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Studies on How Grooming Can Improve the Performance of Fouling Control Coatings

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by

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Abstract

Title: Studies on How Grooming Can Improve the Performance of Fouling Control Coatings

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Biofouling is the accumulation of unwanted organisms on a submerged surface. This can be a major issue to most marine activities. The most common approach to biofouling prevention on ship hulls is the application of fouling control coatings (FCC), which can be categorized as biocidal and biocide-free.

Grooming has been proposed as a proactive method to maintain these coatings and extend their working lives. In 2010, Tribou first defined grooming as the systematic, gentle, and mechanical disruption and removal of fouling on a ship hull. For biocidal coatings, grooming maintains the active biocide contained in the coating, preventing organism attachment. For biocide-free coatings, grooming applies a force that is great enough to remove organisms from the surface.

This thesis investigated the interactions between fouling control coatings and different grooming brush designs. Two separate studies were undertaken to 1) study three different copper-based antifouling coatings, and 2) study biocide-free formulations (one commercial fouling release coating, and three biocide-free coatings). Each biocide-free coating type was groomed with three different brush designs to test varying forces imparted by each brush design.

The purpose of the first study was to apply grooming on copper-based FCC at a copper output level sufficient to prevent fouling. In addition, the first study aims to reduce the environmental loading of copper into the water column with a lower copper content

paint and reduced paint film thickness lost. The first study concluded that weekly grooming with a hybrid brush can maintain all three copper content formulations free of fouling. In addition, the highest-copper content by weight paint, BRA640 (37.1% copper by weight), released the most dissolved copper into the ambient water column. The paint with the moderate copper-by-weight percentage, 6400 (32.9% copper by weight), proved to release the least amount of dissolved copper into the water column while maintaining both paint thickness and a clean surface.

The second study groomed the coatings with three different brush designs (bristle brush, hybrid brush, and stud brush) to determine which brush applied a force great enough to prevent fouling on the surface of biocide-free coatings. It was concluded that biweekly grooming with a hybrid brush significantly reduced fouling on the three experimental biocide free coatings and one commercial fouling release coating. Biweekly grooming with the stud brush, reducing fouling coverage, however damaged the surface of the coatings due to entrapment by hard fouling. It was found that biweekly grooming with the bristle brush removed biofilm, but failed to remove macrofouling.

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Chapter 1 : Introduction

Biofouling is the accumulation of unwanted organisms on a submerged surface. This can be a major issue to marine activities. Within minutes of submersion, microorganisms begin to settle on surfaces growing into an organic film. These early colonizers form an assemblage of attached cells known as microfouling or slime (Callow & Callow, 2002). Following this, macrofouling organisms such as barnacles, tubeworms, and sponges attach to the surface, forming a fouling community. The specific types of fouling organisms depend on the season, latitude, and other factors such as competition and predation (Callow & Callow, 2002). To remove significant growth, physical removal such as brushing and power washing, may be necessary to reduce drag and biodegradation. The increased roughness associated with fouling results in elevated frictional drag that negatively impacts fuel consumption, greenhouse gas emissions, and vessel speed (Schultz *et al.*, 2015). The cost associated with these negative impacts on the entire US Navy mid-sized class has been estimated to be $1 million per ship per year (Schultz *et al.*, 2011).

The most common approach to biofouling prevention on ship hulls is the application of fouling control coatings (FCC) (Swain, 1999, 2010; Swain *et al.*, 2007). These coatings fall into two main categories: antifouling (AF) and biocide free (Swain *et al*, 2006). Copper in the form of cuprous oxide is the most commonly used biocide (Callow & Callow, 2002) and is the ingredient incorporated in the US Navy qualified ablative copper coating, Interspeed BRA 640 (Tribou & Swain, 2017). Upon contact with water, the cuprous ions are immediately oxidized and released into the surrounding water column (Valkirs *et al.*, 2003). These dissolved cupric ions act as a toxin, preventing growth and killing nearby organisms (Schiff *et al.*, 2004). However, some organisms have been shown to withstand copper biocides and preferentially attach to copper antifouling surfaces (Brinson, 2015). The amount of copper released increases with weight percent concentration of cuprous oxide in the antifouling coating. Likewise, mechanical cleaning processes on the hulls of ships agitates the surface, releasing more cuprous oxide into the water column (Valkirs *et al.*, 2003). Eventually, the coating must be replenished as it is depleted, or leached, in order to remain effective at fouling prevention (Tribou and Swain, 2017). The drawback to copper antifouling coatings is the accumulation of copper in the sediments resulting in toxic concentrations to organisms.

Copper-based AF paints may also preferentially attract copper-tolerant species. The pink acorn barnacle, *Amphibalanus amphitrite*, is an invasive species that has been observed to tolerate copper and preferentially recruit on copper coated surfaces (Weiss, 1947). The native copper sensitive barnacle, *Amphibalanus eburneus*, is often outcompeted by *A. amphitrite* on inert surfaces and does not settle on copper surfaces (Brinson, 2017). Even during times of low fouling pressure, a preference for *A. amphitrite* recruitment on higher copper concentration coatings has been observed (Brinson, 2017). The preferential attachment of hard fouling organisms such as *A. amphitrite* increase drag of ship hulls and may damage the surface calling into question the benefits of using of copper-based AF paints.

A viable alternative for biofouling control is silicone fouling release biocide-free coatings. These coatings do not leach toxins to prevent attachment, but rather reduce the adhesion strength of organisms. This allows for easier removal of attached organisms via grooming, cleaning, or hydrodynamic forces resulting from the movement of the ship through water (Callow and Callow, 2002). However, these coatings are more expensive than copper-based coatings, more difficult to apply, and are likely to foul on slow-moving or static structures (Swain, 2017). Therefore, proactive grooming of biocide-free surfaces can provide a solution to prevent the establishment of biofouling communities. The advantages of theses coatings area that they are smooth, reduce the viscous drag of ship hulls and reduce the environmental impact of releasing toxins into the marine environment.

The need to reduce fuel consumption, cost, greenhouse gas emissions, copper-tolerant invasive species, and the release of toxins from copper antifouling paints create a growing call for improved methods to manage biofouling. Both antifouling and biocide-free coatings are most effective at preventing biofouling when paired with a ship hull cleaning or grooming procedure. Ship hull cleaning is a more reactive approach and may require aggressive cleaning that results in damage to the coating and elevated release of copper from antifouling coatings (Tribou and Swain, 2010). In contrast, grooming is the systematic, gentle, and mechanical disruption and removal of fouling on a ship hull (Tribou and Swain, 2017). This is achieved through manual or remote operated vehicles (ROVs) that brush the ship before fouling has time to fully establish on the hull (Tribou & Swain, 2010). Grooming can reduce hull cleaning frequency, reduce dry dock maintenance requirements, minimize damage to coatings, and decrease fuel costs (Hearin *et al.*, 2015). One estimate calculates that if a mid-sized naval ship is actively groomed to maintain a light biofilm, the US Navy could save $12 million per ship over a 15-year period (Schultz *et al.*, 2011).

Grooming has therefore been proposed as a method to maintain copper-based FCC in a fouling free condition without excessive copper loading to the environment and as a method to maintain fouling release coatings free of fouling without damage to the coating. This thesis will investigate the interactions between fouling control coatings and different grooming brush designs. Two separate studies were undertaken:

1. The effect of grooming on three different copper-based antifouling coatings
2. The effect of brush design on grooming four biocide-free formulations

Hypotheses

1) The application of grooming to copper-based fouling control coatings (FCC) will maintain copper output at a level sufficient to prevent fouling.
2) The application of grooming to biocide-free coatings requires that the forces imparted by the brushes must be greater than the adhesion strength of fouling organisms to the surface.

Chapter 2 : Managing Copper-Based Antifouling Paints with Grooming

Abstract

Copper-based paints are the most widely used fouling control coating. This study investigated the impact of weekly grooming on three types of copper-based paints immersed at Port Canaveral, FL: International Interspeed (IS) 6200 (18.9% copper by weight), International Interspeed (IS) 6400 (32.9% copper by weight), and International Interspeed (IS) BRA640 (37.1% copper by weight). International Interguard 264, a white epoxy paint, was used as a control surface. Weekly groomed panels and static ungroomed panels remained immersed for nine months from August 2020 – May 2021. Grooming was performed weekly with a prototype hybrid brush. No fouling occurred on the weekly-groomed panels coated with copper ablative paints. Significantly more copper output occurred on the panels coated with BRA640. This indicates a need for less frequent grooming on higher copper-content paints. The panels coated with IS 6200 had the greatest decrease in dry film thickness. The ungroomed panels showed a recruitment preference by the copper-tolerant barnacle, *A. amphitrite*, on the copper-coated panels compared to the biocide-free epoxy. This demonstrates the need for an effective grooming plan to match both the copper content of the paint and the fouling pressure present in the water.

Introduction

The most common approach to biofouling prevention on ship hulls is the application of fouling control coatings (FCC) (Swain, 1999, 2010; Swain *et al.*, 2007). These coatings fall into two main categories: antifouling (AF) and biocide-free (Swain *et al.*, 2006). AF coatings contain biocides, such as copper, that deter recruitment and make it difficult for organisms to attach and develop (Callow and Callow, 2002). Without a means to control biofouling, these organisms will increase hydrodynamic drag, transit times, fuel consumption, greenhouse gas emissions and operational costs (Swain *et al.*, 2007; Schultz *et al.*, 2011).

For over 200 years, copper-based AF paints have been used to prevent biofouling (Srinivasan and Swain, 2007). The coating used by the US Navy, a copper ablative coating, dissolves away slowly, exposing cuprous oxide over time (Tribou and Swain, 2017). Upon contact with water, the cuprous ions are immediately oxidized and released into the surrounding water column as cupric ions (Valkirs *et al.*, 2003). The dissolved cupric ions act as a toxin, preventing growth and killing nearby organisms (Schiff *et al*., 2004). At toxic levels, cupric ions can inhibit the metabolic process of organisms by inactivating vital processes within the organism (Corner and Sparrow, 1956; Rainbow 1985). After leaching from the ship hull, cupric ions may take several different forms or species. Studies have shown that cupric ions are slowly formed into inorganic and organic complexes, attaching to solids, and becoming less bioavailable (Morel and Hering, 1993). This causes copper to be especially concentrated in harbors, coastal embayments, and shipping lanes where circulation is restricted and contaminant inputs are high (Trefry, 1983; Schiff, 2004).

Today, ninety-nine percent of the US Navy fleet's underwater hull area (>1.1 million m^2) is coated with copper-based AF paint (Tribou and Swain, 2017). In addition, ninety percent of all vessels use copper as an active ingredient in AF coatings (Blossom, 2018). For the copper-based AF to be effective, the release rate must be at least 20 μg Cu cm^{-2} day^{-1} to prevent fouling (Swain 1999) Actual release rates are highly variable, with values between 3.7 and 20 μg cm^{-2} day^{-1} having been reported in the literature (PRC Environmental Management, Inc. 1997; Schiff *et al.*, 2004; Swain 1986: Valkirs *et al*., 1994, 2003). Assuming an average copper leaching rate of 17 μg Cu cm^{-2} day^{-1} (Naval Sea Systems Command, 1997; Seligman and Zirino, 1998), the copper loading from the US Navy fleet can be calculated to be 68,300 kg $year^{-1}$. Using methods from Srinivasan and Swain (2007) and data from the Florida Department of Highway Safety and Motor Vehicles (2019), copper loading for all recreational vessel underwater hull area (6,473,000 million m^2) in Florida can be calculated to be approximately 402,000 kg $year^{-1}$. The copper loading is concentrated in densely populated areas where boat traffic is increased (Figure 2.1). In addition, the amount of copper released increases with weight percent concentration of cuprous oxide in the antifouling coating. Mechanical cleaning processes on the hulls of ships agitates the surface, releasing more cuprous oxide into the water column (Valkirs *et al*, 2003). Therefore, a large portion of the studies show that the actual amount of copper released into the environment is greater than the amount for the AF paint to be effective.

