor in preventing fouling at all temperatures. In fact, comparing the development in biocide release-rate from ActiGuard® to the temperature dependency of fouling accumulation rates, as reported by Egan (1987) gives the plots shown in Figure 10. It is seen, that biocide release rate from ActiGuard® follows the increasing fouling pressure very nicely. This means that Actiguard utilises the biocide effectively. At low temperature where the fouling pressure is low, the release-rate from Actiguard is correspondingly lower. The release-rate however, increases with the increasing fouling pressure arising from higher temperature, and hence no excess of biocide is released unnecessarily.

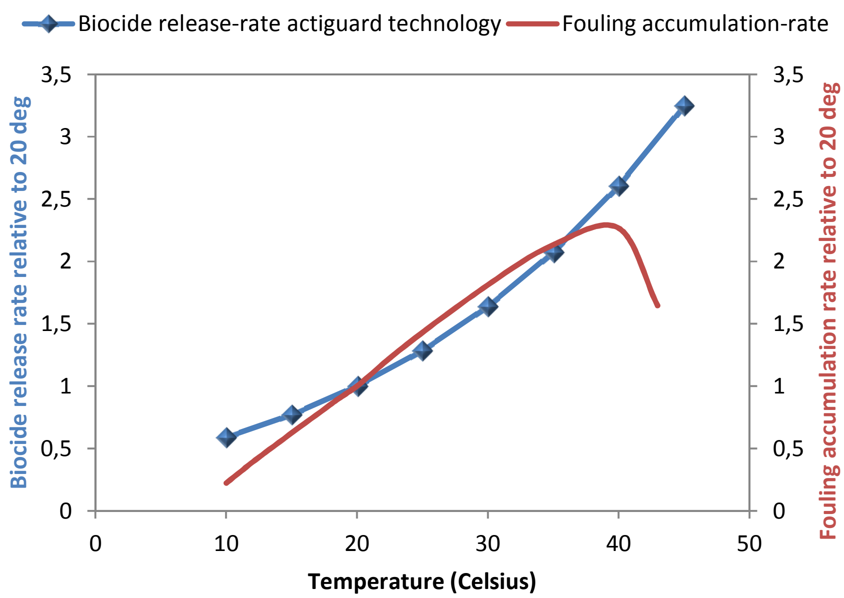

Figure 10: Comparison of development of biocide release-rate from ActiGuard® and fouling pressure as a function of temperature.

Biocide release rate as a function of travelling speed

One major advantages of ActiGuard ® technology vs. any antifouling technology to date (including TBT-based) is the stable biocide release-rate irrespective of travelling speed. Measurements of biocide leaching have been performed on samples immersed dynamically at speeds ranging from 0.08 knots to 20 knots. The results are shown in Figure 11. The figure shows that the release-rate of biocide from ActiGuard® is stable between 0.2 and 20 knots. This means that even at static conditions, where the current is more than 0.2 knots, the biocide release is equal to that of a vessel travelling at 20 knots. And at currents down to 0.1 knots, the release-rate of biocide is 85% that of a ship sailing at full speed. This is a key factor allowing for very low speed and activity of vessels protected against fouling by ActiGuard®. From an environmental perspective, the stable release of biocide irrespective of travelling speed means that less biocide is released into the environment, since the fouling pressure is lower when travelling at higher speeds. Conventional antifouling coatings release more biocide when the flow-rate is higher (Kiil et al. 2002). Due to the lower fouling pressure at higher flow-rates, this is an inefficient utilisation of biocide.

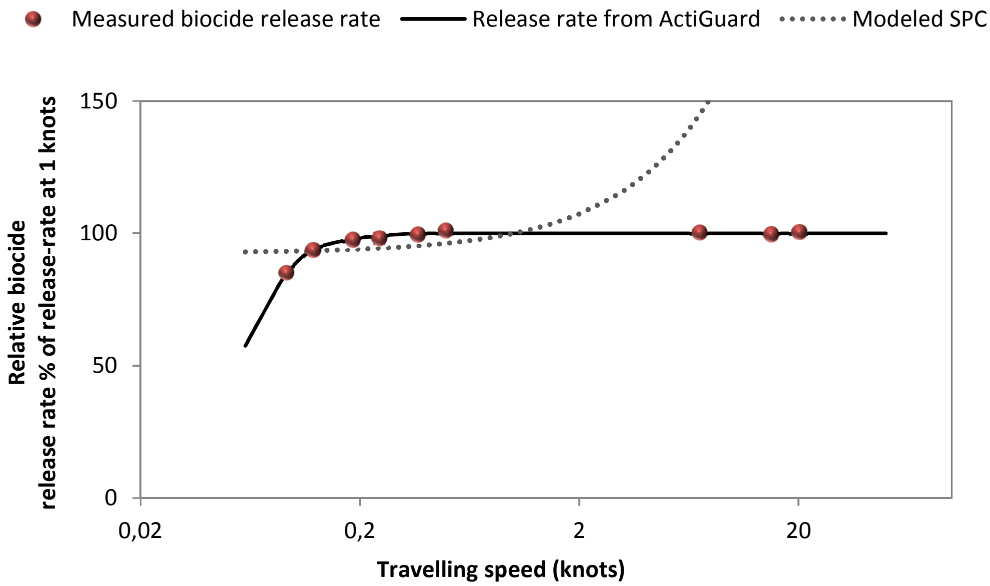

Figure 11: Relative biocide release rate from ActiGuard®as a function of travelling speed. Also indicated is the relative biocide release rate from conventional SPCs (adapted from Kiil et al. 2002). Note the logarithmic scale on the X-axis.

Furthermore, whereas conventional antifouling coating systems are specified according to speed of operation, as well as water-type, when specifying ActiGuard®-based systems, the only operating parameter that needs to be considered is the trading waters of the vessel. This also means that the sailing pattern can be changed during operation without affecting the service-life of the coating.

Conclusions

ActiGuard® is a novel technology, that fuses antifouling and Fouling Release technologies by biocidal activation of a hydrogel-layer. This means that ActiGuard® offers unprecedented fouling control performance while minimising the biocide release to the environment. Taking together, ActiGuard offers:

- Stable biocide release-rate for speeds between 0.2 and 20 knots
- Biocide release-rates that increases with temperature
- Very low biocide-release to the marine environment
- High flexibility during operation of the vessel

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