GE RESEARCH &
DEVELOPMENT CENTER

NONTOXIC, SELF-CLEANING SILICONE FOULING RELEASE COATINGS

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Biofouling on ship hulls presents a significant challenge for the U.S. Navy. Fouling on the hulls of marine vessels has been shown to reduce maximum speed and increase propulsive fuel consumption1. Historically, marine antifouling paints have utilized compounds toxic to marine organisms, such as triorganotin, as a means of combating the fouling problem2. In recent years, the environmental impact of these coatings has come under scrutiny3,4. The application of triorganotin-based paints has been prohibited on smaller vessels (< 25 m) and the U.S. Navy has discontinued its use.

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INTRODUCTION

Biofouling on ship hulls presents a significant challenge for the U.S. Navy. Fouling on the hulls of marine vessels has been shown to reduce maximum speed and increase propulsive fuel consumption[1]. Historically, marine antifouling paints have utilized compounds toxic to marine organisms, such as triorganotin, as a means of combating the fouling problem[2]. In recent years, the environmental impact of these coatings has come under scrutiny[3,4]. The application of triorganotin-based paints has been prohibited on smaller vessels (< 25 m) and the U.S. Navy has discontinued its use.

Copper based ablative paints remain the only currently viable option for marine protection but, although the activity of copper is much less than tin, concerns about copper toxicity effects are likely to lead to future regulations[5]. Current research has focused on employing organic biocides in conjunction with reduced copper concentrations[6].

The costs to the military of combating marine fouling are significant. For example, it is estimated that $34 to $50 million of the Navy's approximately $500 million annual propulsive fuel bill could be saved by the use of an effective antifouling paint. In addition, an estimated $100 million per year is spent for hull cleaning, paint removal, repainting, toxic water and grit disposal, compliance with OSHA requirements during repainting procedures, and labor to remove biofouling[7].

Fouling release coating technologies are under development by commercial marine paint companies and the U.S. Navy in response to the need for lower life cycle costs and a non-toxic alternative to conventional antifouling paints. Fouling organisms may grow on the surface of these coatings, but they adhere poorly and can be removed by cleaning with a water spray or light brushing[8,9,10]. The two leading biofouling release candidates have been fluoropolymers and silicones. This is based on the observed relationship between surface energy and the "non-stick" easy release characteristics of these compounds. However, silicone polymers have shown better fouling release capability than fluoropolymers and other coatings[11,12]. This has been attributed to their being within an optimum range of critical surface tension, which is related to surface energy[13,14]. Other characteristics thought to enhance the superior fouling release ability of silicones are their surface structure, rheology, and the extremely low glass transition temperature (Tg), as reflected in their molecular mobility[11,15,16,17,18]. In addition, fouling coverage on silicone coatings is usually less than the coverage on other nontoxic surfaces[8,19,20].

One method for the enhancement of the performance of silicone fouling release coatings has been oil incorporation[21,22,23]. The earliest example was provided by Milne in which a polymethylphenylsiloxane oil was incorporated into a polydimethyldiphenylsilicone matrix[24,25]. Callow also reported that panels coated with room temperature vulcanizing silicone elastomers containing methylphenylsilicone oils and exposed on a raft near Singapore, had improved antifouling performance relative to coatings without oil[8]. The improvement in fouling release due to the inclusion of oil is also related to the functionality of the silicone matrix into which it has been incorporated; dimethylsiloxane oils are more effective in enhancing fouling release

performance in phenylsilicone functional networks than in methysilicone functional networks[26,27].

Incorporation of oils may allow detachment by slippage as an additional release mechanism[28]. It has been postulated that the surface structure of silicone fouling release coatings is changed when oils migrate to the coating surface. Oils that increase the hydrophobicity of the silicone surface, such as phenylsiloxane oils, improve the fouling release ability of the coating[26,29]. Oil incorporation into an organic matrix does not provide a synergistic effect[30]. This may be attributed to the high flexibility of the polydimethysiloxane backbone, which allows oil to freely diffuse in and out of a coating[31].

