Hempaguard® X5 and Hempaguard® X7: Novel ActiGuard®-based Fouling Defence technologies

Date

Kim Flugt Sørensen, Dorthe Hillerup, Anders Blom, Stefan Møller Olsen

Hempel
Address line one
Address line two
Address line three

Tel: +00 0000 0000
Fax: +00 0000 0000
Email: Name@hempel.com

Hempaguard X5 and X7 are the first products on the market utilising the patented ActiGuard technology.
By fusing hydrogel-based Fouling Release technology with a controlled release of biocide, the novel ActiGuard technology offers unprecedented fuel savings potential.

The initial fuel efficiency offered by silicone-based Fouling Release products is extended dramatically due to the efficient utilisation of a small amount of biocide.

Nevertheless, the antifouling performance of Hempaguard greatly exceeds that of any antifouling systems regardless of sailing speed and water temperature, hence solving the problem of long idle periods in fouling-aggressive waters.

Biofouling and its consequences

The accumulation of biofouling on ship-hulls has adverse effects for the ship operator and the environment.
The increase in skin friction, arising from the added roughness caused by by the fouling organisms, decreases fuel efficiency significantly. This means that more fuel has to be spent for a ship to cover the same distance, and as a consequence the fuel bill and the emission of greenhouse gasses are increased. Heavily fouled ships may need to increase shaft power with up to 86% to compensate for the speed-loss inflicted by the increased drag resistance [Schultz 2007]. However, the extent of biofouling does not have to be high for it to be problematic. Even when the hulls are covered in light slime, the change in shaft power required to counteract the speed loss can amount to about 10 % [Schultz 2007]. Furthermore, in addition to its impact on fuel efficiency, biofouling on ship hulls also works as a vector for translocation of invasive species. It is therefore a necessity to effectively prevent biofouling in order to make marine transportation more cost efficient, but also to preserve the atmosphere and the diversity of the marine flora and fauna.

Antifouling coatings

Historically, fouling has been combatted by antifouling coatings, and these have generally contained high amounts of biocides. Legislation has forced paint manufacturers to disregard the more adverse of the biocides such as the once popular and effective tributyl tin-derivatives. However, even though biocide regulations have become stricter and expanded geographically, most of the antifouling coatings used today still contain high amounts of biocides [Yebra et al. 2004; Pereira and Ankjaergaard 2009]. It is estimated that 3,000 tonnes of copper are released every year to the marine environment by antifouling coatings on ocean going vessels [Yebra et al. 2004].

Fouling Release

An alternative to biocide-based antifouling coatings are Fouling Release coatings, which traditionally do not contain any biocides. Instead, biofouling is prevented by physical means. Generally Fouling Release coatings are characterised by being smooth, flexible, and having a low surface-energy [Yebra et al. 2004]. Originally, Fouling Release coatings worked by releasing fouling rather than deterring it; the natural adhesive of biofouling organisms can only with difficulty wet the surface of a highly hydrophobic silicone coating when immersed in seawater. Therefore the strength of adhesion is low and flexibility of the substrate allows for the motion of seawater to peel off the biofouling organism during operation of the vessel. However, these coatings were dependant on a relatively high activity and speed in order to be efficient in preventing accumulation of biofouling. Typical requirements to this type of Fouling Release coatings were an activity level of 75 % at or above 15 knots to sustain their self-cleanability [Yebra and Catalá 2011].
At these conditions, the siloxane-based coatings showed good performance against shell fouling and macroalgae. However, even at high activities and temperatures, slime still accumulated on the coatings [Yebra and Catalá 2011]. A well-

developed slime layer serves as a substrate for other fouling organisms, ultimately compromising the non-stick properties of the silicone surfaces. Therefore, the fuel-efficiency of the first generation of Fouling Release coatings decreased significantly over time.

