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Friction reduction on recent non-releasing biocidal coatings by a newly designed friction test rig

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ABSTRACT

The drag friction effect of recently developed silicone and polyurethane (PU) paint formulations, containing covalently bound biocide (Econea) were assessed, using a novel rotary test rig.

The immobilization of Econea increased the hydrophobic properties of tested paint formulations, in particular in relation to the reference silicone based paints, where a 32% reduction of the contact angle was registered for the latter.

The formulations containing immobilized Econea showed a positive effect in the drag friction measurements, by reducing the skin frictional drag by 0–16% and 9–20% for silicone and PU based paints, respectively, for the range of tested rotational speeds.

1. Introduction

The shipping industry is highly affected by the biofouling phenomenon. Biofouling, defined as the attachment and growth of aquatic organisms on a total or partially submerged surface in an aqueous environment, is responsible for serious economic and environmental penalties on shipping business [1].

The settlement of aquatic organisms on the ships hulls leads to the modification of the surface roughness, increasing the skin frictional drag between the surface and the sea water, resulting into higher fuel consumption. This leads to higher emission of greenhouse gases, for instance harmful gases such as CO_2, NO_x and SO_x. For example, the International Maritime Organization (IMO) estimated an increase of at least 50% of CO_2 emissions until 2030, under extreme scenarios [2].

Several methods have been used to combat biofouling, since the ancient times. From metal sheathing to the incorporation of heavy metals (copper, arsenic and mercury) into coatings, the latter prevailed and led to the development of potent and durable antifouling coatings [3]. After mid-20th century, Tributyltin (TBT) was used in the antifouling paints, being considered as the most effective antifoulant. However, its use in antifouling paints was banned due to its undesired effects on marine non-target organisms, such as the induction of imposex in female gastropods [1]. Subsequently, copper compounds were used in conjunction with booster biocides such as Econea, Irgarol 1051, Diuron and Zineb [4]. It is relevant to remark that for those biocide based paint formulations' preparation it is crucial to consider the biocide's compatibility with the paint system [5]. Usually, after the biocide(s) inclusion in those paint systems it follows several paint formulation optimization, which can involve the adjustment of several paint additives and limit the biocide content in the system. Nevertheless, the mechanism of action of these paints relies on the release of biocides into the sea, resulting into high concentrations of these booster biocides in areas with abundant shipping activities. To overcome this hurdle, novel biocide-free technologies have been investigated to replace the biocide based coatings.

Recently, researchers have been focusing in combining "foul-release" coatings with hydrogel technology [6,7]. For example, Hempel has been investing in this technology by modifying the surface of commercial PDMS (polydimethylsiloxane) coatings in order to generate a hydrogel on the outermost surface of the PDMS coating. The hydrogel layer helps prevent biofouling settlement by providing a layer of bound water on the surface of the coating, rendering difficult to recognize and adhere to. This enables the coating to keep the surface of the ship clean, even at low speeds [6,7]. Also, the low surface energy of the PDMS provides a weak adhesion to the surface, which facilitates the releasing of biofouling that may have settled. Unfortunately, these paints are less mechanical resistant than conventional antifouling coatings, leading to the development of new approaches aiming to improve these properties while providing an antifouling protection of surfaces.

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Nomenclature

a	radius of the internal cylinder (m)
b	radius of the tank (m)
C_{mc}	drag friction coefficient (dimensionless)
ΔC_{mc}	drag friction coefficient deviation (dimensionless)
θ	contact angle (°)
$\varnothing$	diameter (m)
H	height of the coated cylinder (m)
ρ	fluid density (kg/m^3)
Ω	tank's rotating speed (rad/s)
μ	viscosity of the fluid (Pa s)
Re	Reynold's number
T_q	friction torque generated between the coating and the fluid (N m)
R_a	average roughness (μm)
R_{max}	maximum roughness depth (μm)

Several studies have been carried out to compare the drag resistance of different coating types [8,9]. For instance silicone based foul-release coatings have been compared to tin-free self-polishing coatings. The former has shown positive results in comparison to the latter, mainly due to its surface texture (less rough), creating less frictional drag [8,9]. During motion, the drag of a ship presents two major components: wave-making drag and skin frictional drag. The latter typically accounts for 60–90% of the total resistance and can be reduced by applying an appropriate coating, which softens the surface [9,10]. The skin frictional drag increases when biofouling attaches to the surface of the coating, leading to extreme fuel and maintenance costs of the ships and CO_2 emission, as mentioned previously. For this purpose, it is of utmost importance to assess the coating regarding to the drag friction effect, not only at the initial condition, but also after prolonged immersion in the sea, in order to avoid excessive fuel consumption and subsequent penalties.