Under DARPA contract N00017-96-C1045, we proposed to develop a silicone-based topcoat having substantially extended self-cleaning and fouling release performance. This goal would be achieved by judicious selection of the oil structure that would be incorporated into the silicone topcoat. In addition, we proposed to study whether oil depletion from the coatings occurred. Depletion of oil would result in a precipitous decline in foul release performance. Performance criteria for the coating system were:

- 5-7 year foul release performance
- Ability to self clean at cruising speeds
- Excellent adhesion to steel, aluminum, fiberglass, composites and rubber substrates
- Tear and gouge resistance
- Resistance to cleaning abrasion
- Environmental safety and no toxicity to aquatic species

A team of technologists from the military (NSWC, SPAWAR), academia (FIT, University of Hawaii, SUNY Buffalo), and industry (GE, Bridger Scientific) was assembled to develop a coating system that satisfied the above performance criteria. The work breakdown structure of the program is outlined below (Figure 0.1). The program was divided into 5 tasks:

1. Design, synthesis and testing of foul release paints with improved antifouling and release properties
2. Optimization of the physical and application properties of the coating
3. Environmental impact and toxicological testing
4. Large scale validation
5. Program management.

The technology roadmap for topcoat development utilized by the team is provided in Figure 0.2. In addition to topcoat development, it was deemed necessary to develop new tiecoat compositions as well as a recoat and repair package. The results of our developmental efforts are described by task in the subsequent report. Additional accomplishments include documentation in peer-reviewed journals, patents and presentations as indicated in Appendix A.

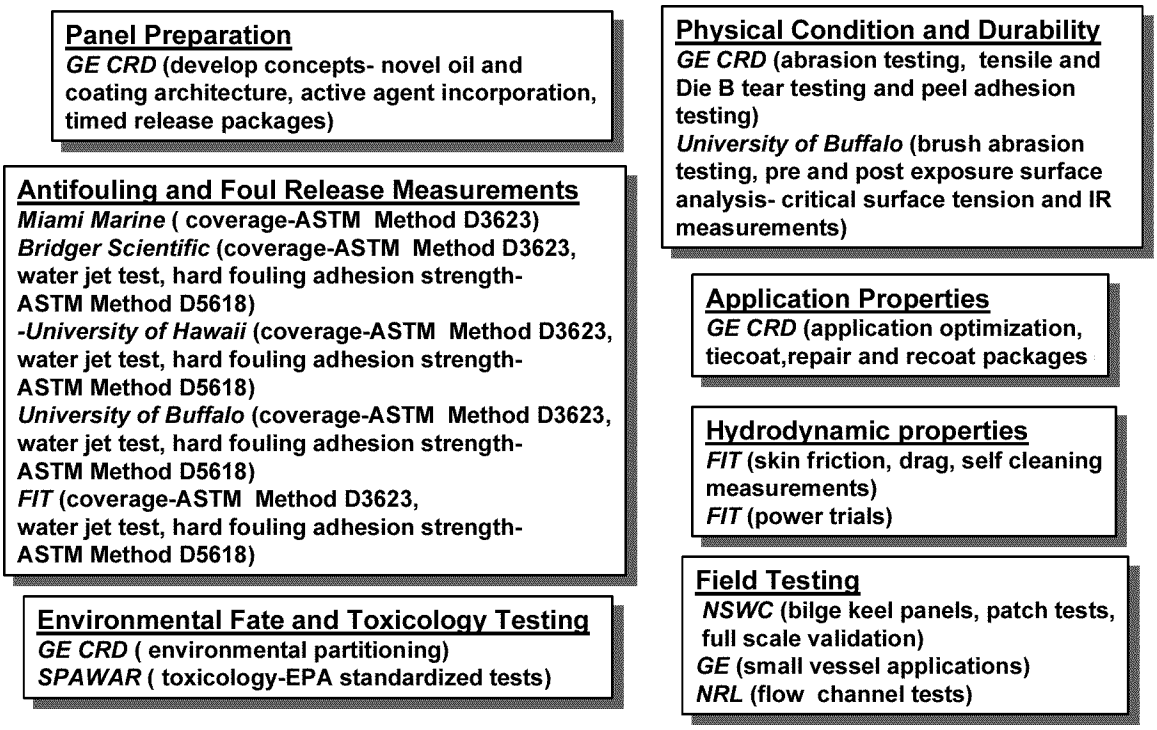

Figure 0.1 Task structure for foul release coating development.