Hydrogel-based Fouling Release

Due to their very low surface energy, Fouling Release coatings have, historically, been based on polydimethylsiloxane binders. Additives of low surface energy polymers, such as silicone oils or phenyl modified polysiloxane oils were implemented in the second generation of Fouling Release coatings. These oils sustained the low surface-energy of the coatings for longer, while they still came out short against biofouling when seawater exposure exceeded one year [Yebra et al. 2003 and Yebra and Catalá 2011]. In 2008, Hempel A/S launched a hydrogel-based Fouling Release coating inspired by state-of-the-art biomedical research. They thereby moved the concept of Fouling Release to the opposite extreme: hydrophilic surfaces. To increase biofouling resistance, these coatings contain a hydrophilic modified silicone polymer that migrates to the surface upon immersion and creates a hydrogel layer at the outermost surface of the coating [Yebra and Catalá 2011]. Figure 1 shows the differences in surface tensions between a 2nd generation pure silicone-based Fouling Release coating, and a 3rd generation hydrogel-based Fouling Release coating. It is seen in the figure that a water droplet adsorbs onto the surface of the hydrogel- based coating, whereas the droplet is stable on the hydrophobic pure silicone coating. The adsorption of water onto the surface is associated with the formation of the hydrogel layer.

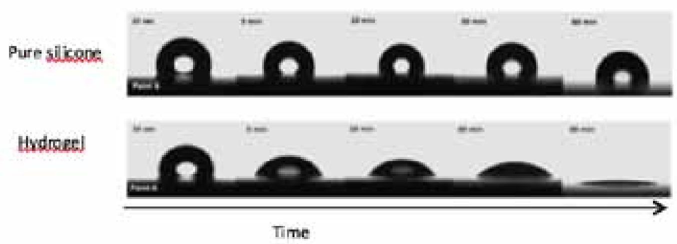


Figure 1: Comparison of development in surface tension between a 2nd generation pure-silicone based Fouling Release coating (top) and a hydrogel-based Fouling Release coating (bottom).

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. The hydrogel-surface offers a potent means to protect against biofouling organisms. Figure 2 shows a comparison of the antifouling performance between a hydrogel-based, a hydrophobic (pure silicone), and a fluoropolymer -based Fouling Release coating. The figure shows the performance after 8 months static immersion in Singapore. It is evident from the figure that the hydrogel-based coating deters biofouling better than any of the other Fouling Release coatings. These results are in agreement with several investigations previously reported in the scientific literature (e.g. Zhang et al. 2013, Zargiel and Swain 2012, Scardino et al. 2012, Zargiel et al. 2011).

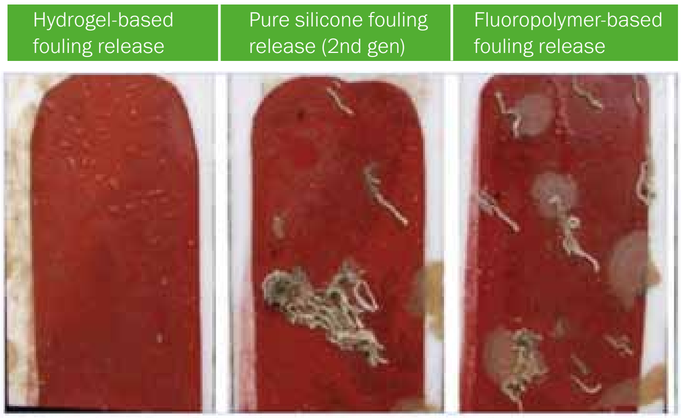


Figure 2: Comparison of static performance of 3 different Fouling Release technologies. The pictures have been taken after 8 months of static immersion in Singapore.

Even though hydrogels offer a significant improvement to the performance of Fouling Release technology, all conventional Fouling Release systems tend to decline in performance over a five-year operational period. Further improvement of the performance is therefore needed to prolong the fuel-efficiency of Fouling Release coatings even further.

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 and

- A very rapid release of biocides from the silicone matrix., which is not optimal for controlled release purposes

Fuel efficiency

Clean Fouling Release coatings are known to have improved fuel-efficiency over conventional antifouling coatings [Schultz 2007]. This is due to the smoothness and lower friction coefficient generally associated to silicone coatings [Yebra and Catalá 2010]. Table 1 shows a summary of differences in friction coefficient when comparing clean Fouling Release coatings to self-polishing antifouling coatings. It is seen that Fouling Release coatings are consistently reported to have less drag-resistance than antifouling coatings. However, these results are all based on freshly immersed coatings, and, in order to retain the fuel efficiency for a given coating, it needs to stay as clean as, or cleaner, than the antifouling counterparts.

