

SUSTAINABLE ENERGY FOR ALL BY DESIGN

Edited by Emanuela Delfino and Carlo Vezzoli

Proceeding of the LeNSes Conference,
Cape Town, South Africa
28-30 September 2016

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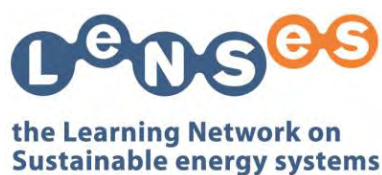
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Edited by: Emanuela Delfino and Carlo Vezzoli

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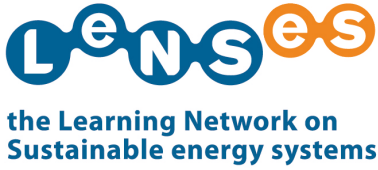
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ANTIFOULING WRAP: A SUSTAINABLE SOLUTION FOR BIOFOULING PREVENTION

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ABSTRACT

The paper presents the results of the first preliminary data on the antifouling properties and water resistance capability of different wrapping polymer films.

Over a period of six months the films were evaluated in comparison to a commercial antifouling paint using both scale samples applied on static immersed surface and on the hull of a real scale sailing boat.

Laboratory tests, in situ tests and visual and photographic inspection, with the support of chromatic analysis software, were performed in order to define, for each products, the biofouling saturation percentage.

For each product under evaluation it has been furthermore evaluated the adhesive capability in water and its cleanability properties.

Key Words: biofouling prevention, self-adhesive film

1. INTRODUCTION

The current research on sustainability applied to yacht design and naval architecture is focused on three main areas: efficiency of the hull shape, efficiency of the propulsion system, and efficiency of the object-environmental interface. The paper presents the results of the first step of the *Antifouling Wrap (AW)* research, developed with a Regione Lombardia government grant, which consists in antifouling properties of commercial products already adopted in other application areas to integrate it with chemistry, nano-topography geometry and product engineering in a further step of study in order to improve their performances.

AW research insists on a strong academic background based on a systematic research both on biofouling growth and on potential risks of antifouling painting. Starting from wrapping systems developed for the terrestrial transport industries and urban furniture, the research is focused on passive systems of hull protection with different kinds of films, easy and safe to apply, remove and replace at the end of the product life cycle. AW aims to be an alternative and sustainable solution for biofouling prevention that fulfills the market demand.

1.1 Scientific background

Marine biofouling is a costly, complex, and environmentally harmful phenomenon caused by the adhesion and accumulation of marine organisms on a surface immersed in water. This unwanted colonization has serious impacts in particular for the marine transport sector and the naval industry (1). Slime films can lead to significant increases in resistance and powering, and heavy calcareous fouling results in powering penalties up to 86% at cruising speed, increasing significantly the fuel consumption and, in turn, greenhouse gas emissions (2).

The International Maritime Organization estimated that, without corrective actions and introduction of new technologies, air emissions due to increased bunker fuel consumption by the world's shipping fleet could increase by between 38% and 72% by 2020 (3). It is estimated that antifouling coatings provide the shipping industry with annual fuel savings of \$60 billion and reduced emissions of 384 million and 3.6 million tonnes, respectively, for carbon dioxide and sulphur dioxide per year.

Numerous studies and research have been developed on biofouling growth and settlement and the impact on the naval industry. Also potentials and risks of antifouling painting are well known (4)(5) and, in particular after the IMO International Convention on the Control of Harmful Anti-fouling Systems on Ships (6), the attention of the international scientific community is concentrated on nontoxic alternatives to biocidal coatings. New antifouling pigments, safer for the environment and humans, green biocides such as ionic liquids and natural products, new organic matrixes and advanced embedding and encapsulating technologies were developed. Another approach followed by academia and industry towards the development of antifouling systems is based on controlling the physicochemical, mechanical, and topographic properties of the hull surface (7)(8). The study of antifouling or fouling release surfaces with special microtextures is one of the main strategies of silicone antifouling products. Even though these products satisfy the efficacy and durability requirements, they are still harmful for the working environment during applying and removing stages.