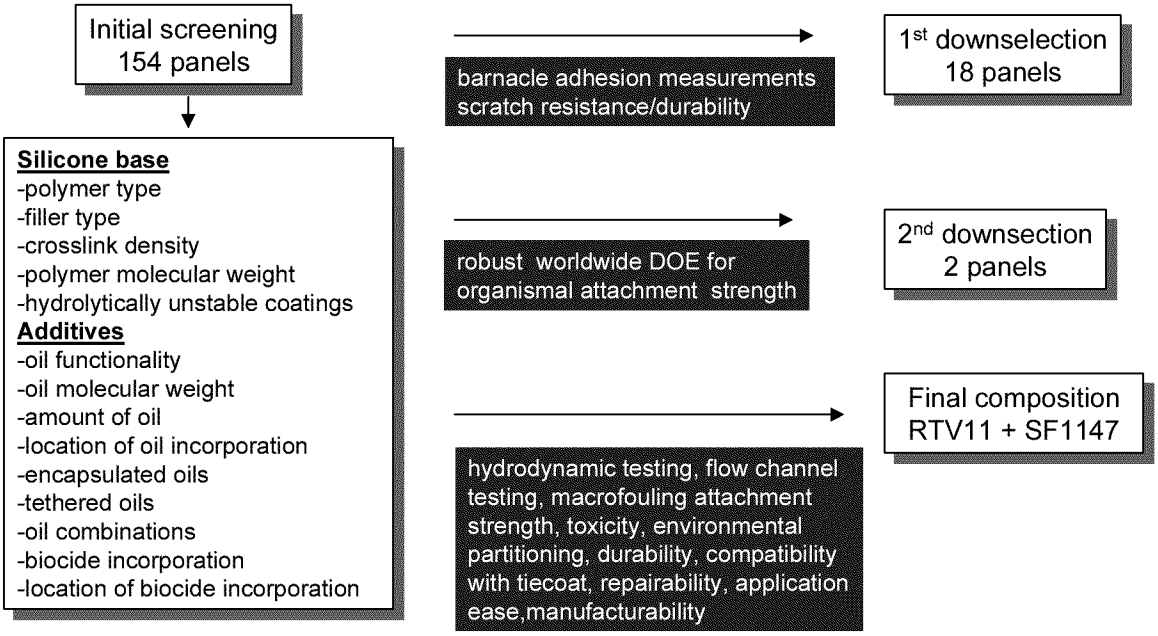

Figure 0.2. Technology process roadmap for topcoat development.

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SUMMARY

Under DARPA contract N00017-96-C0145, GE and it's collaborators (NSWC, SPAWAR, University of Hawaii, SUNY Buffalo, FIT, and Bridger Scientific) have developed a foul-release system comprised of the SEA210A/SCM501C tiecoat and RTV11® amended with 10% SF1147. This system has the following attributes.

- Significantly reduced macrofouling attachment strength compared with the control (RTV11®).

FIT	*Balanus eber*neus (MPa)	*Hydroides* (MPa)
RTV11®	0.067+/-0.031	0.097+/-0.025
RTV11® + SF1147	0.042+/-0.020	0.042+/-0.014
ANOVA Analysis	P = 0.000, N = 770	P = 0.000, N=40

U. Hawaii	*Ostrea* (MPa)	*Hydroides* (MPa)
RTV11®	0.131+/-0.069	0.165+/-0.199
RTV11® + SF1147	0.076+/-0.046	0.090+/-0.048
ANOVA Analysis	P=0.002, N=55	P=0.027, N=56

- Excellent physical properties (tear resistance = 0.103 ± 0.006 MPa, tensile strength = 1.70 ± 0.33 MPa).
- Demonstrated hydrodynamic self-cleaning at less than 20 knots; little difference seen between drag forces obtained on a fouled and clean coating.
- Scratch resistance greater than the RTV11® control; not diminished upon water exposure.
- Excellent interfacial adhesion (peel adhesion strength after 30 days water immersion = 736 ± 25 N/m from large-scale validation).
- Easily sprayable using airless equipment.
- Excellent field performance as demonstrated on small craft (*Balanus improvisus* adhesion strength: 0.034.0+/-0.021MPa; *H. dianthus* adhesion strength: 0.042 +/-0.019 MPa; greater than 2 year life demonstrated.
- Large-scale application demonstrated.
- Recoatability demonstrated on a small vessel.

- Toxicity against diatoms, fish and mysids significantly less than copper control (diatom IC_{50} = 205% extract, fish LC_{50} = >300% extract, mysid LC_{50} = 221% extract; copper 8 %, 10%, and 5% extract).

- Water loss upon water immersion comparable to control (RTV11®) (3.2 ± 1.0 wt %, RTV11® 2.6 ± 0.9 wt %); oil does not exude into the aqueous environment.