Table 1: A summary of the reported differences in friction coefficients between freshly immersed antifouling coatings and freshly immersed Fouling Release coatings. A positive relative difference (Δ)in friction coefficient is in favour of Fouling Release.

Source	Δ Friction coefficient%	Remarks
Weinell et al. (2003)	6.1%	Rotary study. Topcoat on smooth PVC
Candries et al., (2003)	3.5%	Rotary study. Full system on smooth PVC
Schultz (2004) Schultz (2004)	3.0–4.0%	Full system on 304SS. No sandpaper strip
Candries and Atlar (2005)	5.3%	Topcoat on smooth steel. Turbulent boundary layer measurements
Westergaard (2008)	1.4% 5.0%	Towing test. Full system on smooth Al/smooth undercoats Towin test. Full system on Rz50 467 µm panels

ActiGuard-technology and Hempaguard coatings

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.

Silicone properties of Hempaguard coatings

The extremely efficient utilisation of biocide offered by ActiGuard allows for keeping the pigment volume concentration very low, thereby the coatings can resemble conventional Fouling Release coating in their physical properties. In fact, Hempaguard coatings share many of the same physical properties as hydrogel-based Fouling Release coatings. They are based on a silicone elastomer; they have a low content of pigments and fillers (Pigment Volume Concentration or PVC); and they have a low content of Volatile Organic Compounds (VOC). Table 2 below compares some central paint characteristics of two Hempaguard X5 and Hempaguard X7 to those of a hydrogel-based Fouling Release coating (Hempasil X3) and a conventional silylated antifouling coating (Hempel's antifouling dynamic 79560)

Table 2: comparison of central paint parameters for Hempaguard, Hempasil X3 and Hempel's antifouling dynamic coating systems.

	Hempaguard X5	Hempaguard X7	Hempasil X3	Dynamic 79560
VOC	274 g/l	260 g/l	262 g/l	383 g/l
PVC	6%	8.2%	1.8%	41%
Binder-type	Polydimethyl-siloxane	Polydimethyl-siloxane	Polydimethyl-siloxane	Silylated acrylate
Defence	ActiGuard	ActiGuard	Hydrogel	Biocide

The table shows that Hempaguard resembles Hempasil X3 to a great extent when it comes to general paint properties. It should be noted that the deviation on PVC between Hempaguard and Hempasil primarily relate to the biocide content. The similarities between the Hempaguard products and Hempasil X3 are also mirrored in the application properties.

The low amount of biocide in Hempaguard ensures that the coating is very smooth after application. This is a highly distinctive feature of silicone-based Fouling Release coatings [Yebra et al. 2004]. Figure 3 shows the surface morphology obtained using laser profilometry on a fresh Hempaguard coating compared to that of a freshly applied conventional antifouling. It is seen that there is a significant difference in surface roughness of the two coating types.

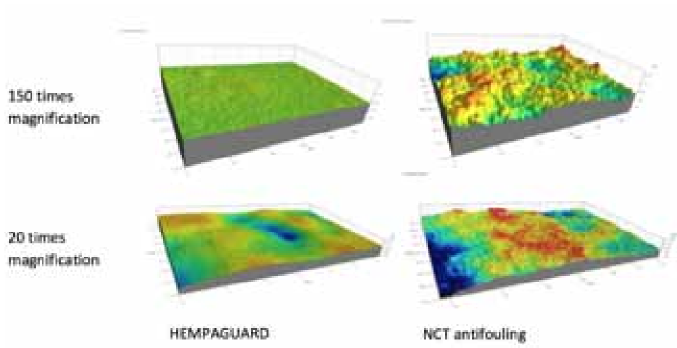


Figure 3: Comparison of the smoothness of Hempaguard coating (left) to that of a conventional silylated antifouling coating (right). Top: high magnification (150 times). Bottom: low magnification (20 times).

When Hempaguard is aged the micro roughness is not changed. Due to the low amounts of biocide no porous leached layer is developed and the surface stays smooth like a traditional fouling release coating. An example of this is seen in Figure 4 below.