1.2 Preliminary data and project rationale

Antifouling technologies have increased due to the advancement of biomimetic science and the research on nonfouling and self-cleaning surfaces. The number of publications which deal with fouling release technology has continuously increased and is currently higher than publications concerning the most efficient chemically active paints. A growing interest in enzyme-based coatings and engineered topographical surfaces as "promising" coatings has appeared in marine applications since the early 2000s, with a number of scientific papers which doubles over the period 2000–2010 (9). Researches are involved in self-cleaning surfaces bioinspired by nature, which is closely related to the surface wettability.

Cells and zoospores can be inhibited on micro- and nano-structural topography, which has also been proved to deter colonization of invertebrate shells and to alter settlement of algae, barnacles, and bacteria (10). The diversity of fouling organisms is vast and the range of adhesion mechanisms used is correspondingly great.

It is often observed that many marine organisms do not become colonized by other species. A diverse range of mechanisms has been considered in natural defence, including settlement-inhibiting micro- and nano-topographies, secreted bioactive molecules, sloughing surface layers, mucus secretions and hydrolytic enzymes (11) (12) (13) (14). The surfaces of many marine animals ranging from shells of molluscs to the skin of sharks and whales have a

complex surface topography in analogy with the ‘self-cleaning’ lotus-leaf effect. It’s often supposed that this surface roughness may have a role in either deterring fouling organisms from attaching or promoting their easy release (15) (16). Appropriately scaled micro/nanostructures have been proved to be very effective for preventing cell attachment (17). In particular, moulded topographies in Polydimethylsiloxane elastomer (PDmse) inspired by the skin of fast-moving sharks at $\sim 1/25$ th of the scale, resulted in an 85% reduction in settlement of zoospores of the macroalga *Ulva* compared with smooth ones (lab experiment testing) (18). Settlement densities of spores of *Ulva* were affected by the complexity of the microtopographical patterns, settlement decreasing as the number of features increased. The number of attached spores per unit area was normalized to the number of spores attached to a smooth control and the data were transformed by taking the natural logarithm ($\ln A/A_0$). These results confirm that the designed nanoforce gradients may be an effective tool and predictive model for the design of unique non-toxic, non-fouling surfaces for marine applications (19).

Even though surfaces with micro-nanostructures have been improved very much, they have not yet been widely used in a real antifouling products. There is no available data on product and process engineering focus on a nanotopography surface for wraps and self-adhesive films. The main gap to fill will be translate in a real product ready to put on the market all the previous studies on antifouling systems and fouling released properties. The only product now commercialized and studied for an antifouling effect is Thorn-D antifouling by Micanti, worldwide patented in the 2006 and placed on the market in the 2011. This self-adhesive foil is made by 3-4 mm nylon fibres applied on a polyester film and can resist up to four years in salt water. This solution, while perfectly matching the requirement of aquaculture industries and offshore structures, is not developed for a speed boat hull: lab tests show that the fibres change the water flow causing extra drag in comparison with a perfectly smooth hull.

2. MATERIALS, TOOLS AND METHODS

The entire AW research activities is developed in 30 month and is organized in four steps: (i) preliminary research and test of self-adhesive films developed for different use and compared with antifouling products on the market to define the state of the art, strategies and scenarios; (ii) definition of the chemical, physical and surface films properties, laboratories and in situ tests (iii) product and processes engineering; (iv) final test on a statistically significant sample of boats.

This paper presents the results of the first preliminary data on the antifouling properties and water resistance capability of different wrap material actually available on the market.

Products already adopted in other application areas, such as anti-graffiti films used in railway transport and protection films developed for landscape architecture and urban furniture are first considered. The study evaluate the adhesive and antifouling properties of the different wrap materials and their capability to resist in the new ecosystem through laboratory and in situ tests.

2.1 Test product selection

The selection of self-adhesive film products already available on the market has been carried out in collaboration with private sector companies working in this field. They were divided according to: chemical proprieties of the film, chemical proprieties of the adhesive, surface properties and process of application.

