Surface treatments for ship hulls - present situation and trends

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Abstract. Targets of the surface treatments of marine hulls have always been to preserve the structural capacity of the hull envelope and to maintain a smooth and clean external surface, thus minimizing the frictional component of motion resistance. These objectives are pursued since a couple of millennia by fighting the chemical and biological phenomena inducing various forms of degradation in the hull base material and/or in the external surface smoothness. As regards the latter aspect, in particular, a most negative effect is represented by the adhesion of biofouling, jeopardizing the resistance performance of the hull. In the past, solutions to this specific problem were found in biocide-releasing paintings, practice that is nowadays unacceptable because of its high environmental impact. New challenges in the field are represented by the possibility of not only maintaining, but also decreasing, the frictional coefficient intrinsic of the hull surface, while preserving excellent properties against fouling adhesion and minimizing environmental impact. The paper, based on publicly available data, analyses recent trends in the commercially available hull coatings and depicts possible development lines for new types of treatments aimed at reducing frictional resistance.

Keywords. Antifouling coatings, fouling release coatings, anti-friction treatments

1. Introduction

Organic coatings of many different types and formulations are frequently applied to metal structures in contact with sea water to prevent corrosion and fouling, while providing specific colour and gloss to the substrate. Since it is impossible to combine all the requirements within one coating, multi-coat systems are essential. The typical layout is composed by an undercoat, a tiecoat and a topcoat. The *undercoat* is in direct contact with the metal. Its main properties are the ability to prevent corrosion of the substrate and a good adhesion to the metal and to the following layer. The *tiecoat* (about 40µm in thickness) is a coupling layer between undercoat and topcoat. The *topcoat* has an antifouling function, i.e. inhibits the settlement of marine organisms, both plants (flora) and animals (fauna). **Figure 1** schematically represents the layers of the coating for the hull.

The dispersion of biocides, poisonous substances added to the coating matrix to kill micro or macro organisms that might settle on the hull, is the first and most used strategy to preserve the integrity and efficiency of hull surfaces. The treatments

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containing these biocidal substances are generally called biocide-based coatings, or antifouling coatings and can be divided in three main categories: i) contact leaching coatings (insoluble matrix or hard bottom or non-sloughing), ii) Controlled Depletion Polymer (CDP) coatings (soluble matrix, ablative bottom) and iii) Self Polishing Copolymer (SPC) coatings (ablative bottom).

Tributyltin (TBT) designates a class of organotin compounds used intensively in the past as biocide in marine coatings. Since a decade, it has been banned by the International Maritime Organisation because it showed to bio-accumulate in the environment affecting many layers of the ecosystem, including invertebrates and vertebrates, even humans. Another popular biocide is copper, having however, as all metals, the same tendency to accumulate. More recently, organic biocides were introduced to lower the impact on the sea environment.

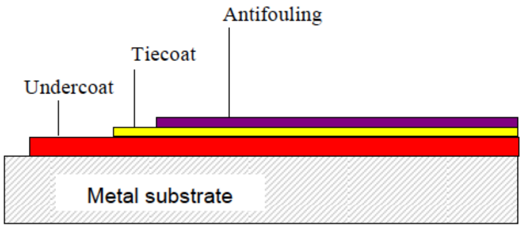

Figure 1. Coating structure for marine hulls.

Since the toxicity of biocides to aqueous organisms and marine environment are still under scrutiny, the coating industry has focussed also on non-biocidal coatings, or fouling release (FR) coatings, minimizing the foulant/surface adhesion and leading to easy removal of the biofoulant by simple mechanical cleaning or hydrodynamic stress during navigation. The most common binders used in the coatings based on this mechanism are Poly(dimethylsiloxane), PDMS (silicones) and fluoropolymers.

This paper focuses on the characteristics of commercial antifouling coatings produced by the main marine coating industries. It also depicts some possible development lines for new types of treatments aimed at reducing frictional resistance in addition to assuring antifouling properties ideally by non-releasing mechanism.