Several experiments have been applied to measure the drag friction of the coatings, including a rough plate or a rotating disc or cylinders [11,14]. The rotating cylinder method consists of measuring the torque generated between the surface of the coated cylinder and the fluid in a cylindrical tank. However, the reported experiments only use the inner cylinder or both the internal and external cylinders in rotation [11,14] and the information about set-ups using a static inner cylinder with rotating external cylinder is scarce. This configuration avoids the drawbacks existing in a conventional test rig, where the torque sensor and the inner cylinder are placed in the same axis and rotate, which can affect the measurement of the torque values, due to possible vibrations during the rotation of the inner cylinder.

The purpose of this work is to carry out characterization techniques on new antifouling coatings, with a major focus on the newly drag friction test rig © IK4-TEKNIKER [15], where the friction generated between a coated static cylinder and the fluid (synthetic sea water) contained in a rotating cylindrical tank was measured. In addition, the surface properties of the coatings were assessed in terms of their mechanical characteristics such as scrubbing and abrasion resistance, as well as adhesion, roughness and wettability properties. These characterization techniques were employed on biocide-free antifouling paints and on newly developed biocidal paints, where a biocide was immobilized in the paint's matrix through covalent bonds [2], aiming to check if the inclusion of biocide showed any improvements on the physical and mechanical properties of the obtained paints.

2. Experimental procedures

2.1. Materials

The testing coatings were applied on naval steel (Grade A) prototypes by ENP (Estaleiros Navais de Peniche, a Portuguese company specialized in painting ship hulls). The characteristics of the paints are presented in Table 1. The paints A and B are the reference paints used for comparative purposes. Paints C, D and E correspond to newly paints with covalently immobilized biocides developed in the frame of a European collaborative project (FOUL-X-SPEL, grant agreement 28552). Sample D is a polyurethane based formulation without any biocide, whereas sample C is composed by the same polyurethane based formulation but with 2.0 wt% of the biocide named Econea, immobilized covalently into the paint matrix. Briefly and prior to the development of final formulation C, several trials and iterative formulations of the paint were performed and assessed with different Econea contents. Finally, the concentration of 2.0 wt% of Econea was determined to be the optimum concentration for enhancing the paint properties both the mechanical–tribological ones and also its antifouling ability. The same criteria were adopted for determining the concentration of Econea on silicone based sample named E.

2.2. Wettability test procedure

The hydrophilicity/hydrophobicity of the samples was measured by determining the contact angle between a droplet of artificial seawater (fluid developed according with ASTM D1141-98) and a painted naval steel flat sample using a goniometer *Surftens UNIVERSAL*. The contact angle was measured vs time by means of image post-processing of an integrated camera on the plane orthogonal to the sample. The data acquisition frequency was of 2.3 Hz, for a total test period time of 300 s for each test, in order to record 700 measurements. At least three measurements were performed for each paint formulation. The volume of the seawater drops used in all tests was of approximately 4 μl.

2.3. Roughness assessment

The average roughness (R_a), which is the arithmetic average of the absolute value of the roughness profile, as well as the maximum roughness depth (R_{max}), defined as the largest single

Table 1
Paint formulations samples.

Paint sample	Supplier's designation	Polymeric matrix	Biocide content (wt%)
A	Hempasil X3	Foul-release Silicone	0.0
B	Olympic +	Self-polishing Acrylic	21.6–22.2 wt% copper (I) oxide and 7.0–7.3 wt% Zineb
C	F0027	Polyurethane	2.0 wt% Econea
D	F0032	Polyurethane	0.0
E	F0033	Silicone	0.56 wt% Econea