A reference antifouling paint has been identified among the products on the market taking into account the relevance of the manufacturer company and level of its distribution.

Film A

repositionable self-adhesive flocked PVC film

Film: 170 μ m PVC cadmium-free calendered and covered with $\pm 725 \mu$ m of PVC fibres

Adhesive: repositionable acrylic clear solvent based

Final thickness: 925 μ m

Application: decorative - automotive and interior design

Film B

transparent PVC self-adhesive film

Film: 120 μ m double-layer polished cadmium-free PVC calendered

Adhesive: repositionable acrylic clear solvent based

Final thickness: 150 μ m

Application: decorative - automotive and nautical-shipping industry

Film C

transparent polyurethane self-adhesive film

Film: 150 μ m polyurethane film coupled with 36 μ m siliconized PET film

Adhesive: permanent acrylic

Final thickness: 150 μ m

Application: impact protection - automotive

Film D

transparent PVC self-adhesive film

Film: 80 μ m shiny PVC calendered and stabilized

Adhesive: permanent acrylic

Final thickness: 80 μ m

Application: decorative - furniture and architecture

Film E

transparent PVC self-adhesive film, resistant to UV rays and abrasions

Film: 36 μ m PET, UV-stabilized

Adhesive: permanent acrylic

Final thickness: 60 μ m

Application: anti-graffiti function - public transportation (busses and trains)

Antifouling Paint (AP)

hydrophilic self-polishing antifouling paint with carbon additive. Thanks to the inorganic compound content (high percentage of copper and presence of pure carbon particles), it has a high antifouling effect both in warm and temperate water.

Final thickness: 60 μ m

Application: pleasure motor and sailing yacht

2.2 Test protocol

The test protocol identifies tools, methods and timing of sample preparation and execution of tests to evaluate the adhesive and antifouling properties of the different wrap materials and their capability to resist in the new ecosystem.

Headquarters of the experiments are the *Sustainable Marine Research and Technology Laboratory* of Politecnico di Milano and *Santa Cecilia Marina* in Dervio, Como Lake.

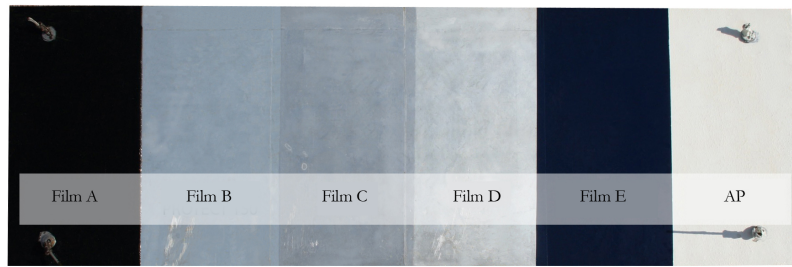
Laboratory tests, in situ tests and visual and photographic inspection, with the support of chromatic analysis software, are performed in order to:

- evaluate the possibility to apply different films selected on double-curved surface;
- verify the adhesive power of the films in water;
- analyse the antifouling effect, quantify and qualify the biofouling growth on the surfaces;
- determine the possibility to clean the wraps instead to replace them.

2.3 Samples in static immersion

The selected products were applied to flat aluminium sheets, 900 x 250 mm size, varnish grease and dust free. The application of the products was performed according to the technical data sheet, each sample has an area of 150 x 250 mm, 15 mm overlapped.

The sample panels were placed in static immersion to a depth of 1 meter, north oriented, with an inclination of 225° to the water line.