2. International Marine Coatings

The products of this company are divided in two series: i) Self Polishing Coatings, based on Lubyon technology, Copper acrylate technology and Silyl acrylate technology ii) Foul release coatings, based on fluopolymer and silicone technologies, as reported below.

2.1. Lubyon® Technology (SPC)

The company claims that Lubyon polymer is 'superhydrophilic', so it creates a lubricating effect at the coating surface, resulting in a low friction, very smooth and slippery surface on immersion, which is maintained throughout the lifetime of the coating. The polymer reacts with seawater via a constant surface active zone, releasing the optimal amount of biocide constantly, over the scheme life, to prevent fouling settlement. This release rate is largely unaffected by seawater temperature. The two main products using this technology are Intercept 8500 LPP, a high performance, low friction, linear polishing polymer (LPP) antifouling and Intercept 7000, a linear polishing antifouling.

2.2. Copper acrylate technology (SPC)

This type of paints are based on copper acrylates, so the products are integrated in an acrylic matrix to which different pendent groups of the main chain are added, however without tin. Like in self-polishing paints containing tin, the pendent groups are considered to be released in contact with sea water. The main products based on this technology are Interflex 8700 SPC, a high solids, high performance, TBT free, copper free, low friction antifouling, Intersmooth 360 SPC and Intersmooth 365 SPC, high performance, TBT free antifouling systems.

2.3. Silyl Acrylate or Methacrylate polymer technology (SPC)

Also for these paints, the pendent groups, silyl acrylates, are considered to be released when interacting with sea water, and their self-polishing effect is coupled with the controlled release of biocides. Products based on this technology are Intersmooth 7465Si SPC and Intersmooth 7475Si SPC, high solids, high performance, TBT free, low friction antifouling systems.

2.4. Fluoropolymer technology (FR)

The coatings based on this technology are designed to tackle the problem of slime on vessel performance. The company reports that the Intersleek range delivers outstanding micro and macro fouling control with better static resistance even in warm waters and that effectively releases slime even at low speeds. The main products are Intersleek 1100SR, a three component advanced fluoropolymer foul release coating, and Intersleek 1000, which is claimed by the company to be the first fouling control coating that incorporates bio-renewable raw material to deliver enhanced vessel performance throughout the dry-docking cycle.

2.5. Silicone technology (FR)

Even if the technology is very similar to that of fluoropolymers, in general the application of a force to the joint deforms the rubbery silicone and the resin peels away from the marine adhesive in a process which is slower than for fluoropolymers, which have lower surface-free energy, but requires less energy. The mechanical locking of biological glues is minimised and slippage and fouling-release are enhanced [1]. The coating based on this technology is Intersleek 757, a three pack, silicone elastomer foul release coating.

3. Nippon Paint

The products of this company are Self Polishing Coatings (SPC), divided in four series of products: LF-Sea, A-LF-Sea and ECOLOFLEX, containing biocides, and

AQUATERRAS, biocide free; in addition, a foul release (FR) coating is produced: ECOLOSILK, based on silicone polymers, as reported below.

3.1. LF-Sea Series (SPC)

As mentioned by the company, this is a biomimetic low-friction antifouling that works using a patented ‘water-trapping function’, depending on the particular roughness profile of the coating, to lower the hydrodynamic footprint of the hull. Stable and long term antifouling is guaranteed by the use of a self-smoothing copper-silyl-acrylate hydrolysis technology. The main products are LF-Sea 150-250 HyB, which fulfil the antifouling characteristic through their copper-silyl-acrylate hybrid copolymers, while LF-Sea 400-600 HyB contains cuprous oxide, too.