TASK 1. DESIGN, SYNTHESIS AND TESTING OF FOUL RELEASE PAINTS WITH IMPROVED ANTIFOULING AND RELEASE PROPERTIES

SECTION 1. 1 BASELINE MODEL STUDIES

Model silicone foul release coatings with controlled molecular architecture were evaluated to determine the effect of compositional variables such as filler loading and crosslink density on pseudobarnacle and barnacle attachment strengths. Pseudobarnacle adhesion values correlated with filler loadings in both condensation and hydrosilylation cured silicones. Variation of crosslink density of hydrosilylation-cured silicones had an insignificant effect on attachment strength. A significant correlation was obtained between the modulus of the coatings and pseudobarnacle adhesion values as predicted by the Kendall equation. However, the mode of failure upon detachment of the pseudobarnacle was dependent upon the crosslink density; samples with high crosslink density failed cohesively within the silicone. Barnacle adhesion profiles mirrored pseudobarnacle adhesion in hydrosilylation cured systems.

INTRODUCTION

There are many reports on the utility of silicones as foul release coatings; however, there are few reports of the effect of compositional variables of the coating on bioadhesion strength. Wynne has compared the fouling release performance of a filled condensation cured RTV (RTV11®) with that of an unfilled hydrosilylation system[1]. Bauch and Tonge found different pseudobarnacle adhesion performance within the class of polydimethylsilicones but no systematic variation in architecture was reported[2]. In this section, we describe our experiments in which we have controlled the molecular architecture of both condensation cured and hydrosilylation cured silicone coatings and examined the relationship between coating composition (crosslink density and filler loading) and organismal adhesion strengths.

EXPERIMENTAL

Materials

Silicone polymers, Karstedt's catalyst, dibutyltin bis (acetylacetonate), fumed silica, tetraethylorthosilicate, calcium carbonate, and SS4155 were obtained from GE Silicones. Aluminum panels were obtained from the Q-Panel Company.

Model silicone foul release. coatings

A condensation curable coating with 0% filler was prepared by combining 100 g of dimethoxymethylsiloxy terminated polydimethylsiloxane (MW = 3100, 0.032 moles) with 3.56 g tetraethylorthosilicate (0.017 moles) and 0.65 g dibutyltin bis (acetylacetonate) (1.5 mmoles). As an example of a filled system, a coating with 13% filler was prepared by combining 87 g of dimethoxymethylsiloxy terminated polymer (0.028 moles), 13 g calcium carbonate (0.129 moles), 3 g tetraethylorthosilicate (0.014moles) and 0.65 g dibutyltinbis(acetylacetonate) (1.5 mmoles). Samples were dispensed onto aluminum panels primed with SS4155 using a scalpel blade. Samples were allowed to cure for 7 days prior to testing.

A master batch for hydrosilylation curable model systems was prepared by combining 200 g of hexamethydisilazane treated fumed silica and 800 g of vinylterminated polydimethylsiloxane (equivalent weight = 4111). The master batch was combined with additional vinyl polymer if necessary, mixtures of crosslinkable hydride polymer (equivalent weight = 102) and linear hydride (equivalent weight = 1257) so that the ratio of total hydride to vinyl was maintained at 1.2. Ten mg of tetravinyltetramethylcyclotetrasiloxane (0.000023 moles) was added to the mixture, followed by 10 μl of Karstedt's catalyst (10.9% Pt, 4.8 μmoles Pt). The amounts of master batch, linear vinyl, linear hydride, and crosslinkable hydride polymers for the different coating systems are given in Table 1.1.1.

Table 1.1.1. Composition of hydrosilylation curable model systems.

Coating Type	**Master Batch (g)**	**Vinyl Polymer (g)**	**Linear Hydride (g)**	**Crosslinking Hydride (g)**
16% filler 50/50 hydride ratio	80	5.0	13.5	1.1
16% filler 25/75 hydride ratio	80	10.6	7.28	1.78
16% filler 0/100 hydride ratio	80	17.4		2.56
10% filler 50/50 hydride ratio	50	34	14.5	1.12
5% filler 50/50 hydride ratio	25	58	15.3	1.24

Aluminum panels were coated using the procedure described above for the condensation curable systems.

Field Exposure

Panels were exposed at the Florida Institute of Technology (FIT) exposure and testing platform in the Indian River Lagoon for approximately one month to allow for barnacle accumulation. The shear strength of barnacles to the coatings was measured using ASTM method D5618 in which a force is applied parallel to the base of the barnacle until the barnacle detached[3].