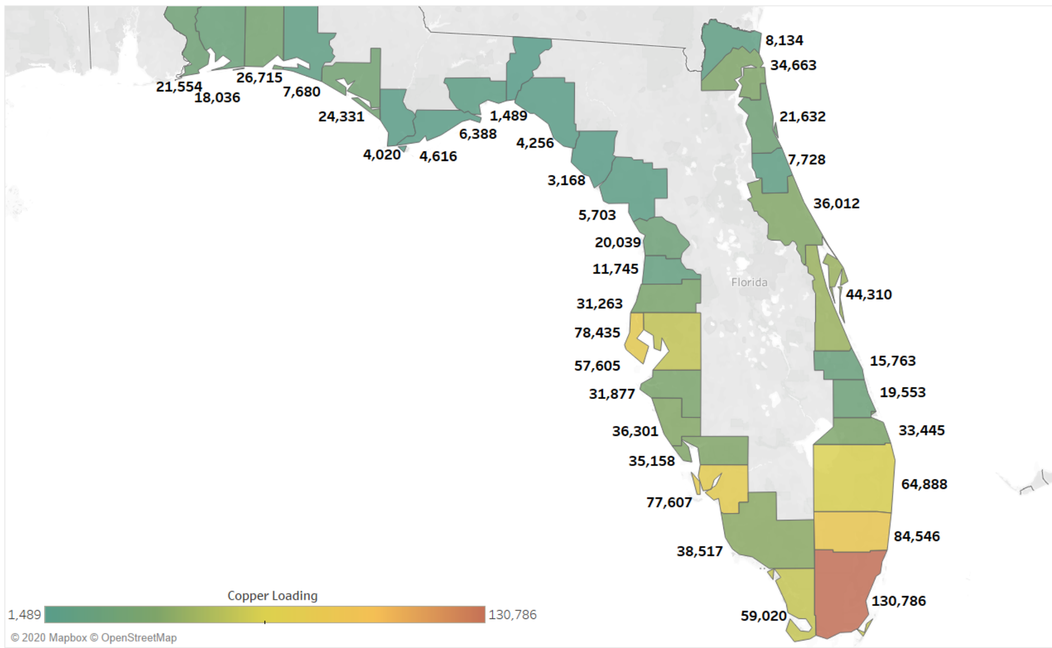

Figure 2.1: Copper loading (g/day) from all recreational vessels by county in the State of Florida (data extrpolated from Florida Highway Safety and Motor Vehicles, 2019) Analyzed in Tableau 2020.2

Copper is a naturally occurring element and required in trace amounts as an essential micronutrient. However, ship hulls painted with copper-based AF coatings contribute significant amounts of copper into seawater. The National Recommended Water Quality Criteria (WQC) lists copper as a priority pollutant with recommended dissolved copper concentrations in the marine environmental to not exceed 4.8 μg/L and an instantaneous concentration of 30 μg/L (EPA, 2016; Valkirs *et al*., 1994). Dissolved copper concentration has exceeded the WQC for marinas in San Diego Bay (Schiff *et al.*, 2007), San Francisco Bay (Flegal and Sanuda-Wilhelmy, 1993), and Indian River Lagoon, Florida (Srinivasan and Swain, 2007; Trefry, 2010). Due to cupric ions propensity to form complexes, the copper levels in biological tissues and sediments have been found to be higher in marinas and harbors (Srinivasan and Swain, 2007).

Copper levels exceeding water quality criteria have caused regulatory controls such as Total Maximum Daily Loads and National Pollution Discharge Elimination System permit restrictions to limit the loading and concentration of copper in harbors, yacht basins, and marinas (Port of San Diego). In addition, the State of Washington intends to phase out the use of copper-based and antifouling paints entirely by 2026 (Blossom, 2018).

Copper-based AF paints have also attracted copper-tolerant invasive species that often dominate these surfaces. As one of the busiest ports in the Western Hemisphere, Port Canaveral is an ideal location to observe copper tolerance. Over 3 million tons of cargo move through cargo ships, cruise ships, Navy ships and submarines, all of which travel widely, making this port highly susceptible to ecological invasions (Braun *et al*., 2002; Floerl and Inglis, 2005). The pink acorn barnacle, *Amphibalanus amphitrite*, is an invasive species that has been observed to tolerate copper and preferentially recruit on copper coated surfaces (Weiss, 1947). The native copper sensitive barnacle, *Amphibalanus eburneus*, is often outcompeted by *A. amphitrite* on inert surfaces and cannot settle on copper surfaces (Brinson, 2017). Other invasive species that have been observed to settle on copper coated surfaces at Port Canaveral include *Hydroides elegans* and *W. subtorquata complex* (Brinson, 2017). Even during times of low fouling pressure, a preference for *A. amphitrite* recruitment on higher copper concentration coatings has been observed (Brinson, 2017).

With environmental health in mind, it is important to find the correct interaction between ship hull maintenance and copper-based AF coatings to reduce fouling pressure, copper output, the presence of copper-tolerant invasive species, dry dock time, and drag. The purpose of this study is to investigate the interactions between three different classes of copper-based AF coatings and weekly grooming. Previous studies have found that weekly and monthly grooming were sufficient to prevent fouling on copper ablative paints, specifically BRA640 (Tribou and Swain, 2017; Hunsucker *et al*., 2019) This study compared how grooming affects fouling recruitment and copper leaching rates for three copper-based antifouling paints. It was hypothesized that the application of grooming to copper-based AF paints will maintain copper output at a level sufficient to prevent fouling.

Methods

The experiments were conducted at Florida Institute of Technology's seawater test facility located in Port Canaveral, FL (Figure 2.2). The average salinity at this location is

Figure 2.2: A diagram highlighting the location of the field test site in Port Canaveral, Florida

34 ± 2 ppt, and the average water temperature is 27 ± 2 °C (Braga, 2018). Biofouling is high year-round, although seasonality is seen with different fouling organisms. During the warmer months (June, July, August) fouling communities are dominated by encrusting bryozoan, calcareous tubeworms, and barnacles. During the cooler months (December, January, February) arborescent bryozoan and biofilm dominate. Port Canaveral has a large population of invasive benthic invertebrates likely due to the mix of recreational and commercial ships, prevalence of anthropogenic hard substrates and high-water retention times (Floerl and Inglis, 2005).

Three different ship hull paints were chosen for these experiments: International Interspeed 6200 (18.9% copper by weight) and International Interspeed 6400 (32.9% copper by weight) are controlled depletion polymer (CDP) self-polishing antifouling systems. International Interspeed BRA640 (37.1% copper by weight) is an ablative antifouling. All three copper-based AF coatings were used as the experimental copper treatment. International Interguard epoxy in white was used as the inert control.

The paints were applied as four replicates on 10 x 20 cm (4 x 8 inch) steel panels. The panels were first sanded with 80 grit sandpaper and cleaned with lint-less rags soaked with acetone. Paints were mixed mechanically with a high-speed mixer. All panels were first coated with Interguard 264 white epoxy as a standard barrier coat. Interguard white epoxy is a two-part epoxy which was mixed in a 4:1 ratio recommended in the International Paints' product datasheet (PDS) manuals. The epoxy coat was applied with a roller to the standard 156-micron wet film thickness (WFT). The copper paints were applied approximately 1.5 hours after the epoxy coat was applied, while the epoxy coat was still tacky. Nine panels were coated with International BRA640 to 204-micron WFT, nine with International 6400 to 208-micron WFT, and ten with International 6200 to 215-micron WFT (Table 2.1)/

Table 2.1: List of experimental paints with copper content by weight, grooming frequency, and sample replicates

Sample Name	Copper by Weight	Grooming Frequency	Sample Replicates
6200	18.9%	Every Week	6
6400	32.9%	Every Week	5
BRA640	37.1%	Every Week	5
264 Epoxy	0	Never	5
6200	18.9%	Never	5
6400	32.9%	Never	4
BRA640	37.1%	Never	4

Sixteen of the copper coated panels were randomly placed and flush mounted to two weighted frames coated with black BRA640. The remaining 12 copper-coated panels and four epoxy control panels were randomly hung on a PVC deployment frame (Figure 2.3).

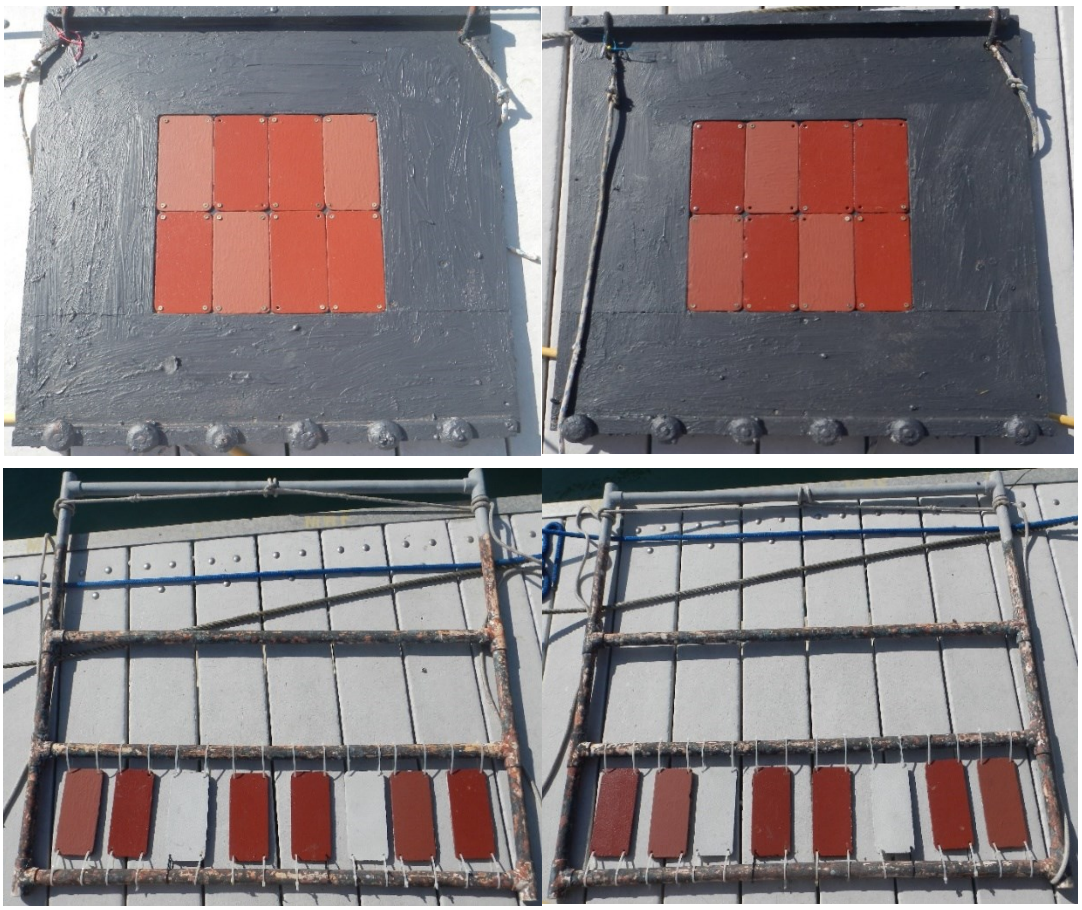

Figure 2.3: Photo of weekly groomed frames (Top) and ungroomed frame (bottom)

The panels were statically immersed at a 30 cm water depth. Underwater grooming was performed weekly on the 16 flush mounted frames with a two-brush prototype rotating grooming tool. The hybrid prototype brush heads were made with one row of bristle filaments and one row of rubber nitrile studs (Figure 2.4).