3.2. A-LF-Sea Series (SPC)

A-LF-Sea is the Advanced type of current LF-Sea in fuel saving performance. The mechanism of A-LF-Sea is claimed to mimic tuna, which can swim at more than 100 km per hour thanks to a special mucus over their skin. A new improved hydro-gel maximises the water-trapping effect that provides low-friction. The long-term low friction performance is ensured by incorporating this into Nippon Paint’s self polishing copper silyl acrylate antifouling. The main products are A-LF-Sea 150-250, obtaining the antifouling characteristic through their copper-silyl-acrylate copolymers, while A-LF-Sea 400-600 contains cuprous oxide, too.

3.3. ECOLOFLEX SPC Standard series

The original self-polishing antifouling paints developed by Nippon Paint are ECOLOFLEX SPC Standard series. The company says that these antifouling paints work by slow and predictable exposure of fresh antifouling surface thanks to an hydrolysis process of the resins. Cuprous oxide is present in all these coatings as toxic pigment. The self polishing properties are based on different binder systems: copper acrylate for ECOFLEX SPC 200, and ‘metal’ acrylate for ECOFLEX SPC 100-200 HS.

3.4. ECOLOFLEX SPC Hybrid (HyB) series

Nippon Paint’s ECOLOFLEX HyB series was developed to further improve the performance and predictability of the standard series. As indicated by the company, this has been achieved by combining copper acrylate and silyl resins in a unique hybrid copolymer. This provides longer service life by providing very accurate polishing rates and eliminating skeleton layers on the coating’s surface. This guarantees a constant exposition of a fresh antifouling film on the ship’s surface. The main products are ECOLOFLEX SPC 150-250 HyB, based on copper silyl acrylate polymers and cuprous oxide as biocide; ECOLOFLEX SPC 400-600 HyB based on copper silyl acrylate polymers.

3.5. AQUATERRAS Series (SPC)

The technology reported for this product is based on hydrophilic and hydrophobic micro domain structure of the coating, derived from medical anti-thrombogenic polymers, and continuous hydrolysis of the binder, which constantly exposes the active micro domain structure to sea water. The company declares that the flat and smooth surface, attributed to the absence of biocides, i.e. heavy pigments, is maintained over time due to the continuous hydrolysis reaction.

3.6. ECOLOSILK (FR)

This product is a biocide-free antifouling paint based on the technology of the silicone elastomers: a low frictional resistance, preventing ship fouling organisms from settling, is realized by the silicone elastomer featuring water repelling properties. Since the product is not of a polishing type, it has less film deterioration and almost no chemical degradation.

4. Chugoku Marine Paints (CMP)

This company, too, produces coatings belonging to the categories of self polishing and of foul release coatings. The former one includes five series of products: SEAFLO NEO CF PREMIUM, SEAFLO NEO Z Series, SEAFLO NEO Series, SEAGRANDPRIX 880 HS PLUS and SEAGRANDPRIX 880 HS. In addition, a foul release product, BIOCLEAN Series, is based on silicone polymers.

4.1. SEAFLO NEO CF PREMIUM (SPC)

The company declares that this is the latest high performance antifouling, combining zinc acrylate binder with a pharmaceutical agent to cope with the challenge of barnacles. When the antifouling hydrolysis polymer dissolves, biocides are released and the polymer provides anti-fouling performance. The cross-linked zinc acrylate polymer is decomposed in small molecular structures, which dissolves in seawater.

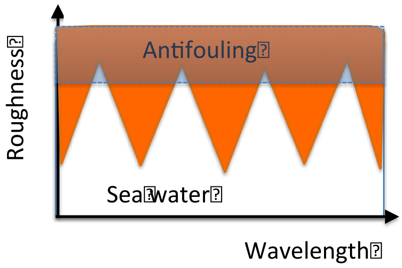

Figure 2. Magnification of the coating-water interface.