Laboratory Testing

Tensile properties of the model foul release coatings were obtained in accordance with ASTM Method D412 using 1-1.5 mm thick sheets of the cured coating. Contact angle measurements were performed according to literature methods using a Rame-Hart NRL100 goniometer. Critical surface tensions were calculated using Zisman plots[4]. Surface roughness was determined using Park Universal Scanning Probe operating in the contact mode at a 1 Hz line scan rate.

Pseudobarnacle Adhesion Tests

Pseudobarnacle adhesion measurements were performed using a modification of ASTM D5618[5]. Wooden studs of known diameter were glued to the surface using Epoxi-Patch obtained from the

Dexter Corporation. The glue was allowed to harden for 5 days before testing. In this case, the force gauge was mounted on a traveling rack that moved at 0.63 cm/sec or 0.08 cm/sec parallel to the coating surface (Figure 1.1.1). Velocity of the traveling rack within the range tested had no effect on pseudobarnacle adhesion values ($P = 0.174$, $df = 59$).

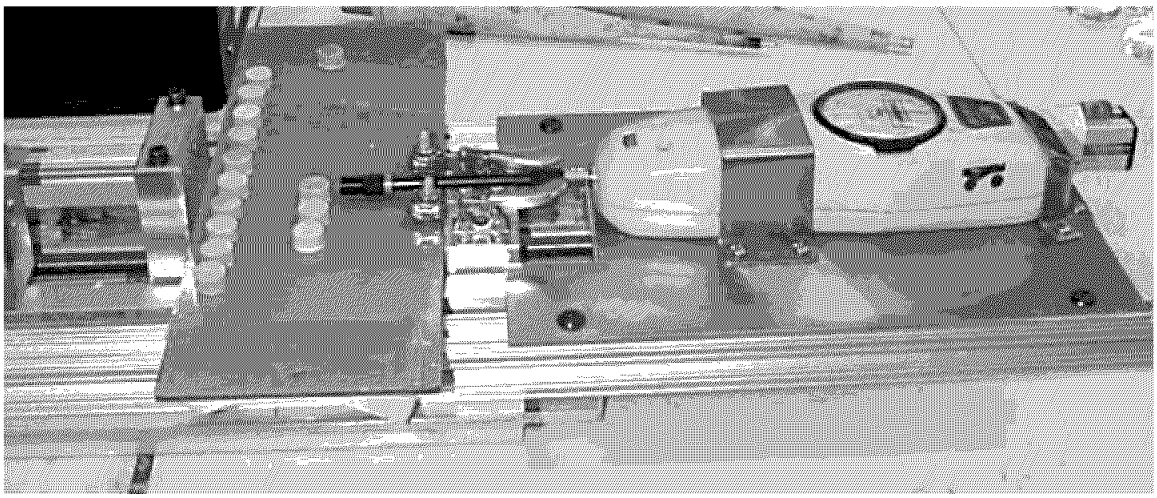
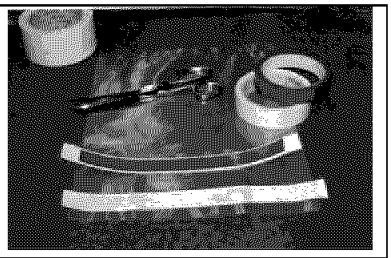
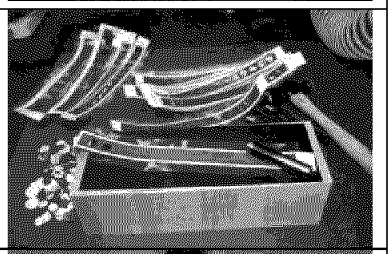
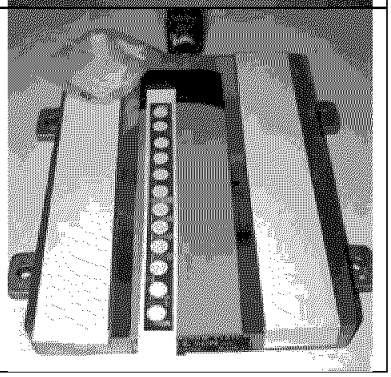
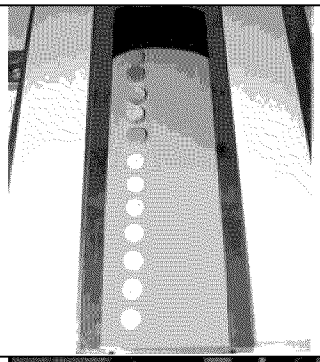
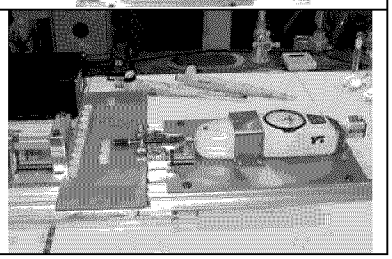