Figure 2.4: Photo of the hybrid grooming brush

Dry Film Thickness (DFT) Measurements

Dry Film Thickness (DFT) measurements were taken on each copper panel face to monitor coating loss over time. A Fischer Deltascope DFT gauge (Fischer Technology, Inc. Windsor, CT, USA) (± 5% accuracy) equipped with a waterproof tip was used to measure dry film thickness. Ten DFT measurements were randomly taken per panel, half an inch from the edge, while panels remained wet. DFT measurements were taken at initial immersion and every month of immersion. DFT measurements were then converted to average loss rates using a linear density of 5.76 g cm^{-1} for cuprous oxide at a % loading by volume as specified for each paint. The following formula (Equation 2.1) was used to calculate an equivalent total copper loss rate in µg cm^{2} day^{-1}:

$$Total\ copper\ loss\ rate\ (\mu g\ cm^{2}\ day^{-1}) = \frac{Density\ Cu_2O\ (g\ cm^{-3})(10^{6}\mu g\ g^{-1}) \times thickness\ loss\ (cm) \times loading\ by\ volume}{days\ immersion}$$

Equation 2.1: Equation to calculate equivalent total copper loss rate from change in thickness

This value reflects any copper losses due to both mechanical removal and characteristic losses due to coating chemistry.

Biofouling

Panels were visually assessed monthly using a modified ASTM D990-05 method. This method assesses the total percent cover of all benthic fouling organisms that are directly attached to the surface of the panels. Initial algae cover is recorded as “biofilm,” but as the algae progresses, it may be labelled as “green algae.” Fouling organisms that are mature enough to be identified with the naked eye were identified and recorded as part of the total percent cover on the panel by taxonomic group.

Results

The panel sets were analyzed each month for fouling cover and dry film thickness (DFT). Differences were found in the total amount of fouling cover for each panel set because of the time of year that they were exposed (Lieberman, 2016). All three formulations of copper panels had a higher coverage of the copper-tolerant barnacle *A. amphitrite* than the epoxy panels. The highest copper content panel, BRA640, recruited barnacles slower than the lower copper content panels. DFT for the ungroomed panels was measured at the time of immersion and removal from the test site due to high biofouling coverage. On 31 July 2020, the panel sets were removed from the test site due to Hurricane Isaias. The panels were re-immersed on 4 August 2020 and assessment commenced on 7 August 2020.

Coating Thickness Loss

The 6200 coating had the greatest change in film thickness (microns) over 12 months of immersion for the weekly groomed coatings (Figure 2.6). 6200 on average lost (99 ± 13) microns thickness, 6400 on average lost (29 ± 7) microns in thickness, and BRA640 on average lost (67 ± 6) microns in thickness.

The total average DFT losses were used to calculate theoretical copper loss rates (Equation 2.1). The weekly groomed panels values were found to be (21 ± 6), (14 ± 7), and (28 ± 6) $\mu g\ cm^{-2}\ day^{-1}$ for 6200, 6400, and BRA640, respectively (Figure 2.5). The differences between copper loss rates for 6400 and BRA640 was significant ($p = 0.02$, $\alpha = 0.05$). The difference between the copper loss rates for 6200 and 6400 was insignificant ($p = 0.12$, $\alpha = 0.05$). The difference between the copper loss rates 6200 and BRA640 was also insignificant ($p = 0.11$, $\alpha = 0.05$). The ungroomed panels values were found to be (3 ± 5), (2 (± 5), and (12 ± 2), respectively. For the ungroomed panels, the difference between copper loss rates for both the ungroomed 6200 and BRA640 and the ungroomed 6400 and BRA640 were significant ($p = 0.03$ and $p = 0.01$, respectively, $\alpha = 0.05$). The difference between the copper loss rates for the ungroomed 6200 and 6400 were insignificant (p = 68, α = 0.05). The difference between copper loss rates for each coating type and grooming frequency (ungroomed and groomed weekly) was significant for 6200, 6400, and BRA640 (p = 0.002, p = 0.03, and p = 0.002, respectively, α = 0.05).

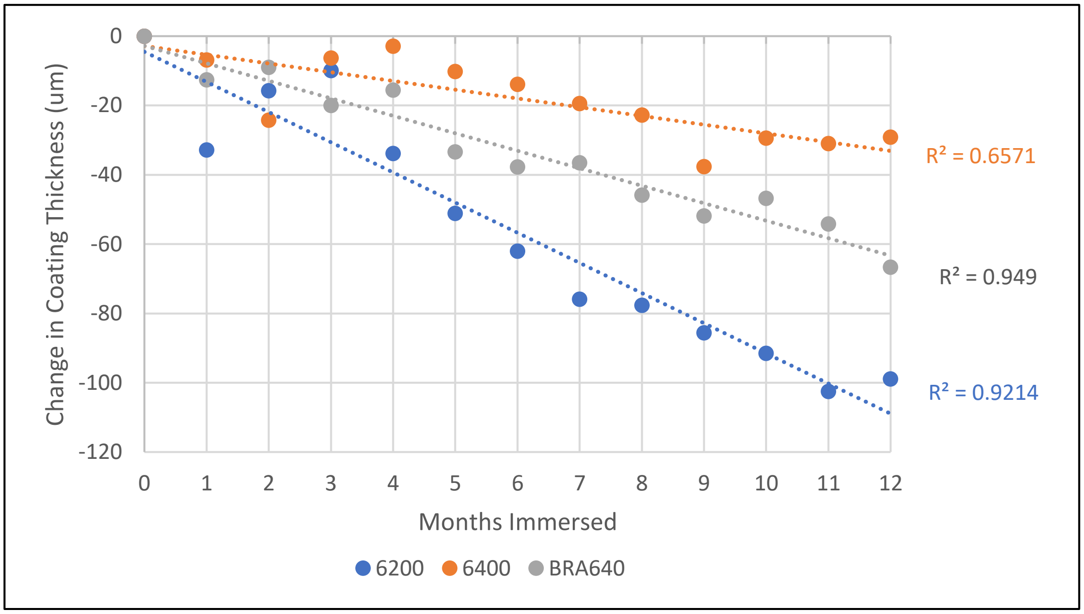

Figure 2.6: Change in coating thickness (microns) for the weekly groomed panels

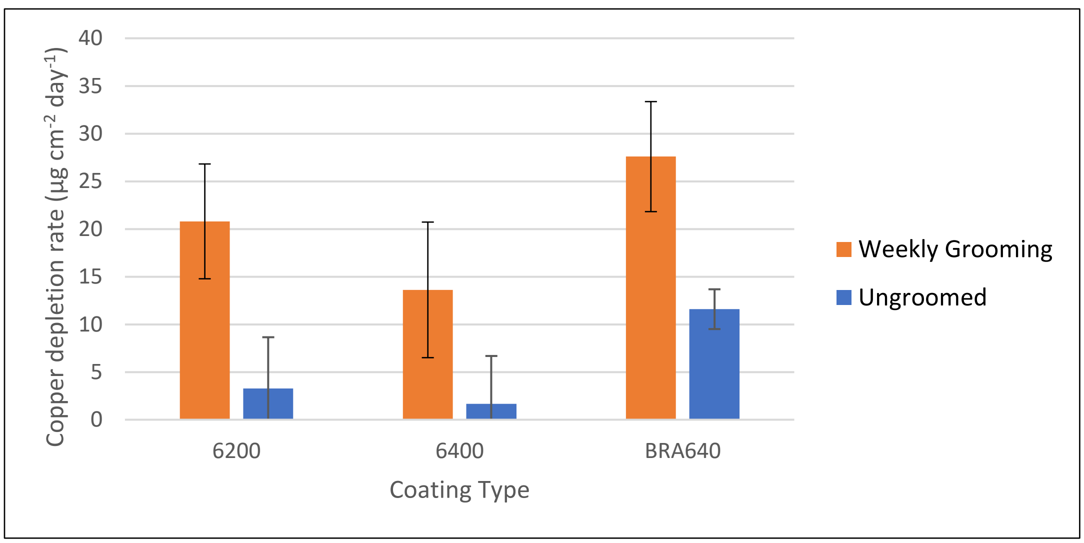

Figure 2.5: Copper depletion rate for panels coated with 6200, 6400, and BRA640.

Biofouling

After 12 months of immersion, the weekly groomed panels remained largely free of fouling. Biofilm began appearing on the panels after seven months of immersion and this may coincide with the warmer temperatures and increased light in the summer months (Figure 2.7, Figure 2.8).