For this coating, the Friction Increase Ratio (FIR) Theory is introduced and explained as follows: friction resistance is mainly attributed to the roughness of coating surfaces. Normally roughness control of ship bottom paint surface is conducted by measuring the roughness height (peak height, Rz). However, double cylinder tests, flow simulations and tank tests conducted by researchers in connection with CMP indicated significant contribution of the roughness wavelength (distance between peaks, RSm) to the friction resistance (**Errore. L'origine riferimento non è stata trovata.**).

Then a simple relation for the calculation of fuel saving has been proposed:

$$FIR\ \% = 2,62 * R_z^2 / RSm.$$

For this coating, FIR = 1,2 % is reported, with respect to conventional antifouling paints, whose FIR = 10,7%.

4.2. SEAFLO NEO Z Series (SPC)

These products are indicated as innovative hydrolysis polymers, contributing to fuel saving, forming a smooth surface with extremely low friction resistance. The smooth surface, due to the excellent balance of pigments, polymer and technique of dispersion, contributes to a remarkable fuel saving. Some of the main products belonging to this series are: the SEAFLO NEO 500 Z, defined as a high-performance hydrolysis antifouling based on a zinc acrylate polymer providing long-term antifouling protection, low friction and reduced fuel consumption; the SEAFLO NEO SL Z, defined as a high-performance hydrolysis antifouling based on a special silyl methacrylate polymer with a higher solids percentage than standard hydrolysis paints. For this coatings, FIR = 1,2 % is reported, with respect to conventional antifouling paints, whose FIR = 10,7%.

4.3. SEAFLO NEO Series (SPC)

These products are claimed to exhibit an excellent self-leveling property, which enables the formation of “low roughness and long wavelength” ultra-smooth low-friction coating films right after application. The binder is based on silyl acrylate polymers. For this coating, a FIR = 1,2 % is reported, with respect to conventional antifouling paints, whose FIR = 7,9 %.

4.4. SEAGRANDPRIX 880 HS PLUS (SPC)

The only information given by the company is that this product is characterised by a high polishing rate binder and a special toxic ingredient from the pharmaceutical industry, which boosts the performance of the product to the level of outstanding. For this coating, a FIR = 6,9 % is reported, in comparison to similar conventional antifouling paints, whose FIR = 10,7%.

4.5. SEAGRANDPRIX 880 HS (SPC)

Also for this product, the binder type is not specified, and it is defined as a hydrolysing self-polishing tin free antifouling paint. For this coating, FIR = 6,9 % is reported, with respect to similar conventional antifouling paints, whose FIR = 12-15 %.

4.6. BIOCLEAN series (FR)

The company bases its fouling release coatings on silicone elastomers. The two products commercially available are CMP BIOCLEAN HB, a three-pack silicone elastomer and CMP BIOCLEAN R, a one pack, silicone elastomer foul release coating.

5. Hempel's Marine Paints

A number of products are developed by this company, which proposes several antifouling coatings based on chemically hydrolysing nano acrylate technology and silylated acrylate technology (SPC), zinc carboxylate technology (SPC), and rosin based antifoulings (SPC). All antifoulings are reinforced with patented microfibre technology for a higher mechanical strength. In addition, products based on silicone technology are reported as fouling release coatings; finally, innovative fouling defence coatings, combining silicone-hydrogel with the controlled release of efficient fouling preventing biocides, are proposed.

5.1. Nano acrylate technology (SPC)

In nano acrylate antifouling hull coatings, nano capsules control polishing. When seawater comes into contact with the nano capsules, it penetrates the hydrophobic outer shell. The hydrophilic inner core chemically hydrolyses and then expands, breaking through the outer shell to enable controlled polishing. This means that an immediate antifouling protection is obtained, without the need for water friction. Some of the products belonging to this category are: Globic 9000, defined as a high solids chemically hydrolysing SPC antifouling based on nano acrylate technology. It offers leading low friction properties, self-smoothening, and very fine control of polishing. It combines best possible binder and biocide package for premium performance in different trading speeds. For Globic 8000, the definition of the product is the same of Globic 9000, but the latter results especially effective for slower steaming and frequent idle days, due to the strong biocide package with 3 biocides.