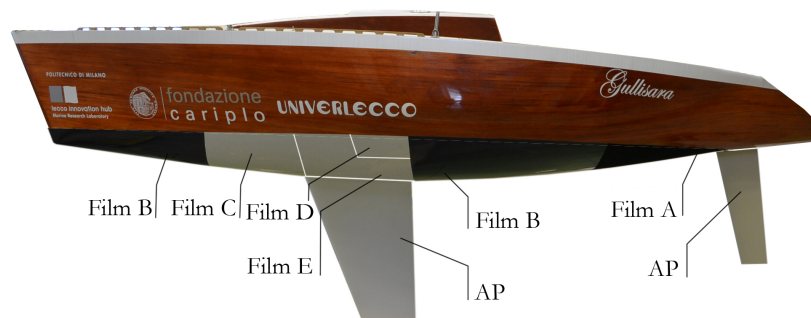
[Figure 1] Reference diagram to place the product samples on panels

2.3 Real scale sample

The selected products were applied on the hull of a 7 meters sailing boat. The boat body, rudder and keel were sanded, feared, coated with an epoxy primer coat, and cleaned of any grease and oil. In particularly, special care was paid to the removal of bubbles and scratch that could affect the tightness of the products immersed in water. The products application was performed according to the technical data sheet and by a specialized technician. The boat hull was longitudinally divided into 5 sectors, and the products were arranged according to their possibilities to application on double curved surface. The antifouling paint was applied only on the keel and the rudder surface.

Launches and mooring stages were performed in order not to deface or damage the films surfaces, using interior hangers fixed on keel prisoners to hauling and appropriate mooring lines.

During the observation period the vessel sailed for at least 6 hours per week, with an average speed between 4 and 6 knots.



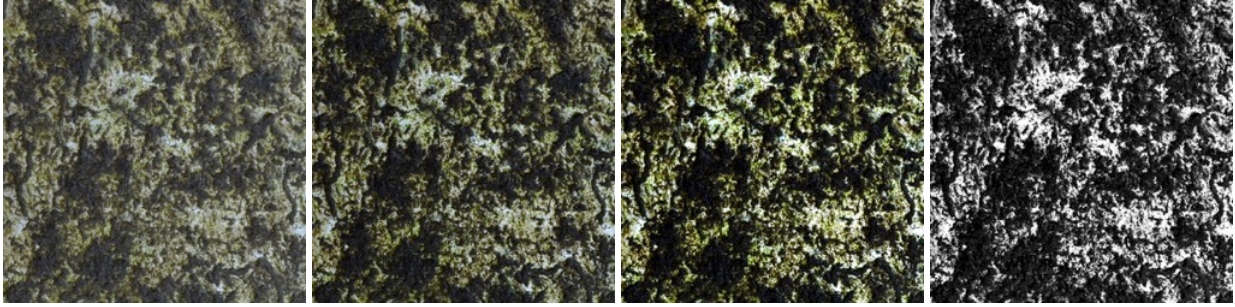
[Figure 2] Reference diagram to place the product samples on boat hull

2.4 Data collection methods

The data relating to the possibility to apply different films selected on double-curved surface was performed during the samples application stages. The adhesive capacity of the products in water, the quantity and quality of biofouling growth and the possibility to clean the film were acquired by visual investigation and/or by a camera at regular intervals of a month for a period of 6 months.

The results images were processed through photo-editing tools and computer analysis for the definition of the biofouling saturation percentage. In particular, the following steps were performed:

- adjustment of brightness (-10%) and contrast (+ 100%);
- tonal values correction to reflected light exclusion;
- exposure adjustment to highlight the biofouling on the film colour background (+ 9%, 0%, 5%);
- colour dropout with a selective filter of green and yellow channels;
- white and black channels reverse on A and B films;
- black channel proportion on 200,000 pixels.



[Figure 3] Photo editing and computer analysis:
1. original image, 2. brightness and contrast, 3. exposure, 4. B / W Image with selective filter

3. RESULTS

The following results refer to six months of testing divided in 2 steps: from June to September and from October to December 2015. Results are divided as defined by the Test protocol: 3.1 apply on double-curved surface, 3.2 adhesive power of the films in water, 3.3 quantify and qualify the biofouling growth on samples, 3.4 possibility to clean the samples.