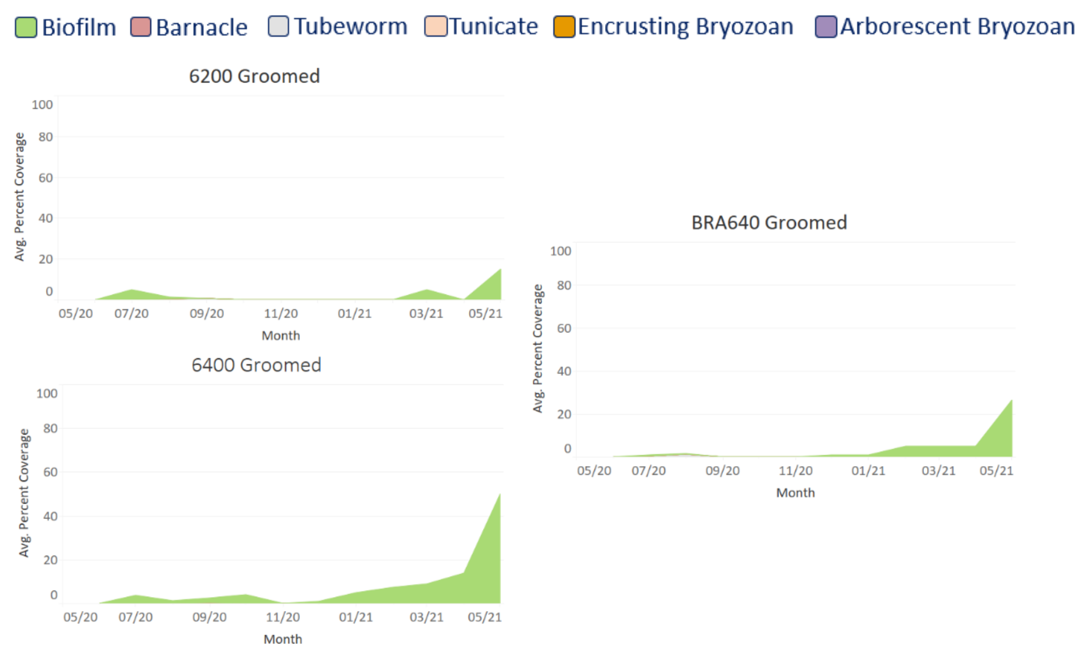

Figure 2.7: Percentage fouling coverage of groomed surfaces

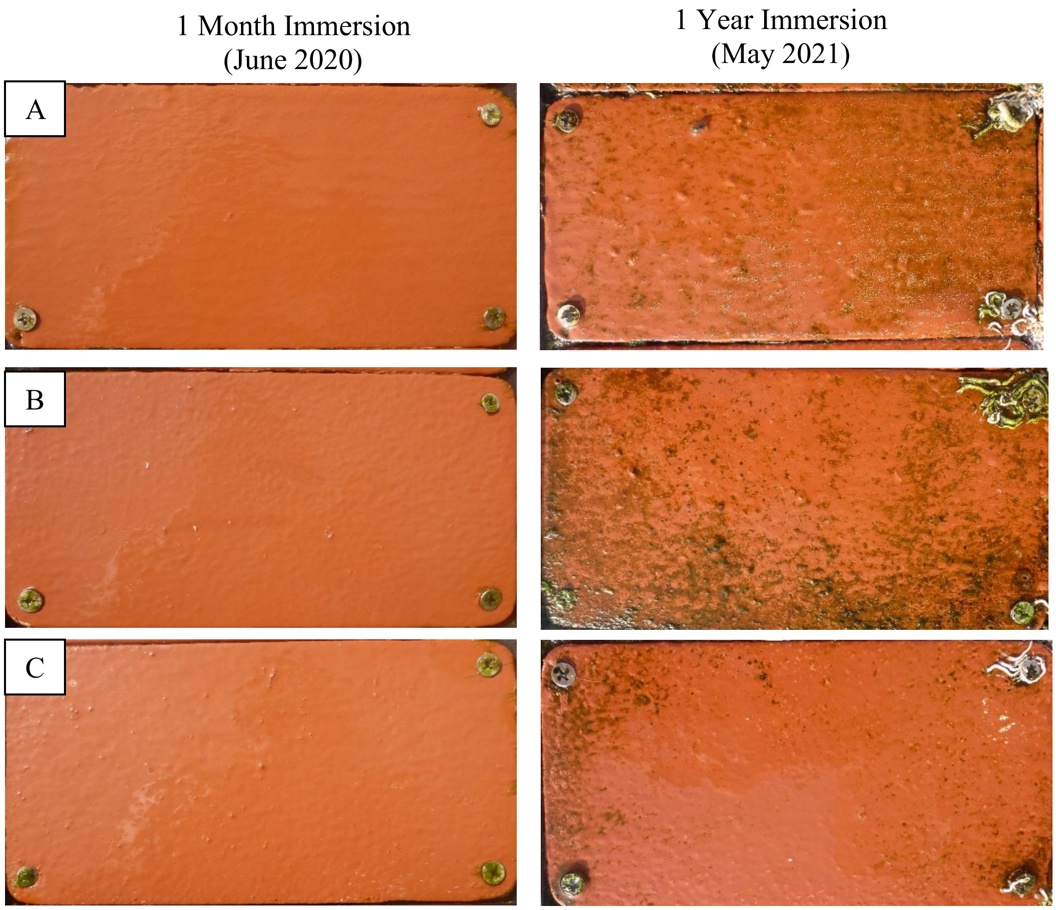

Figure 2.8: Photograph of 6200 (A), 6400 (B), and BRA640 (C) taken one month after immersion (June 2020) and after 1 year of immersion (May 2021).

The ungroomed panels quickly became fouled with biofilm after one week of immersion (Figure 2.9). Calcareous tubeworms established themselves on all panels after one month of immersion, comprising 33%, 23%, and 23% of all organisms for 6200, 6400, and BRA640, respectively. However, the calcareous tubeworms were eventually out competed by barnacle recruitment and did not contribute more than 10% coverage on the copper panels for the remainder of the experiment. The copper tolerant barnacle, *A. amphitrite*, were first established on the 6200 panels with 11% total coverage after one month. *A. amphitrite* contributed 83% of the total coverage for 6200 and 6400 after two months of immersion. BRA640 did not exhibit as quick recruitment of *A. amphitrite*, with just 55% total coverage after 5 months. After nine months of immersion, *A. amphitrite* comprised an average percent coverage of 86%, 84%, and 86% for 6200, 6400, and BRA640, respectively.

The epoxy control panels did not become dominated by *A. amphitrite*. The native, copper-sensitive barnacle, *A. eburneus*, became established on the panels and contributed 10% of the total coverage by the end of nine months of immersion. The epoxy panels experienced seasonal fluctuations in coverage, with barnacle establishment in the winter months and encrusting bryozoan coverage in the summer months.

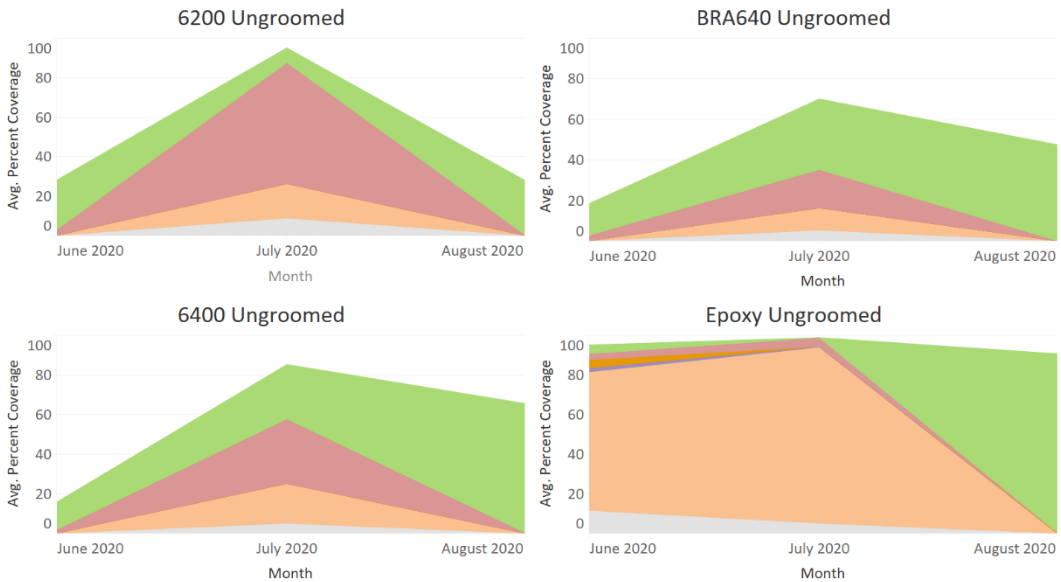

Figure 2.10: Fouling percentage coverage on the ungroomed panels from June 2020 - August 2020. Panels removed from the water in August due to Hurricane Isaias

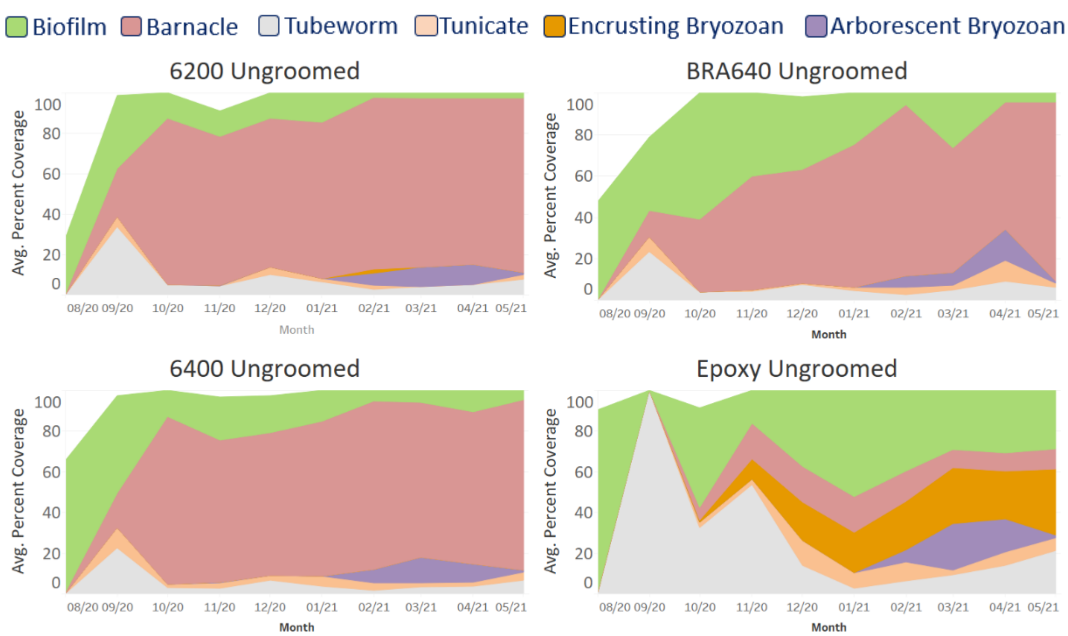

Figure 2.9: Percentage fouling coverage of ungroomed surfaces August 2020-May 2021.

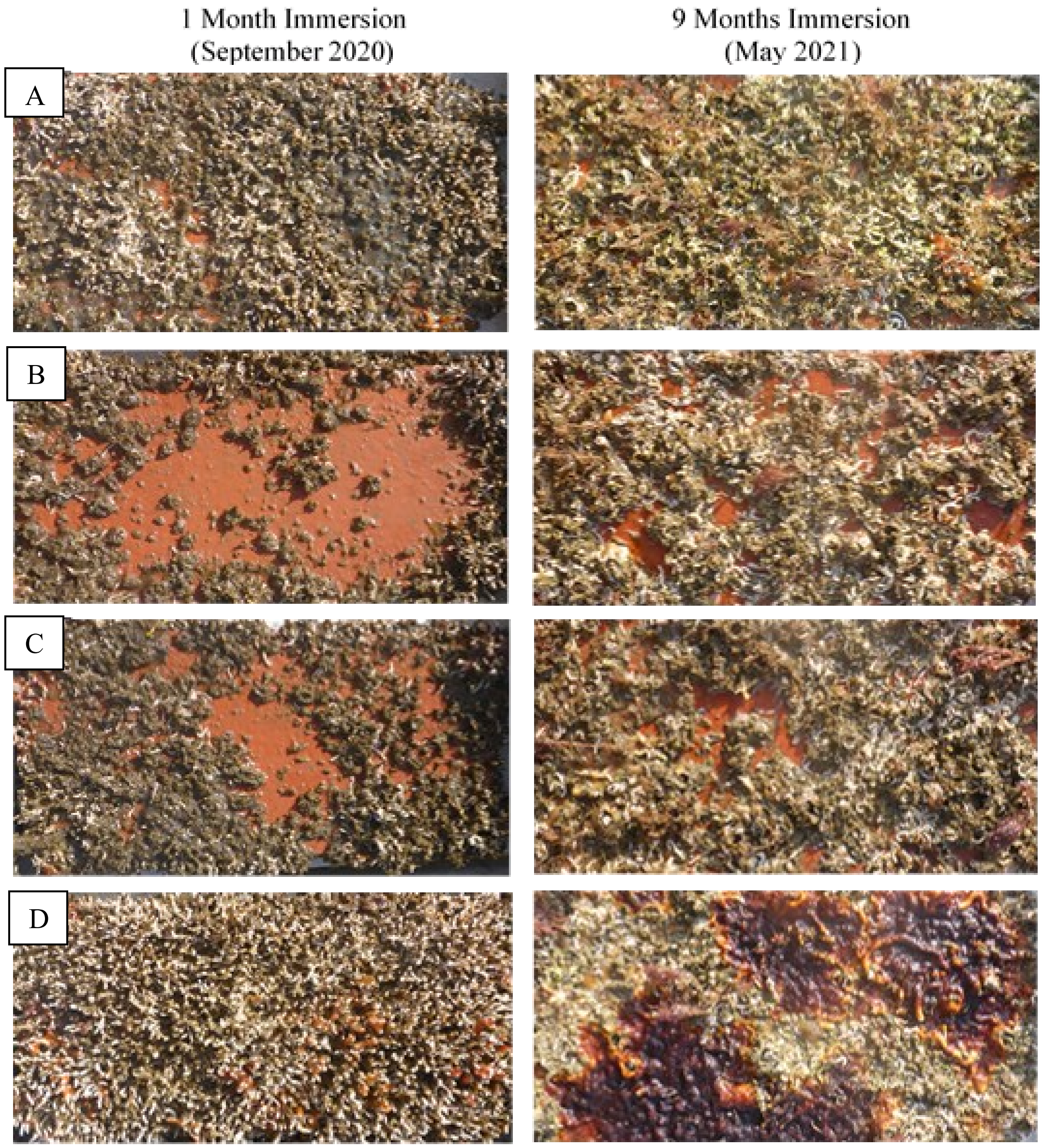

Figure 2.11: Photographs of ungroomed 6200 (A), 6400 (B), BRA640 (C), and Epoxy (D) following one month of immersion (September 2020) and nine months of immersion (May 2021).