5.2. Silylated Acrylate Technology (SPC)

The company declares that the silylated acrylate technology features perfect polishing with exceptionally low leached layers and best-in-class biocides to give the optimal antifouling performance. The basic process is reported as follows: when seawater penetrates the outer layer, it starts chemical hydrolysis. As the level of hydrolysis increases, the polymer becomes soluble, forming a very thin leach layer and releasing the biocide. The leach layer is progressively eroded from the surface, exposing a fresh coating layer underneath. As the silylated acrylate film is relatively impermeable, water penetrates only the first few microns of the coating, ensuring excellent performance even over long docking intervals. The coatings of the Dynamic series are based on this technology: Dynamic 9000 is defined as a high solids chemically hydrolysing Silyl Acrylate Antifouling. It contains a boosted concentration of high grade biocides to prevent fouling under aggressive trading conditions.

5.3. Rosin Based Technology (SPC)

Gum rosin is the most common raw material in antifouling coatings, having been used for over 100 years. Hempel says that for more reliable long-term fouling control, some of their rosin-based coatings use synthetic rosin, a rosin treated to make it more resistant to cracking and to give better polishing control. The zinc carboxylate ensures that the leach layer remains low and releases a controlled level of biocide throughout the docking interval. The Oceanic+ series of products bases its action on this technology. OCEANIC+ 7390, for example, is defined as a high solids SPC antifouling based on zinc carboxylate and acrylic binders, which delivers strong predictable antifouling protection through a very stable selfpolishing mechanism, which is based on chemical hydrolysis and a strong 3 components biocide package. Also the OLYMPIC+ antifouling coatings are based on gum rosin, delivering good antifouling performance and assuring good adhesion on a wide range of substrates and existing coatings. An example of this products is OLYMPIC+72950, which is defined as a high solids selfpolishing antifouling based on acrylic binders.

5.4. Silicone Based Technology (FR)

The company proposes also the hydrogel technology, by which silicone-based hull coatings give excellent fouling control. This technology is claimed to be innovative in that hydrogel tricks fouling organisms making them to perceive the hull as liquid. In particular hydrogel consists of a network of polymer chains absorbing water to a level of more than 99%. This gives it the capability of minimising protein and bacterial adhesion – and of making the hull appear as liquid to fouling organisms. HEMPASIL X3+ is defined as a fouling release two-component coating based on silicone hydrogel technology, biocide free..

5.5. Actiguard technology (Fouling Defence)

Actiguard technology combines silicone-hydrogel with the controlled release of fouling preventing biocides. Its formulation is designed to store and diffuse biocide over an extended period, while preserving the coating's long-term stability and mechanical properties. Examples of this technology are HEMPAGUARD coatings, as HEMPAGUARD X5, defined as an advanced fouling defence coating which utilizes the added effect of advanced hydrogel silicone and an efficient fouling preventing biocide. This boosts the antifouling barrier and prolongs the fouling free period. The product is based on silicone, and cures after addition of a crosslinker. A hydrogel micro layer prevents fouling organisms firmly adhering while the silicone polymers facilitate self-cleaning.

6. Sigma Coatings

Sigma Coatings produces several SPC coatings, represented by ECOFLEET series, NEXEON series and SAILADVANCE series; on the other hand, fouling release products, represented by the SIGMAGLIDE series, are based on the silicone technology.

6.1. PPG SIGMA ECOFLEET® series (SPC)

The patented hydrolysable binder system delivers the active ingredients through a consistent and reliable linear self-polishing mechanism. This product range currently features four main products: PPG SIGMA ECOFLEET 290-530-690-270, Linear self-polishing antifoulings, with 55%, 60%, 70% and 62% volume solids, respectively.