Figure 1.1.1 Pseudobarnacle adhesion tester.

Table 1.1.2. Pseudobarnacle sample preparation.

Step 1. Make tape strips.	
Step 2. Cut holes.	
Step 3. Mix and apply epoxy.	

Step 4. Apply wooden dowels and cure.	
Step 5 Measure adhesion.	

X-ray Photoelectron Spectroscopy (XPS)

The XPS measurements were conducted in a Surface Science Instruments SSX-100 system, employing a monochromatic Al kα source (600μ spot). A fixed pass energy of 150 eV was used for survey scans, and 50 eV for high resolution scans of individual core levels. The surface charging that occurred due to the non-conductive nature of the samples were neutralized with 1-2 eV low energy electrons from an electron flood gun. Atomic compositions were computed from XPS peaks using empirically determined sensitivity factors derived from measurements on standard materials. The C1s signal was curve fit using mixed Gaussian/Lorentzian line shapes. The binding energy of the C 1s signal from the hydrocarbon at 284.6 eV was used as an internal calibration of the absolute binding energy scale.

Pressure Volume Temperature Measurements (PVT)

PVT measurements were performed using the GNOMIX PVT system that employs the bellows-piezometer principle of PVT measurement. The coating (1-2 g) was contained in a rigid sample cell, one end of which was closed by a flexible bellows. The sample was surrounded within the cell by a "sample cup" formed from 0.025 mm nickel film. The space in the sample cell not taken up by the assembly was filled with mercury under vacuum. The sample cell was placed in a pressure vessel. Temperature was maintained constant and pressure was increased up to 200 Mpa. Volume changes in the contents of the sample cell (mercury plus sample) were reflected in an elongation or contraction of the flexible bellows. The length change of the bellows was converted into a volume change of the sample itself, making use of the known cross-sectional area of the bellows and the known PVT properties of the confining mercury. The accuracy of the equipment is +/- 0.002 cm^3/g to 250°C, and 0.004 cm^3/g at higher temperatures, with a sensitivity of better than 0.0005 cm^3/g. Bulk moduli were calculated from the slope of the pressure versus volume strain curve at room temperature.

RESULTS AND DISCUSSION

Condensation Curable Silicone Coatings

In order to quantify the effect of filler loading on organismal detachment strengths, moisture curable silicone networks containing 0% to 29% calcium carbonate were prepared by the reaction of dimethymethylsiloxy endcapped polydimethylsiloxane with tetraethylorthosilicate and the appropriate filler amount using dibutyltinbis(acetylacetonate) as the catalyst. Pseudobarnacle adhesion values were obtained rather than barnacle adhesion values to decrease the standard error in measurement as well as decrease the experimental time and serendipity of barnacle settlement. We confirmed that over large ranges in organismal adhesion, an excellent correlation existed between pseudobarnacle adhesion strength and barnacle adhesion strength ($df = 60$, $p = 0.000$, $R_{Pearson} = 0.885$).

Pseudobarnacle adhesion values were shown to increase as the filler loading increased (Figure 1.1.2, $df = 99$, $p = 0.000$). As the filler loading increased, the tensile strength of the coating also increased; thus, the higher the tensile strength of the coating, the greater the pseudobarnacle adhesion (Figure 1.1.3). Therefore, coatings with the greatest durability and strength will be the least effective in terms of facile removal of fouling organisms.