3.1 Apply on double-curved surface

The capability of the film to bond single curved or double curved surface is expressed according to 4 levels of qualitative effectiveness:

- optimal (the film can perfectly adapt to double curved surface and small details): Film B and Film C
- good (the film can be applied on double curvature surfaces with large radius): Film A
- low (the film adheres to single curvature surfaces only): Film D
- scares (difficulty in application on single curved surfaces): Film E

The Antifouling paint, for its specifically proprieties, can be perfectly applied on double curved surfaces.

3.2 Adhesive power of the films in water

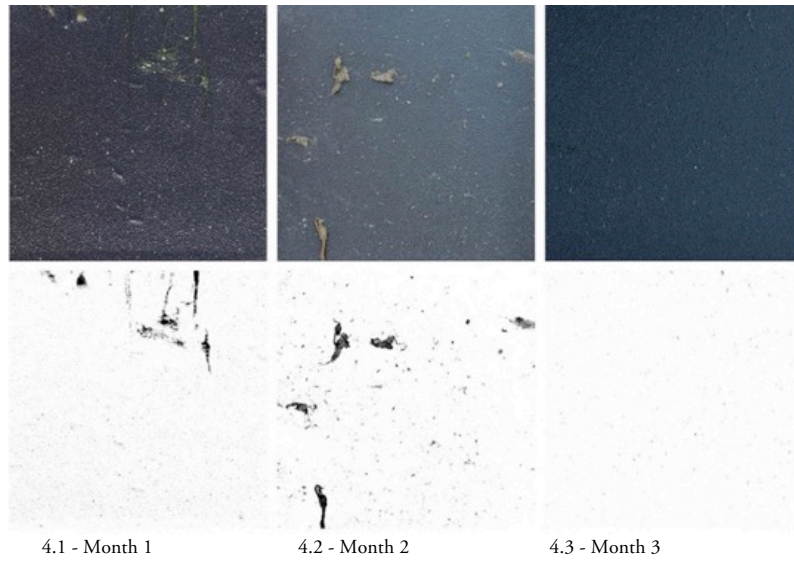
The adhesive capability in water of the selected films and antifouling painting is suitable, excepted for the Film A both applied on samples in static immersion and on the boat hull. It's reported the first detachment mark of the Film A samples on the second month of test. At the fourth month the sample was completely detached from the panel.

3.3 Quantify and qualify the biofouling growth on samples

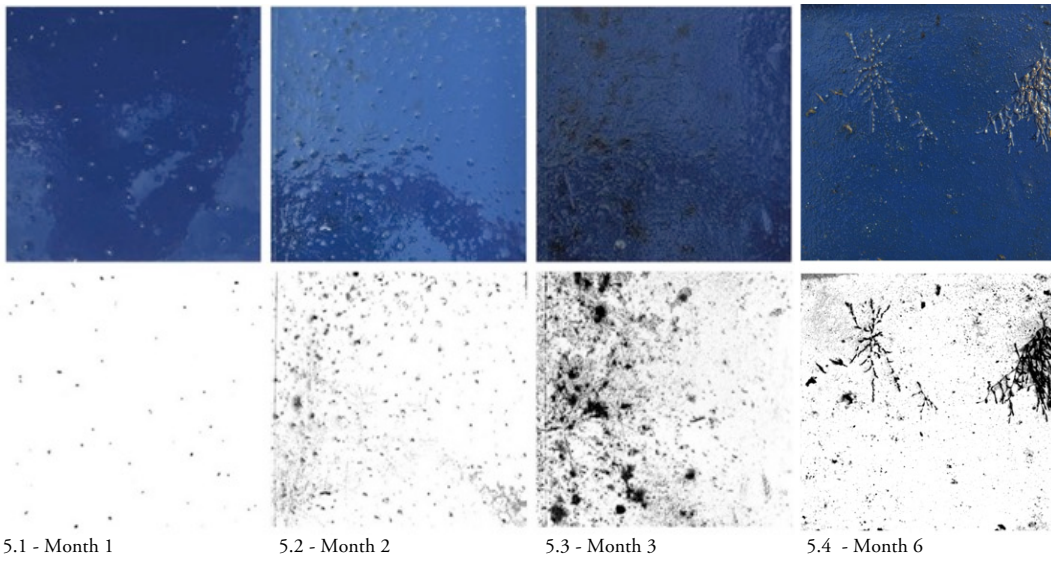
The average growth data on biofouling quantity is expressed in percentage. The data below are referred to the samples in static immersion at the first, second, third and sixth month of test. At the third month it's arranged a cleaning stages in order to compare summer and autumn results.