6.2. PPG SIGMA NEXEON™ series (SPC)

The PPG SIGMA NEXEON antifouling range is based on linear, self-polishing binder technology and instant low-friction, high-performance/low-roughness active ingredients. The company declares that it provides up to 25% lower roughness at application and, therefore, contributes to about 2.5% fuel savings right from day one when the ship starts sailing. The high-performance active ingredients, together with the linear self-polishing binder, maintain premium antifouling performance and hull smoothness. Another important characteristic is reported: due to the absence of copper, PPG SIGMA NEXEON coatings do not have the 'whitening' effect that is common with copper-containing products. The product range currently includes two main products, PPG SIGMA NEXEON 710 and 750, defined as instant low-friction antifouling.

6.3. PPG SIGMA SAILADVANCE™ series (SPC)

SIGMA SAILADVANCE products have been developed with the primary aim of reducing energy and therefore lowering total operational costs. A self-smoothing mechanism reduces the friction on the ship's hull and a technology based on Controlled Surface active Polymers (CSP) acts on the coating/water interface as a lubricant, supporting a laminar flow and thereby lowering the hull friction when the ship is sailing. In addition, these CSP's create a 'slippery surface' increasing the resistance to fouling when the ship is not sailing and, therefore, extending the tolerance to idle days. The SIGMA SAILADVANCE product range currently has four products: SIGMA SAILADVANCE RX-GX-MX (formerly known as 700)-DX (formerly known as 800), defined as low friction, self-lubricating, linear self-polishing antifoulings based on hydrolysable polymer binder composition, which differ for the volume of solids and the idle time tolerance.

6.4. PPG SIGMAGLIDE® series (FR)

These products are based on a 100% pure silicone binder. It is declared by the company that *SIGMAGLIDE* 1290 product utilises a breakthrough dynamic surface regeneration technology to eliminate slime problems. PPG's R&D team has been able to design the optimal configuration for the silicone coating surface. This results in a significantly increased silicone density that slime organisms do not perceive as a substrate.

7. Future trends

As apparent from the previous review of existing coatings, while many products are still based on biocide releasing techniques (even though based on substances less noxious for the environment than those adopted in previous decades) the trend seems to be given by products based on prevention/dissuasion of microorganisms from adhering to the hull. In this context, Self Polishing Surfaces, based on a controlled depletion of the surface aiming at removing the attached micro-organisms and at smoothing the hull surface, are still used. The cutting-edge technologies seem however to be focused on obtaining stable micro and nano characteristics of the surface in order to achieve the target. Bio inspired micro- and nano-textures, such as complex topographies that mimic the skin of sharks and lotus leaves, can inhibit biofouling and exhibit 'self-cleaning' properties, thus representing a promising approach to develop antifouling polymer coatings. Micro or nano-characteristics of surfaces, controlled to obtain anti-fouling properties, can be tuned to obtain anti-friction effects, too. Recently, highly non-wetting, micro-patterned, or nano-patterned hydrophobic surfaces have captured attention as new means of providing an air layer air barrier between the water and the hull then reducing the skin friction drag [2-6]. Well-tailored surface structures, typically coated with hydrophobic materials, can create a composite interface with liquid by retaining air between the structures and minimizing the liquid contact to the solid surface [7-11]. Another possible technology is represented by the use of Lubricant-Impregnated Surfaces (or Liquid Infused Surfaces), LIS, which are realised by a micro/nanostructured surface (metallic or polymeric) in which an appropriate lubricating liquid is infused. The liquid penetrates into the surface pores, being trapped by the surface morphology. In this way, the interface with the water sea is realised by the infused liquid, inducing a relevant drag reduction [12] but also an effective anti-fouling action [13]. The application of the above mentioned techniques to ships is, however, restrained by two main reasons: the difficulty to apply micro/nanotechnology procedures on large areas like those represented by ship hulls and the difficulty of obtaining good stability and durability in long-term applications, because of the harsh conditions of the marine environment. Large challenges lie ahead for the development of these materials into viable commercial products.

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