Discussion

This study investigated the interactions between three different concentrations of copper-based AF coatings and weekly grooming. All three concentrations of copper-based AF were maintained free of fouling with weekly grooming throughout the duration of the experiment. Weekly grooming with the rotating hybrid brushed proved effective at eliminating hard fouling organisms, such as barnacles and calcareous tubeworms.

The ungroomed panels demonstrated that the copper-based antifouling paints will not keep a surface free of fouling without grooming. Although BRA640 experienced slower barnacle recruitment, all three copper coatings were nearly completely covered in barnacles and tubeworms by the end of the experiment. Hard fouling organisms, particularly barnacles, create the highest drag penalty of any fouling organism (Shultz *et al*., 2011). The barnacles at this test site, *A. amphitrite*, contributed significantly more coverage on the copper paints than the biocide-free control. Therefore, where copper-tolerant organisms dominant, such as *A. amphitrite*, a copper-based AF paint will not be as effective at preventing hard fouling attachment than a biocide-free alternative.

In addition to the increased drag associated with the heavy settlement of *A. amphitrite*, there are issues associated with the settlement of this invasive species. Invasive species may have higher fecundity and greater larval success than native species (Ferrario *et al.,* 2017). This allows an invasive species to out-compete native species and reduce the biodiversity of the benthic community. *A. amphitrite* also provides a foundation for other organisms to colonize. Less copper tolerant species can then be transported to new areas around the world (Floerl *et al.*, 2004). Reducing fouling through ship hull management can mitigate the impacts of copper-tolerant invasive species.

Weekly grooming impacted coating thickness differently on the copper-coated panels. Panels coated with 6200 experienced the greatest amount of coating loss throughout the experiment, with 99 microns lost. Panels coated with 6400 lost the least amount of coating thickness with 29 microns lost. This indicates that although 6200 is a lower copper-content paint (18.9%), it loses significantly more paint than the 6400 higher copper-content paint (32.9%) to maintain copper output at a level that maintains the surface free of fouling. In addition, BRA640 (37.1% copper by weight) lost more thickness than 6400 with 66 microns lost. This higher copper content paint may not need as frequent grooming to maintain the surface free of fouling.

The life cycle of the paint must also be considered when selecting a copper concentration and grooming frequency. The US Navy allows for a 25 μm per year wear rate when applying a thickness of 380 μm of copper ablative to their ship hulls (Tribou and Swain, 2017). This targets a 12-year dry-docking cycle. Following three years of service, in-water hull cleaning is often required to remove fouling (US Navy, 2006; EPA, 2011). Using thickness loss rates from this study, 6200 would have to be applied every three and a half years whereas 6400 would have to be applied every thirteen years. Frequent dry dock time increases both waste production and manpower associated with the application of ship hull paint (Byrnes and Dunn, 2020). By selecting a paint such as 6400 that maintains thickness with weekly in water grooming reduces the environmental and economic consequences of frequent dry dock time.

The coating thickness loss for the ungroomed panels estimated a theoretical copper output below 20 μg Cu cm^{-2} day^{-1} for all copper coated panels. BRA640 had the largest theoretical copper output of (12 ± 2) μg cm^{-2} day^{-1}. All the ungroomed panels were completely fouled within two months of immersion. This indicates grooming is necessary to maintain copper output at a level sufficient to prevent fouling.

The coating thickness loss calculated a theoretical output above 20 μg Cu cm^{-2} day^{-1} for both BRA640 and 6200. Panels coated with BRA640 exhibited a copper output of (28 ± 6) μg cm^{-2} day^{-1}. This is greater than the copper output for the panels coated with 6200 (23 ± 6) μg cm^{-2} day^{-1} and 6400 (14 ± 7) μg cm^{-2} day^{-1}. 6400, with the lowest copper output was maintained free of fouling. In addition, less frequent grooming can both reduce coating loss and copper loading.

The copper loading in ambient water can be calculated using the wetted hull area and the release rate of copper (Equation 2.1) (Srinivasan and Swain, 2007).

$$\textit{Copper Loading} = \textit{Wetted hull area} \times \textit{Release Rate of Copper} \times \textit{Days in Port}$$

Equation 2.2: Theoretical Copper loading

For one ship with a 3,000 m^2 hull area painted with BRA640, this would amount to 291.6 kg $year^{-1}$ of dissolved copper released into the water column. In comparison, if the ship hull were painted with 6400, this would amount to 149.0 kg $year^{-1}$ of dissolved copper released into the water column. Srinivasan and Swain (2007) estimated that the copper loading in Port Canaveral from the seven cruise ships that use the port is estimated to be about 1.4 tons $year^{-1}$ based on a leaching rate of 17 µg cm^{-2} day^{-1}. It is important to note that it is difficult to accurately determine the bioavailability of the copper because it is affected by different abiotic and biotic components within the aquatic environment (Meyer, 2002).

It is vital to reduce the excess amount of copper being leached in the ambient water column while simultaneously maintain the surface free of fouling. Panels coated with 6400 were maintained free of fouling while having the lowest theoretical copper output. Therefore, an effective grooming plan combined with a coating such as 6400 can both eliminate fouling and reduce environmental risk from excessive copper release rates.

Conclusion

Weekly grooming with a hybrid brush at Port Canaveral can maintain copper-based AF paints free of fouling. Dry film thickness measurements demonstrated that the three copper-based coatings responded differently to grooming. The grooming method and frequency need to be matched to the coating type and fouling pressure encountered by the coating. The fouling recruitment to the copper-based coatings at Port Canaveral was dominated by *A. amphitrite*.

Chapter 3 : Improving the Use of Biocide-free Coatings Through Grooming

Abstract

Biocide-free fouling release (FR) coatings are a nontoxic alternative to biocidal-containing antifouling (AF) paints. Biocide-free coatings reduce the adhesion strength of the fouling organisms, making them easier to remove either from hydrodynamic forces generated when a ship is underway or by cleaning or grooming. For biocide-free coatings to be effective, the forces imparted to on the surface must be greater than the adhesion strength of the fouling organisms. This study assessed the effectiveness of grooming with three different grooming brushes on three experimental biocide-free coatings and one commercial FR coating. The three grooming brushes were selected for their increasing force imparted on the surface. The coatings were placed under static immersion at Port Canaveral, FL and groomed on a biweekly frequency. The results showed that the hybrid brush reduced fouling attachment while preventing coating damage. It can be concluded application of grooming to biocide-free coatings can be effective at maintaining the surface if the forces imparted by the brushes are greater than the adhesion strength of fouling organisms.

Introduction

Concerns over the negative environmental impacts of AF paints have led to increase interest in biocide-free paints (Swain, 1998). Silicone-containing biocide-free paints are nontoxic, but require a different approach to the traditional AF paints. Biocide-free paints do not kill the fouling organisms, but rather reduce the adhesion strength of the fouling organism once it settles on the surface (Schultz *et al.*, 1999). As such, a ship hull may become fouled if it spends an excessive period in port. Therefore, the efficacy of the biocide-free paints is determined by their ability to self-clean through hydrodynamic forces or the ease at which they can be cleaned (Schultz *et al.*, 1999). The hydrodynamic or grooming forces must be employed at a value that is greater than the adhesion strength of the attached organism.

The adoption of nontoxic biocide-free and FR coatings requires an effective in water cleaning plan to maintain the ship full free of fouling. The current practice is to mechanically clean ship hulls when they become heavily fouled (Hearin *et al.*, 2015). This reactive approach tends to damage silicone biocide-free coatings (Tribou and Swain, 2010). One option is to incorporate a proactive and gentle grooming program for the coating (Tribou and Swain, 2010). Biocide-free coatings can be enhanced by grooming to maintain an active surface and to prevent the establishment of fouling (Tribou and Swain, 2010, 2015). Different types of grooming brushes impart different forces on a coating when grooming commences. Therefore, for biocide-free coatings to be effective, a plan must be established to match the coating with the grooming brush design and grooming interval.

This study was designed to investigate the effectiveness of three different vertically rotating brushes to maintain one commercial FR coating and three experimental coatings free of fouling. The research was designed to understand the relationships between brushes, different fouling release surfaces and fouling adhesion.

Methods

On August 11, 2020, 64 coated aluminum panels (4 in x 8 in) were immersed at the Florida Institute of Technology test site located at Port Canaveral, Florida. Three of the coatings were experimental formulations from North Dakota State University. They included a siloxane-polyurethane FR coating (A4-20), silicone oil additive in siloxane-polyurethane FR coating (A4-SO-0021), and amphiphilic additive in siloxane-polyurethane FR coating (A4-SMAA-#54) (Table 3.1). The fourth coating, Intersleek IS-1100SR, was included as a control. The panels (16 replicates of four coatings) were randomly attached to one of four PVC sheets (36 in x 36) coated with IS-1100SR. The frames were suspended approximately 0.5 m below the water surface from a static immersion raft moored at the Cape Marina at Port Canaveral, Florida from August, 2020 to June, 2021.

Table 3.1: List of surfaces immersed, composition, grooming treatment, number of replicates, and date exposed.

Sample Name	Composition	Grooming Treatment	Sample Replicates	Date Exposed at Port Canaveral
A4-20	Siloxane-Polyurethane Fouling Release Coating	1 thru 4	A thru D	August 21, 2020
A4-SO-0021	Silicone Oil added to Siloxane-Polyurethane FR Coating	1 thru 4	A thru D	August 21, 2020
A4-SMAA-#54	Amphiphilic additive in Siloxane-Polyurethane FR Coating	1 thru 4	A thru D	August 21, 2020
IS-1100SR	Intersleek 1100SR Fouling Release Coating	1 thru 4	A thru D	August 21, 2020

Grooming Brushes

The grooming tool was a prototype two-brush rotating grooming tool with interchangeable brushes (Figure 3.1). Three different 10-centimeter diameter grooming brushes were used to prevent and control fouling on the panels. These include a polypropylene bristle grooming (bristle) brush, hybrid polypropylene bristle and rubber stud grooming (hybrid) brush, and a nitrile rubber stud grooming (stud) brush (Figure 3.3).

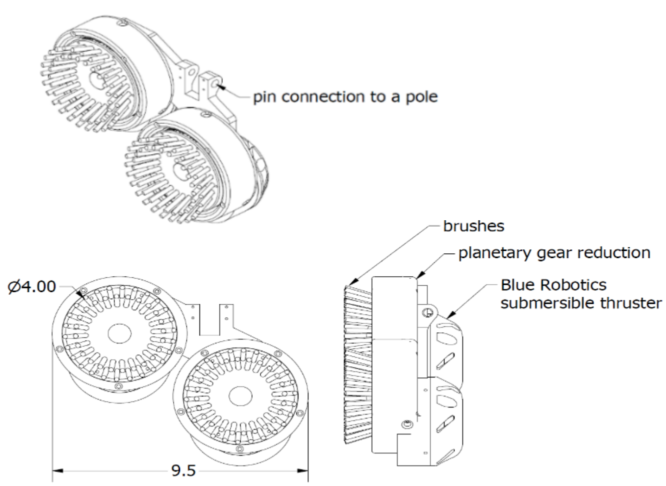

Figure 3.1: Prototype two-brush rotating grooming tool

Figure 3.3: Polypropylene bristled grooming brush (A), hybrid polypropylene bristle/rubber stud brush (B). nitrile rubber stud brush (C)

The grooming racks were subjected to different grooming treatments every two weeks (Figure 3.2). Grooming rack A remained ungroomed as a control. Grooming rack B was groomed with the bristle brush, grooming rack C was groomed with the hybrid brush, and grooming rack D was grooming with the stud brush (Table 3.2).