[Table 3.1] Biofouling quantity on static immersion samples

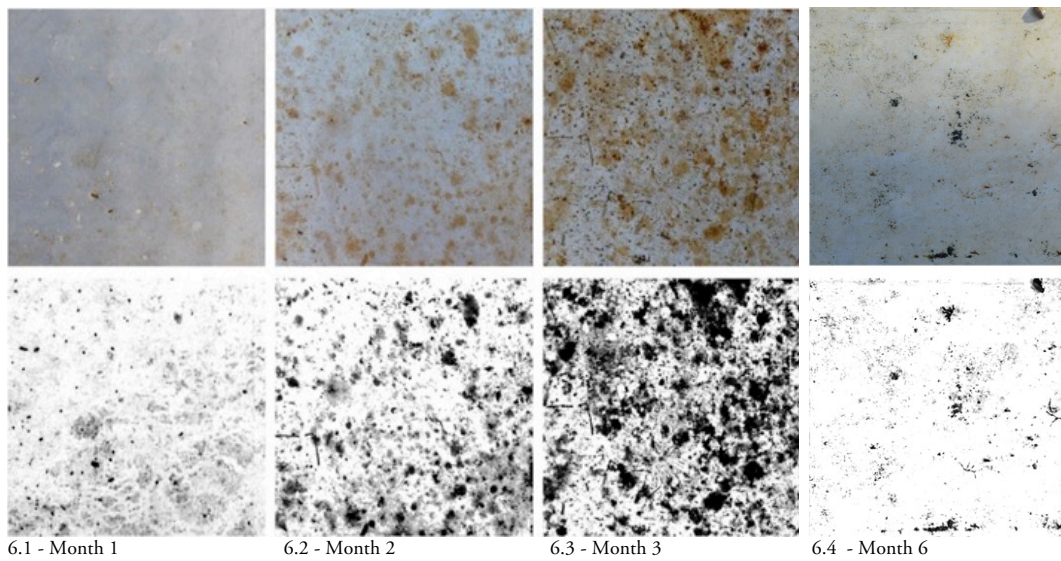
	Film A	Film B	Film C	Film D	Film E	AP
Month1	2%	1%	7%	1%	1%	1%
Month2	2%	4%	11%	11%	2%	1%
Month 3	1%	13%	35%	26%	14%	2%
Month 6 (3+3)	dnf	8%	5%	4%	6%	1%



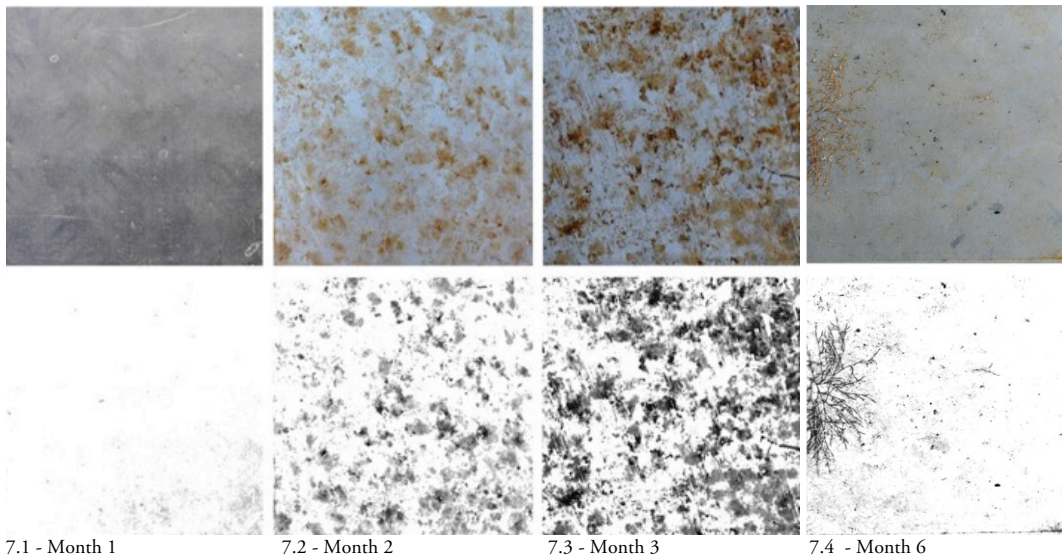
[Figure 4] *Film A* at (4.1) first, (4.2) second, (4.3) third month of test