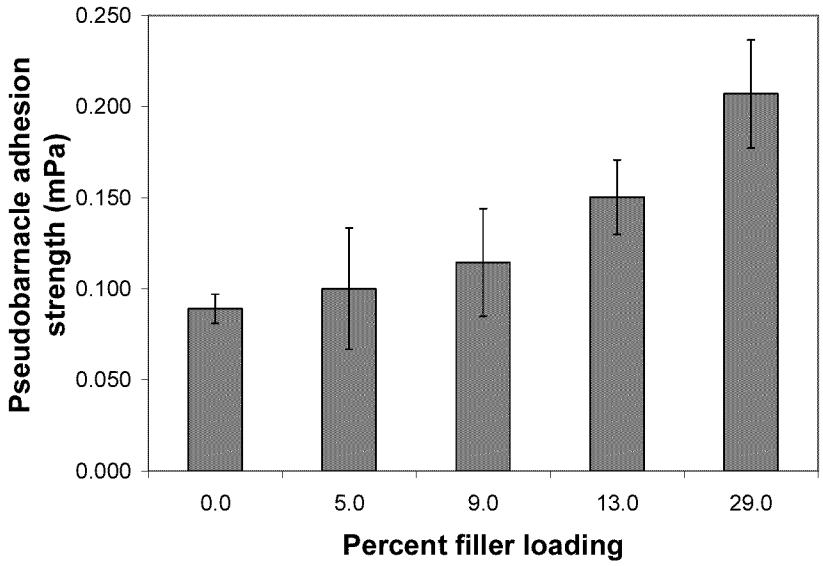


Figure 1.1.2. Effect of filler loading on pseudobarnacle adhesion strength in condensation cured systems ($df = 99$, $p = 0.000$). Error bars represent one standard deviation.

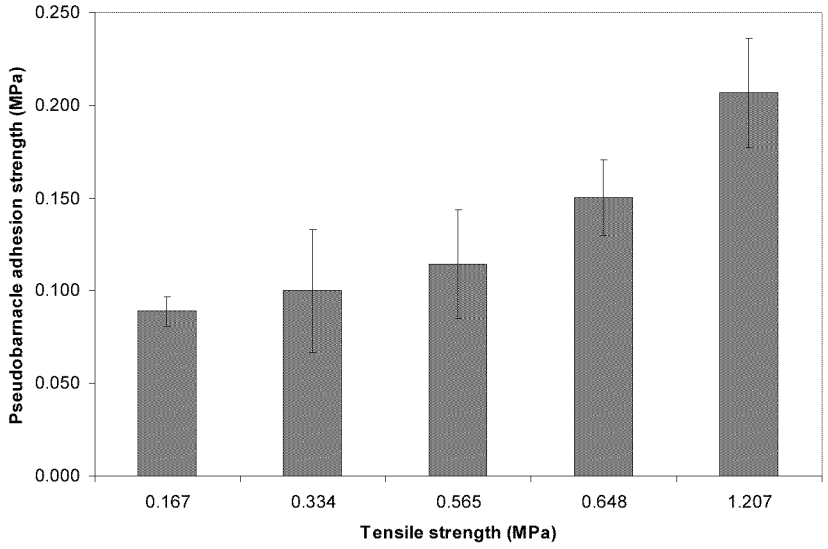
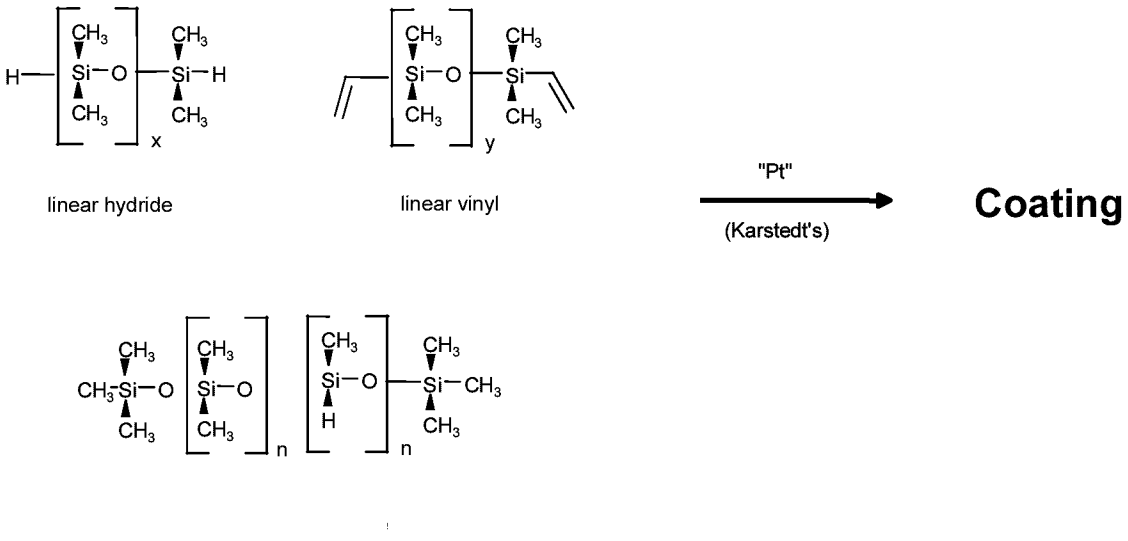


Figure 1.1.3. Correlation of pseudobarnacle adhesion strength with tensile strength of condensation cured silicones (df = 99, p = 0.000). Error bars represent one standard deviation.