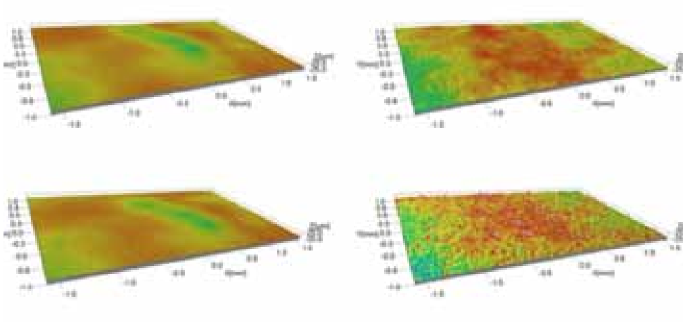


Figure 4: Smoothness of Hempaguard before and after ageing, showing that roughness does not increase.

Biocide content
The biocide content of Hempaguard coatings is significantly lower than that of conventional antifouling coatings. Figure 5 shows the average biocide content per square centimetre coating for the two Hempaguard systems compared to a conventional silylated acrylate antifouling coating. It is evident from the figure that the biocide content in a typical specification of a Hempaguard coating is almost negligible compared to that of a conventional antifouling coating.

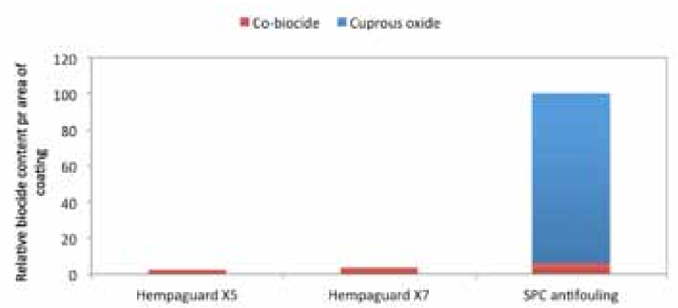


Figure 5: Average biocide content pr. area of coating. The calculation is based on conventional specifications (150 µm DFT for Hempaguard and 280 µm for the antifouling system).

Performance testing

Static performance tests
Several performance tests have been made in order to assess the antifouling performance of the Hempaguard systems. Figure 6 shows the comparison of Hempaguard coatings to Hempasil X3 during static immersion at different locations around the world. It is evident from the figure, that irrespective of the marine environment, the Hempaguard systems perform significantly better than the current state-of-the-art hydrogel-based Fouling Release technology

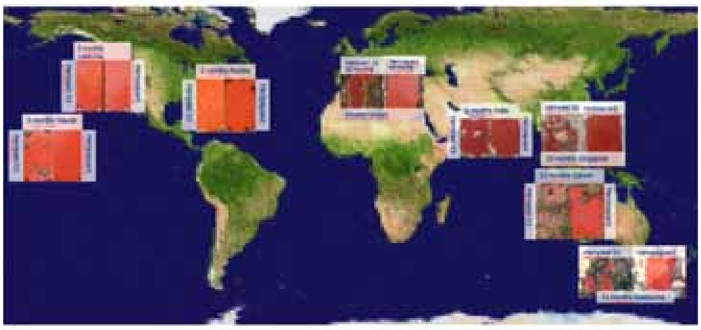


Figure 6: overview of test-sites and results of direct comparisons between Hempasil X3 and Hempaguard in static tests around the world. (World map adapted from: http://commons.wikimedia.org/wiki/File:Whole_world_-_land_and_oceans.jpg

Fouling protection of scratches
Damages are prone to occur on all antifouling systems including Fouling Release coatings. Until now, Fouling Release systems have been defence-less once damaged. However, ActiGuard provides a window of defence for the coating even after damage.

Figure 7: Pictures of damaged panels after 20 months immersion in Spain.
Left: illustration of the panel's damage-patterns. Middle: Hempasil X3 with heavy fouling on damaged areas. Right: Hempaguard coating.