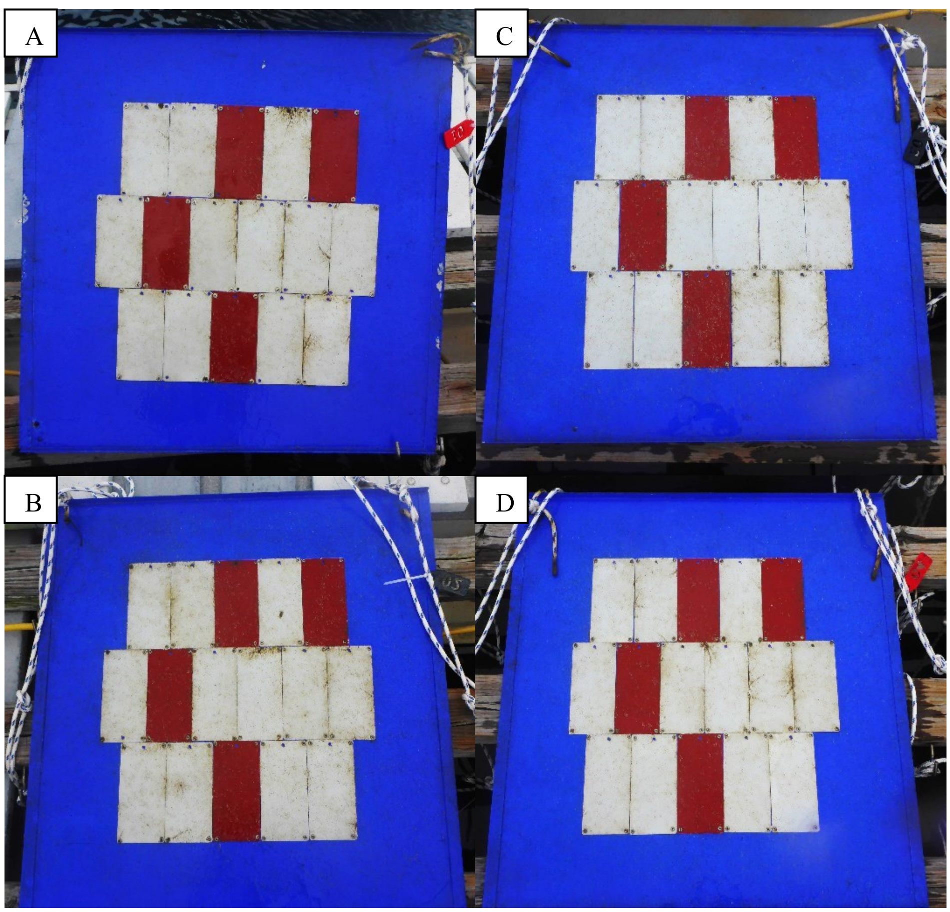

Figure 3.2: Photographs of the ungroomed rack (A), groomed biweekly with the bristle brush (B), hybrid brush (C), and stud brush (D).

Table 3.2: List of grooming treatments, immersion methods, and grooming frequencies.

Rack	Grooming Treatment	Grooming Frequency
A	Ungroomed	Never
B	10milØ Polypropylene bristle brush	Every Two Weeks
C	Hybrid polypropylene / rubber brush	Every Two Weeks
D	0.18inØ rubber stud brush	Every Two Weeks

The three brush designs were selected to provide different grooming forces. The brushes were calibrated by measuring the forces imparted to 3D printed barnacles attached to a floating element using a Futek load cell (Figure 3.4). The bristle brush imparted the least force, followed by the hybrid and stud brush. These values can then be related to the adhesion strength of the organisms to the coatings.

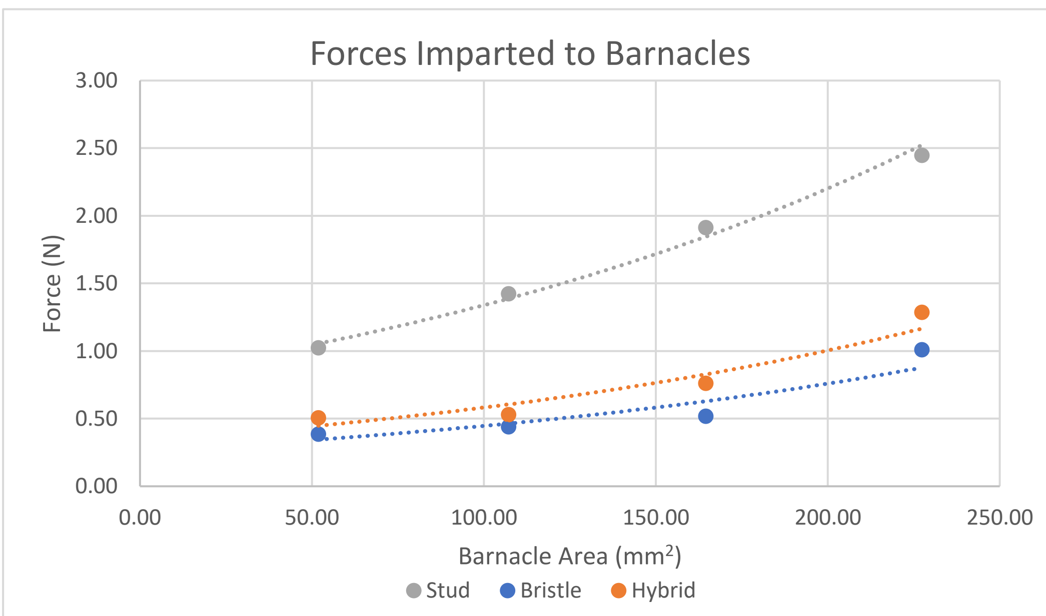

Figure 3.4: Forces Imparted to barnacles by the stud, hybrid, and bristle brushes.

Biofouling

The biofouling pressure at the test site was assessed visually every two weeks before and after grooming. Biofouling intensity and organism types were visually assessed per ASTM D6690-05 (2011) in which the total percentage of all benthic fouling organisms that are directly attached to the surface of the panels are documented. If a fouling type was present at <1% cover, a value of 1 was given. Fouling that became established at the edge of the panels was not included in total percentage cover (edge effect was 1 cm from the edge). The water temperature and salinity were also recorded daily at the test site to assess water quality.

Fouling Adhesion Measurements

The adhesion strength of hard fouling organisms was measured to better understand the forces required to effectively groom each coating. The shear adhesions strengths of barnacles (*Balanus eburneus*) and tubeworms (*Hydroides elegans*) to the coatings were measured using ASTM D5619-94 (ASTM 2011; Swain and Shultz, 1999). A hand-held force gauge was used to apply a force to the base of the hard fouling organism until the organism detached. The baseplates of the organisms were then scanned, and the base area was calculated using ImageJ software. Pixel to area determination was based in a 3-point calibration and computations were validated by inclusion of an object of known dimensions with each data set analyzed. Adhesion shear strength, tau, was calculated by dividing shear force, F (N), required to remove the organisms by the surface area, A (mm^2), of attachment (tau = F/A).

Results

The test panels were immersed during the month of August, 2020. Grooming was performed every two weeks until May, 2021. Barnacle and tubeworm adhesion measurements were taken in November, 2020.

Biofouling

The ungroomed control surfaces all showed rapid accumulation of fouling (Figure 3.5). The experimental coatings were initially dominated with biofilm (

). By the end of the experiment, encrusting bryozoan accounted for 60-70% of total biofouling coverage on all three experimental panels. Barnacles accounted for 8-9% of total biofouling coverage. The IS-1100SR control fouled slower than the experimental coatings. After three months of immersion, the IS-1100SR control panels were significantly less fouled than all three experimental coatings. ($p = 0.0002$, $p = 0.0001$ and $p = 0.0001$ for A4-SO-0021, A4-SMAA-#54, and A4-20, respectively, $\alpha = 0.05$). The IS-1100SR panels did not become completely fouled until nearly six months after immersion. In addition, calcareous tubeworms compromised approximately 50% of total biofouling coverage, whereas the experimental panels only accumulated 18-20% calcareous tubeworm coverage.

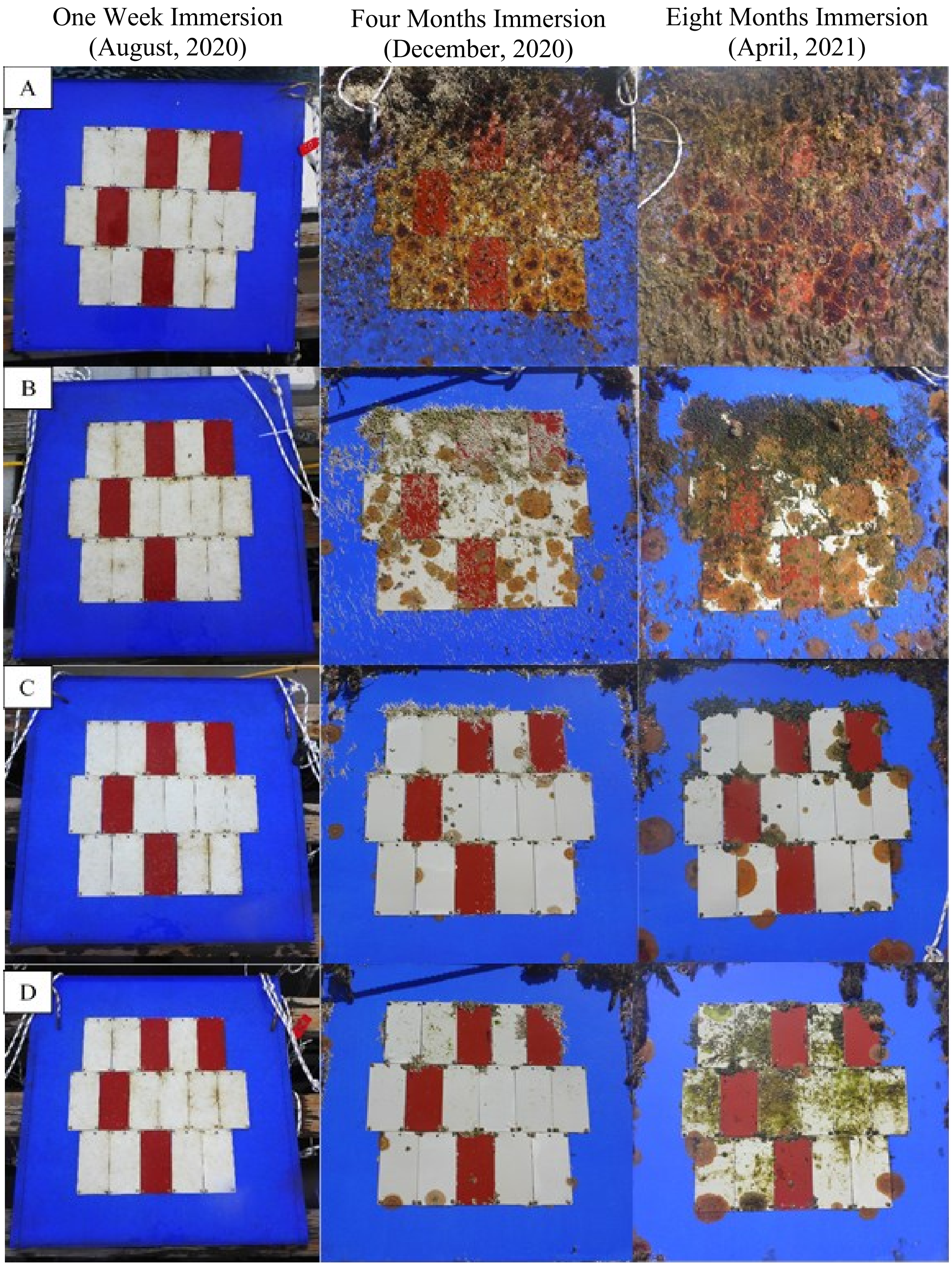

Figure 3.5: Photographs of the ungroomed rack (A), groomed biweekly with the bristle brush (B), hybrid brush (C), and stud brush (D) taken one week after immersion (August, 2020), four months after immersion (December, 2020), and eight months after immersion (April, 2020).