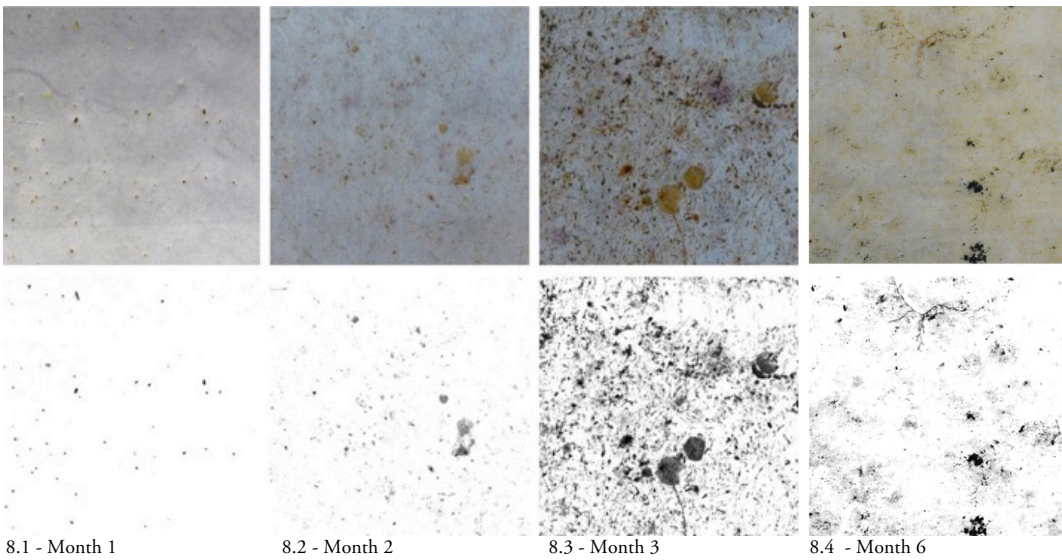
[Figure 5] *Film B* at (5.1) first, (5.2) second, (5.3) third and (5.4) sixth month of test



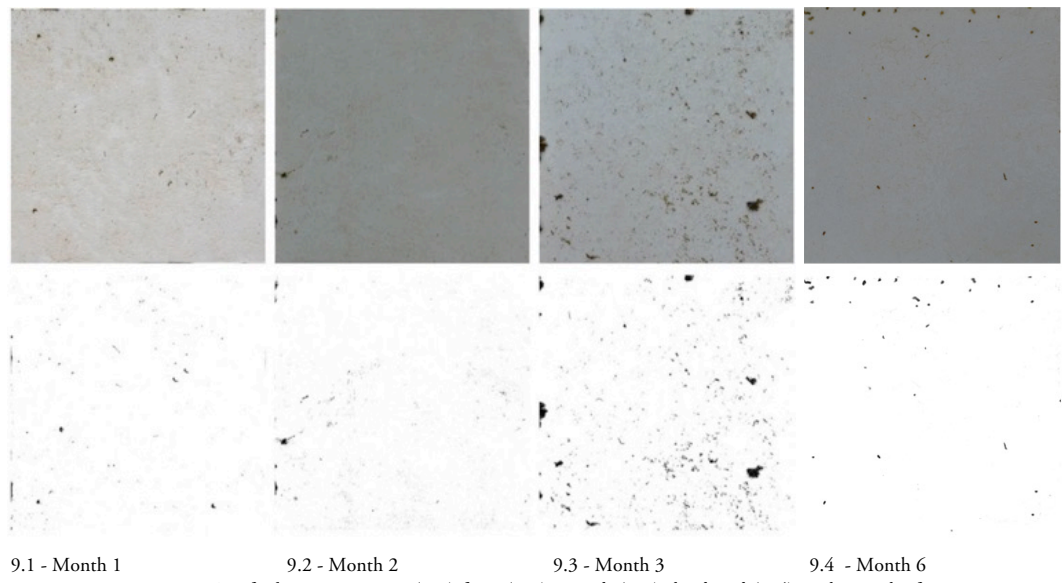
[Figure 6] *Film C* at (6.1) first, (6.2) second, (6.3) third and (6.4) sixth month of test