Figure 7 shows the results of static immersion of panels where a heavy damage was inflicted on one quarter of the coating before immersion. The damage was inflicted by scratching two diagonal lines in the panels using a knife. This was followed by scraping off of the right triangle of coating using a spatula. It is seen that Hempaguard coatings are still able to deter fouling after infliction of significant damages. However, as the coating acts as reservoir for ActiGuard removing the coating in its entirety will also remove the protecting agent. The performance of damaged areas of Hempaguard is therefore limited compared to that of an intact coating. For damaged coatings immersed under harsh fouling conditions in Singapore, the protection of the damages has been seen to hold for between 2 to 4 months during static immersion.
In addition to rough damages inflicted by a spatula, lighter damages inflicted by roughening by sandpaper have also been tested. Figure 8 shows the results of these tests. It is seen that whereas the conventional Fouling Release coating has lower performance after roughening, Hempaguard retains its good performance even at static conditions.

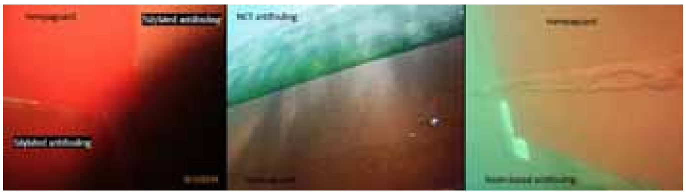
Figure 8: Pictures of panels damaged by sandpapering. Left: Hempasil X3 compared to Hempaguard after 19 months immersion in Spain. Right: Hempasil X3 compared to Hempaguard after 11 months immersion in Singapore.

Conclusions

Figure 9: Pictures of a test patch after 22 months in service. The area on the pictures is scratched but still shows excellent performance.

Real-life testing

Several ship trials have demonstrated the efficacy of ActiGuard technology. Figure 10 shows the performance of Hempaguard-coatings compared to three different conventional antifouling coatings on test patches on ocean going vessels. The three test patches represents 2 vessel-types, and 2 different levels of activity. In all of the tests, Hempaguard out-performs the antifouling systems.
Also, it is seen that one of the vessels has had idle periods of up to 20 days, without the condition of the test patch was compromised.



Vessel type: general cargo Operation time: 19 months Activity: 69% Idle periods: 8 & 10 days	Vessel type: oil tanker Operation time: 22 months Activity: 85% Idle periods: 13 & 11 days	Vessel type: general cargo Operation time: 16 months Activity: 66% Idle periods: 20 & 17 days

Figure 10: Pictures of test patches of HEMPAGUARD® on commercial vessels.

Since the launch of the technology more than 250 full ship vessels have been applied pictures from under water inspections of some of these vessels are shown below.

Figure 11: Condition of a Hempaguard coating on a container ship after 24 months of operation.

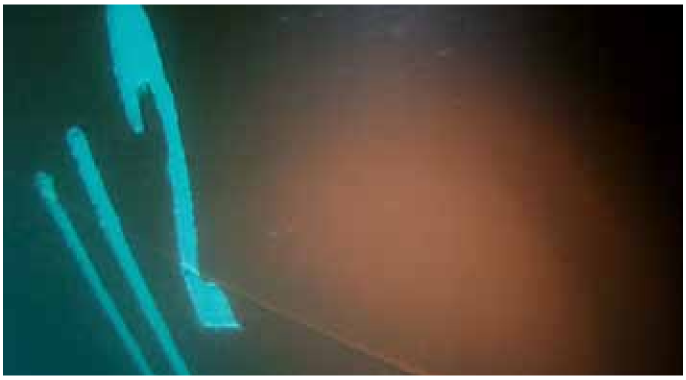


Figure 11 shows the condition of the first full HEMPAGUARD ship applied after 14 months of operation. As can be seen from the figure, the coating was in perfect condition and completely slime free.

Conclusions

Hempaguard X5 and X7 are newly developed Fouling Defence systems. They are based on ActiGuard, a biocide-activated hydrogel that has been shown to keep the surface free from fouling during extended immersion. Because Hempaguard coatings are based on silicone binder systems Hempaguard offers unprecedented long-term fuel-efficiency by keeping a very smooth hull free from fouling for longer than any alternative technologies available. Considering the limited amount of biocide utilised in ActiGuard to efficiently prevent biofouling and the significantly improved fuel-efficiency, Hempaguard can be considered the most efficient and environmentally friendly Fouling Control coating ever developed. In summary Hempaguard offers:

- Fuel-efficiency due to very smooth binder systems
- Highly efficient antifouling performance
- Fouling protection over scratches and smaller damages
- Limited biocide-release to the marine environment

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