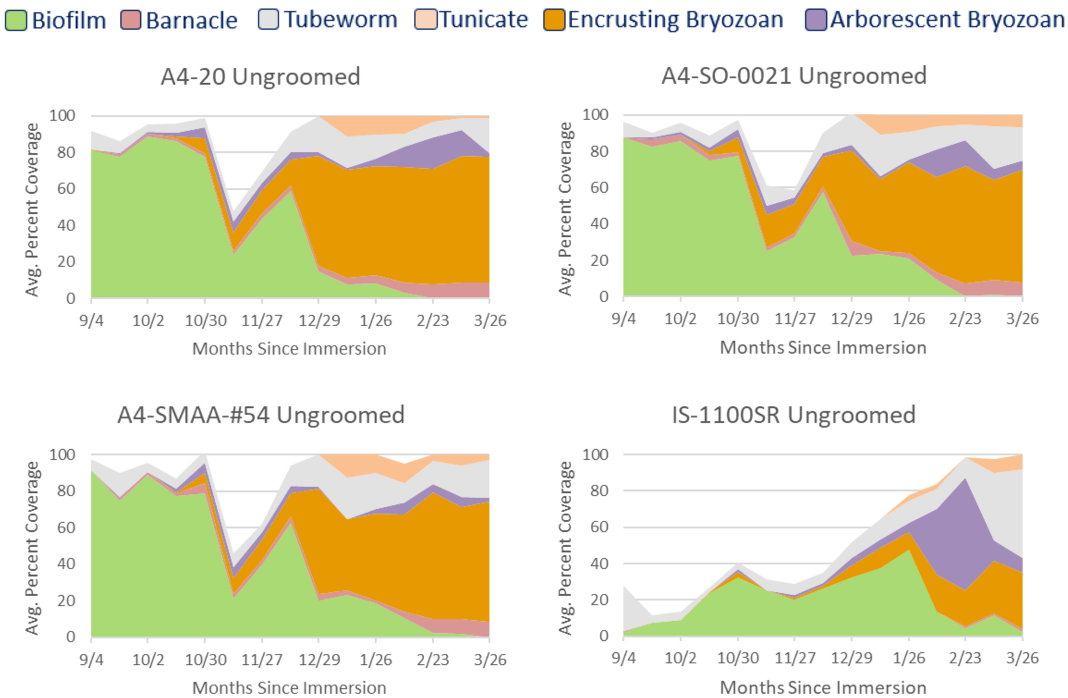

Figure 3.6: Percentage fouling coverage of ungroomed surfaces

Grooming was effective at reducing fouling accumulation on all the experimental and IS-1100SR coatings; however, differences were observed in recruitment both among the brush type and coatings. The hybrid brush was the most effective, followed by the stud and bristle brush types.

Bristle Brush

The bristle brush was able to control fouling on IS-1100SR for three months (Figure 3.7). However, these panels became dominated by tubeworms and encrusting bryozoans after four months of immersion. No barnacles attached to the surface of the IS-1100SR panels.

Biweekly grooming with the bristle brush was not effective at maintaining the experimental coatings free of biofouling. For the first three months of immersion, the bristle brush removed the biofilm which was present on the control (i.e., ungroomed) panels. However, after three months of immersion, hard fouling began to dominate, and the bristle brush was unable to remove these organisms. By March, 2021, approximately 80% of A4-20 and A4-SMAA-#54 bristle brush panels were fouled. Tubeworms and encrusting bryozoan contributed approximately 25% and 30% of the total percentage coverage, respectively. Barnacles contributed the greatest percent coverage to the A4-20 bristle brush panels with 25% total coverage. The A4-SO-0021 bristle brush panels were the most fouled at 93% total coverage. No significant differences were observed between total fouling coverage and fouling type on the experimental panels ($p > 0.05$).

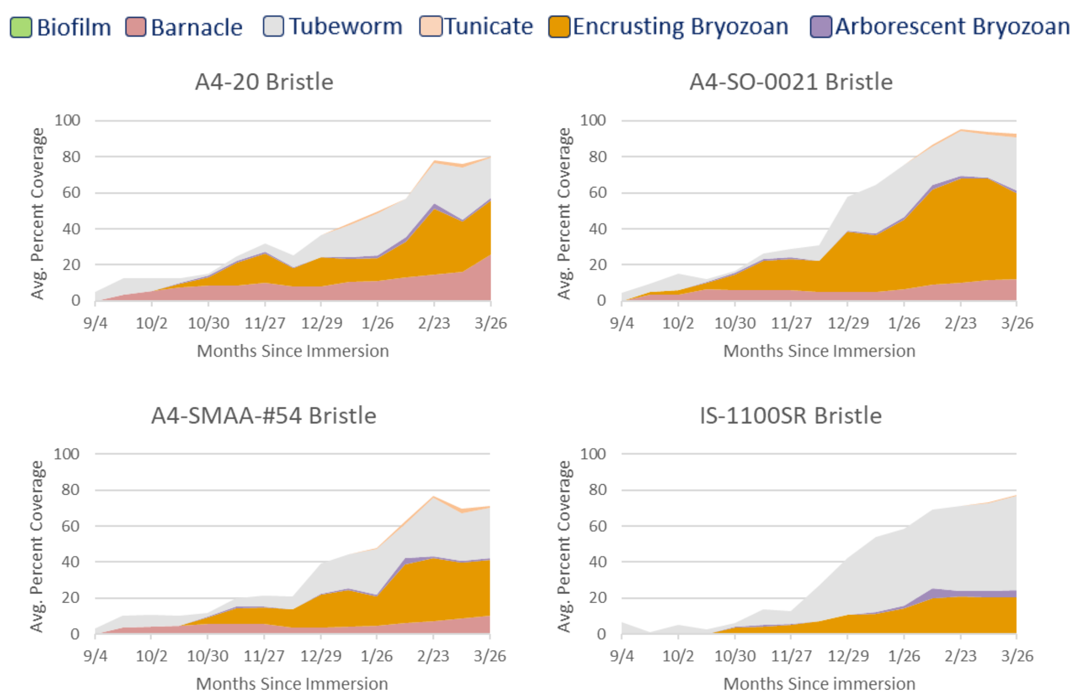

Figure 3.7: Percentage fouling coverage of panels groomed biweekly with the bristle brush.

Hybrid Brush

The hybrid brush was the most effective at preventing biofouling on all coatings. All coatings remained below 10% of total biofouling coverage by applying biweekly grooming with the hybrid brush (Figure 3.8). Barnacles occupied 5.5% of the A4-SO-0021 surface at the end of the experiment, which was the greatest macrofouling present on the coatings. This demonstrated that with the correct brush design grooming can be used to control biofouling on both the experimental and commercial IS-1100SR. No significant differences were observed between total fouling coverage and fouling type on the experimental panels ($p > 0.05$).

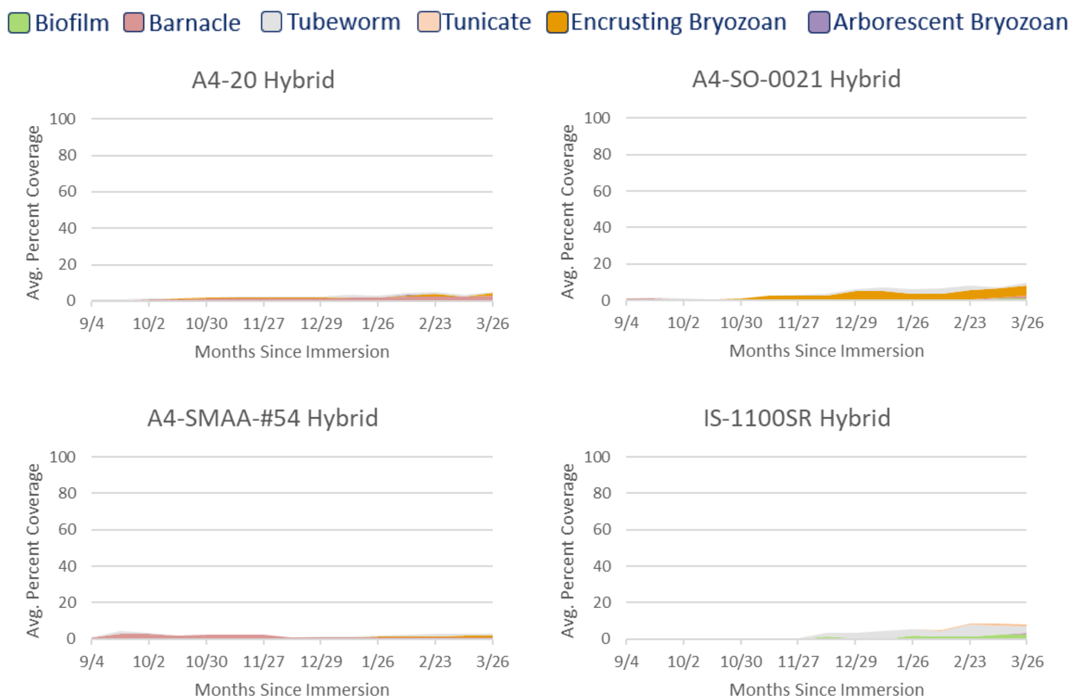

Figure 3.8: Percentage fouling coverage of panels groomed biweekly with the hybrid brush

Stud Brush

All coatings were maintained free of biofouling through biweekly grooming with the stud brush. The three experimental coatings and IS-1100SR exhibited less than 5% total biofouling coverage (Figure 3.9). However, the experimental coatings began to be damaged in November 2020. This was due to the entrainment of calcareous tubeworms, which caused scratching of the coating when removed. Biofilm began attaching to the exposed scratches which then led to the attachment of barnacles. This may also be attributed to warmer temperatures and greater sunlight. The IS-1100SR panels were significantly (α = 0.05) less fouled than the A4-SO-0021 panels (p = 0.02), A4-SMAA-#54 panels (p = 0.04), and A4-20 panels (p = 0.03).

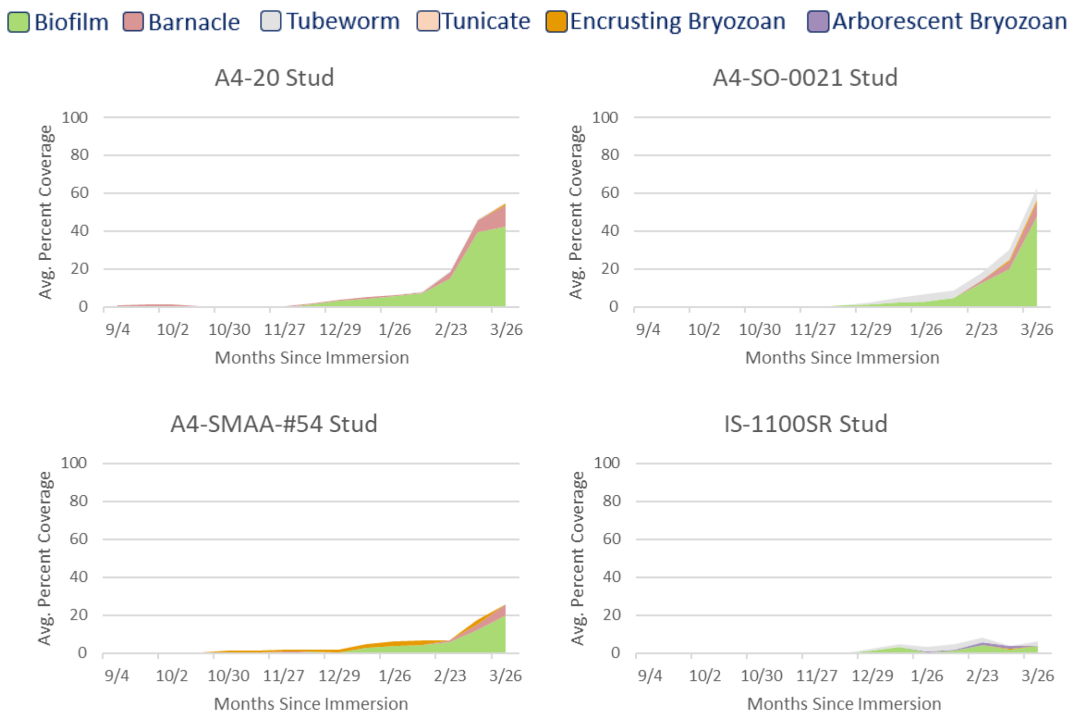

Figure 3.9: Percentage fouling coverage of panels groomed biweekly with the stud brush

Adhesion Measurements

The shear force required to remove barnacles and tubeworms varied among different coatings (Figure 3.10). Barnacles were not recruited to the IS-1100SR panels and therefore values from previous studies will be used. Tribou *et al.* (2010) measured an average barnacle adhesion strength of 0.099 MPa. Barnacles recruited to all the experimental coatings. A4-SMAA-#54 had the significantly lower average barnacle adhesion strength of 0.22 MPa (Figure 3.10A) than the other two experiment coatings (p < 0.0001, α = 0.05). A4-20 and A4-SO-0021 had similar average barnacle adhesion strength with 0.57 MPa and 0.55 MPa, respectively. The barnacle adhesion strength of IS-1100SR is significantly (p < 0.0001, α = 0.05) lower than all three experimental coatings. The average tubeworm adhesion strengths for the three experimental coatings were 0.20 MPa, 0.19 MPa, and 0.16 MPa for A4-SMAA-#54, A4-20, and A4-SO-0021, respectively (Figure 3.10B). IS-1100SR exhibited the lowest average tubeworm adhesion strength of 0.08 MPa, but this was not statistically significant ($\alpha = 0.05$) probably due to the low number of readings.