[Figure 7] *Film D* at (7.1) first, (7.2) second, (7.3) third and (7.4) sixth month of test



[Figure 8] *Film D* at (8.1) first, (8.2) second, (8.3) third and (8.4) sixth month of test



[Figure 9] *Antifouling Painting* at (9.1) first, (9.2) second, (9.3) third and (9.4) sixth month of test

From the results obtained by visual comparison between the samples in static immersion and samples applied at real scale boat it's possible to observe a substantial qualitative correspondence. The comparison between the first test

phase carried out during summer period and autumn period highlights a reduction of biofouling growth for all the film under test. Conversely, the antifouling paint applied to the static sample shows to lose its antifouling properties if not affected by phenomena of water flow.

In addition to that, comparing the results obtained on the films applied on the hull boat to the ones on the static samples it's possible to underline that on the hull surface some barnacles and molluscs started to appear from the third month of observation, both in summer and in autumn especially in the bottom area of the hull. This phenomenon interested all the samples tested with the exception of the flocked PVC film (Film A) and the antifouling paint. It is therefore to be emphasized that the results obtained with the Film A could be considered qualitatively comparable to the ones obtained with the antifouling paint used as a reference.

3.4 Cleanability of the samples

In order to evaluate the cleanability properties of the film tested all the samples were submitted to different washing procedures. After the first month of observation all the samples preserved the possibility to be perfectly cleaned just using fresh water with the aid of a sponge. After a period of three and six months the result obtained using pressure washer produced a result corresponding to the 95% of the initial situation. During this cleaning procedure any deterioration or damage phenomena was noticed on the films and the water used for cleaning got dirty only because of the presence of slime.

However it was noted that after the first cleaning treatment the biofouling tends to grow faster compared to new films.

The antifouling paint showed worse cleanability performance both at the end of the first month and at the end of the full test period. After a period of three and six months the result obtained using pressure washer produced indeed a result corresponding to the 90% of the initial situation. However, in this case, taking into account the self-polishing properties of the paint, the degradation of the surface is evident and the water used for cleaning got dirty not only because of the presence of slime, but also of debris and paint particles.

4. CONCLUSION AND FUTURE DEVELOPMENTS

The performed tests provide an experimental confirmation on different parameters which are considered relevant in the biofouling prevention research. In particular, the Film A achieves good results in terms of antifouling effect and cleanability. It's therefore experimentally demonstrated that the flocked surface has fouling release and self-cleaning properties. These first results lead us to explore the following areas of investigation.

- Film surface design: characterization of the film coating with different surface textures. It's considered appropriate to run a comparative effectiveness study to evaluate the antifouling effect of different surface textures taking into account the academic research on micro- and nano-topography.
- Frictional resistance of rugged surfaces: verification of the potential increase of the resistance induced by different textures sliding into water. The test will be carried out by naval basin experimental method on flat sheets samples and hull model samples.
- Integration of antibacterial compounds: integration, in the film chemical formulation, of antibacterial compounds with different active ingredients, as well as deducing from the literature and from other areas of application.

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