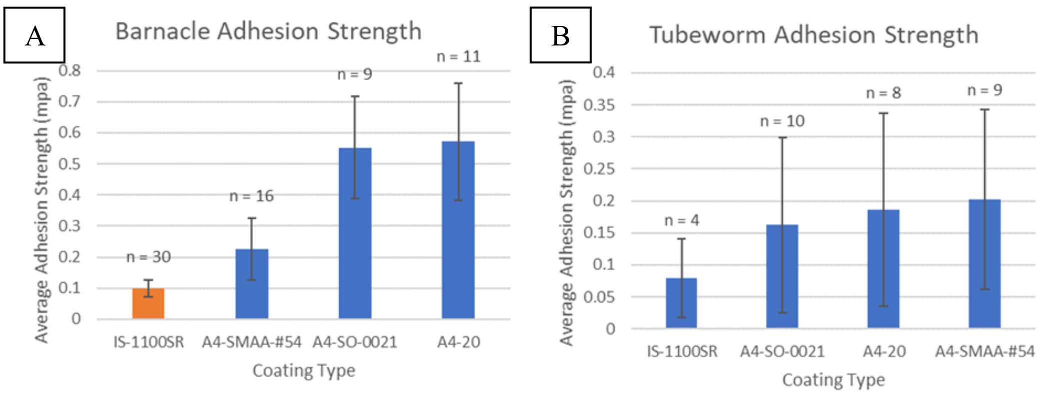

Figure 3.10: Average adhesion strength of barnacles (A) and calcareous tubeworms (B). Tribou *et al.* (2011) collected data for barnacle adhesion strength for IS-1100SR

Discussion

All three grooming procedures reduced fouling on the three experimental and one commercial biocide-free coatings. The bristle brush eliminated soft fouling, such as biofilm, from the surfaces but was unable to remove macrofouling, such as encrusting bryozoan and barnacles. Hearin *et al.* (2015) performed a grooming study on International Intersleek 900, a fouling release coating like IS-1100SR. This study found a five-bristle brush push underwater grooming tool was also effective at removing biofilm when groomed weekly. However, the tool could not remove macrofouling such as tubeworms and encrusting bryozoan. Hearin *et al.* (2016) then determined the same brush was effective at preventing macrofouling settlement at a grooming frequency of three times per week. This study agrees favorably with these studies as the bristle brush did not prevent the establishment of macrofoulers with a biweekly grooming interval.

Biweekly grooming with the hybrid brush successfully prevented fouling on all biocide-free panels. This indicates that the incorporation of the nitrile rubber studs on the grooming tool provide large enough force to remove macrofoulers from the surface. The stud brush was initially very successful at preventing fouling on the surfaces. However, the stud brush resulted in coating damage and was unable to remove the biofilm that settled in the scratches. The hybrid brush, which includes both the bristles and nitrile rubber studs, was the best design for preventing fouling on the surface. In these experiments, grooming was applied at a biweekly frequency. This lengthened the grooming frequency applied by Hearin *et al.* (2016), who determined a grooming frequency of three times per week was required to be effective for bristle brushes.

When the force imparted by the grooming tool was greater than the adhesion strength of hard fouling organisms, the coatings were maintained free of biofouling. This was achieved using the hybrid and stud brushes. The bristles were necessary to remove biofilm from the surfaces and the studs to impart sufficient forces to remove hard fouling. The present stud brush design caused coating damage due to entrainment of removed macrofouling. These tests emphasize the importance of the brush design to match the fouling type, fouling adhesion and coating toughness.

Barnacle adhesion strength can be related to the brush removal forces. The brush removal stress is equal to the force divided by base area. As the barnacle diameter increases, the shear stress imparted to barnacles by the same force decreases (Figure 3.11). The barnacle adhesion strength (Figure 3.10A) was measured on large, fully established barnacles. With adhesion strengths ranging from 0.22-0.57 MPa, the shear stress of the brushes was unable to overcome the adhesion strength of the barnacles. IS-1100SR had a previously measured barnacle adhesion strength of 0.099 MPa. For the IS-1100SR panels, the shear stress of the brushes was large enough to overcome the adhesion strength of the barnacles on the panels.

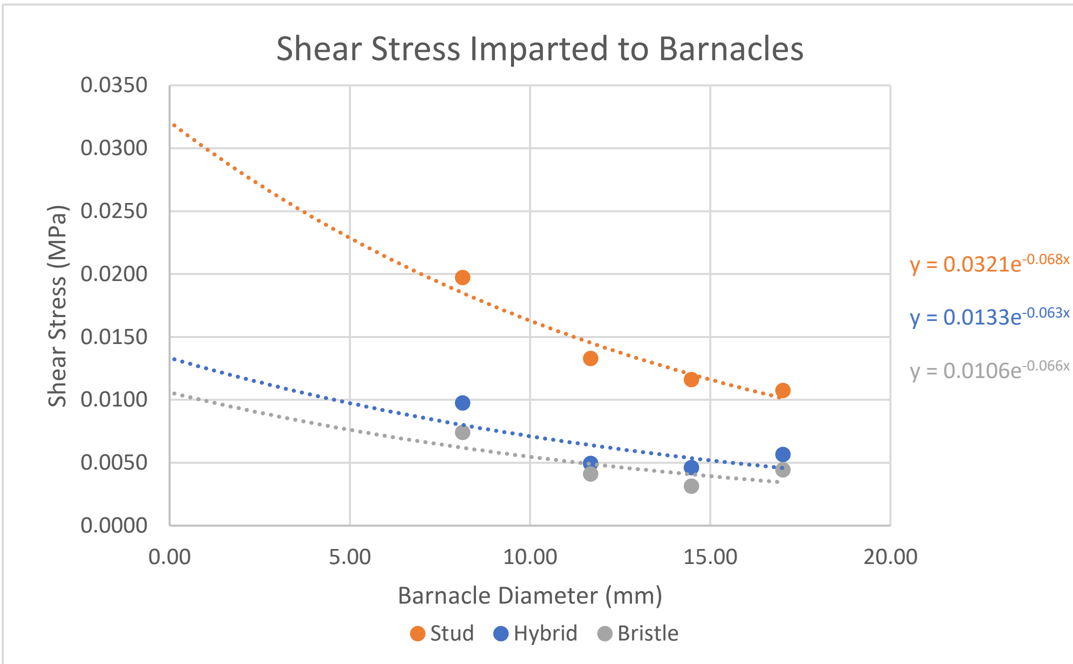

Figure 3.11: Shear stress (MPa) imparted to barnacles by diameter (mm)

The shear stress imparted to barnacles decreases as the barnacle base diameter increases. Therefore, for in water grooming to be effective on biocide-free coatings, the coating must be groomed while the barnacles are small.

Fouling type must also be considered when determining efficacy of grooming on biocide-free coatings. A Waltz *et al.* (2020) study compared the adhesion strength of encrusting bryozoan to barnacles and tubeworms on Intersleek 970. The encrusting bryozoan adhesion strength ranged from 0.020 to 0.083 MPa, which was lower than the adhesion strength of barnacles and tubeworms. This suggests that the hybrid and stud brush were able to effectively remove encrusting bryozoan from the surface, but the bristle brush did not apply enough force for removal. However, encrusting bryozoans could be missed by a grooming tool that can remove higher form fouling taxa such as barnacles and tubeworms (Hearin *et al.,* 2016). This then leaves room for the encrusting bryozoan to grow. The low form of encrusting bryozoan also allows them to remain attached to ship hulls even when subjected to high speeds. Their attachment will increase the drag of the ship, increasing fuel costs and consumption. Encrusting bryozoans also provide a habitat to other invertebrates, potentially transporting non-native species from port to port (e.g. Sellheim *et al.*, 2010). The design of a grooming tool that effectively removes low form taxa such as encrusting bryozoans is necessary to maintain biocide-free coatings free of fouling.

Conclusion

This study demonstrated that existing commercial fouling release coatings can be maintained free of fouling through biweekly grooming while imparting minimal coating damage. Biweekly grooming with a hybrid brush was shown to be very effective at preventing the establishing of macrofouling on the surfaces of fouling release coatings. This provides a viable method to clean ship hulls that are in port or at anchor and unable to remove fouling through hydrodynamic forces. Fouling release coatings, which are biocide-free, also reduce the environmental impact of biocide input at ports and marinas. The combination of an effective grooming tool and grooming interval make a tougher fouling release coating an alternative to traditional biocide-based coatings.

Chapter 4 : Conclusion

Differences in the efficacy of grooming brushes to prevent biofouling on antifouling (AF) and fouling release (FR) coatings were found to be related to the coating type and brush design. Biofouling on all the copper-based AF paints was prevented when groomed every 14 days with a hybrid brush. This ensured that copper ions remained present at concentrations sufficient to prevent recruitment to the surface. Differences were recorded in the rate at which the coatings were removed and at which copper was released. The lowest copper-content paint (6200) lost significantly more dry film thickness than the high copper-content paint (BRA640), which was necessary to maintain its antifouling action. The greater loss of dry film thickness means that the 6200 would have a shorter design life and vessels using this paint would require more frequent dry docking and recoating.

The grooming tests applied to the FR coatings, demonstrated that ship hulls coated with these nontoxic alternatives can be maintained free of fouling without the use of biocides. A biweekly grooming plan with a hybrid brush cleaned the surfaces of both the experimental and commercial FR coating. This was related to the forces imparted by the brushes to the adhesion strength of the organisms. It was shown that the brush design selected for grooming needed to match the fouling type, fouling size and adhesion strength, and coating durability. Biocide-free fouling release coatings in combination with a well design grooming program are a viable alternative to AF coatings.

Chapter 5 : Future Research Recommendations

As nations move towards decarbonization and sustainable engineering, the environmental and economic impact of maintaining ship hull coatings in a smooth and fouling free condition cannot be overlooked. Future research should continue to develop underwater grooming methods that are able to prevent the recruitment of biofouling without damaging the coating. This includes the development of coating formulations to work in synergy with grooming, the design of brushes to work with existing commercial coating formulations, and the development of underwater robots by which to apply in-water grooming/cleaning.

Studies should be performed to understand how to match coatings and the different biofouling pressures encountered at different locations with a well-designed grooming program.

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