Hydrosilylation Cured Silicone Coatings

Hydrosilylation cured silicones have an advantage in that both the filler loading and crosslink density can be controlled. This allows for a complete description of the molecular architecture. Coatings were prepared according to Scheme 1.1.1 in which the ratio of crosslinkable polydimethylmethylhydridesiloxane with multiple hydride groups on the polymer chain and hydride terminated polydimethylsiloxane was varied between 50/50 and 100/0, while the overall ratio of hydride to vinyl groups was maintained at a ratio of 1.2/1. Filler loadings were also varied from 5 to 16% for a composition that contained a 50/50 crosslinker to linear hydride ratio.



Scheme 1.1.1. Hydrosilylation cured model system.

Meyer has suggested that fouling release ability is related to the critical surface tension of the coating[6]. We performed critical surface tension measurements to confirm that the surface energy of the coating did not change upon variation of filler loading in hydrosilylation-cured coatings. No change was observed as the filler level was increased from 5 to 16% (Figure 1.1.4). Surface profiles were also obtained which indicated that filler level had no appreciable effect on surface roughness (Figure 1.1.5).

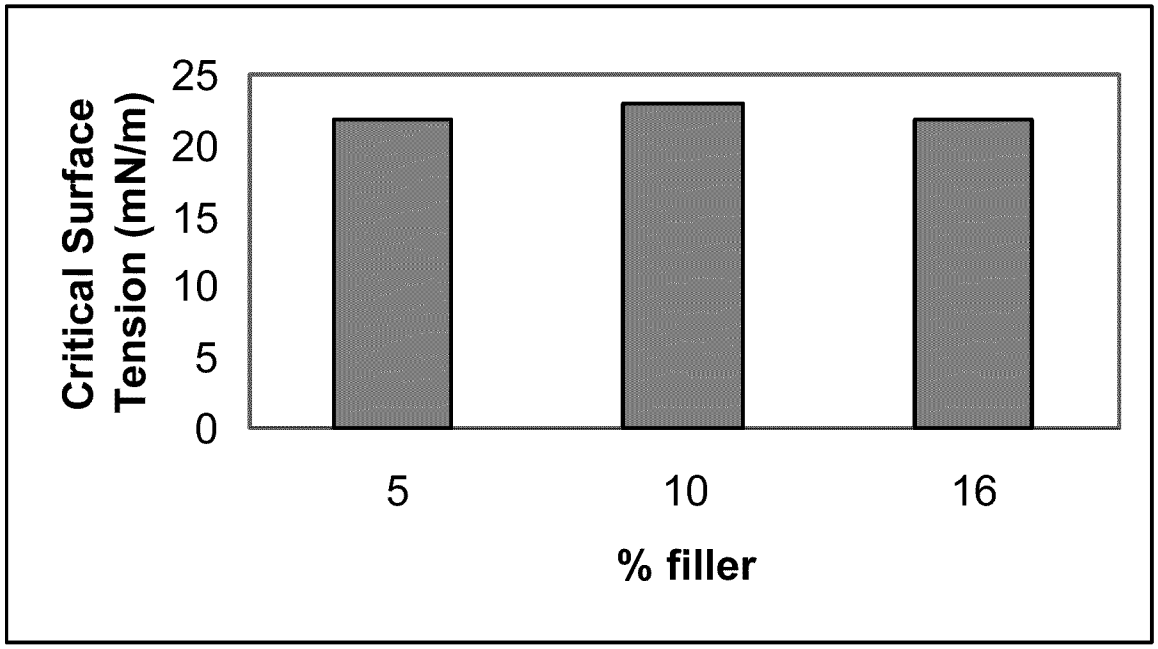


Figure 1.1.4. Effect of filler loading on critical surface tension of hydrosilylation cured silicone coating.

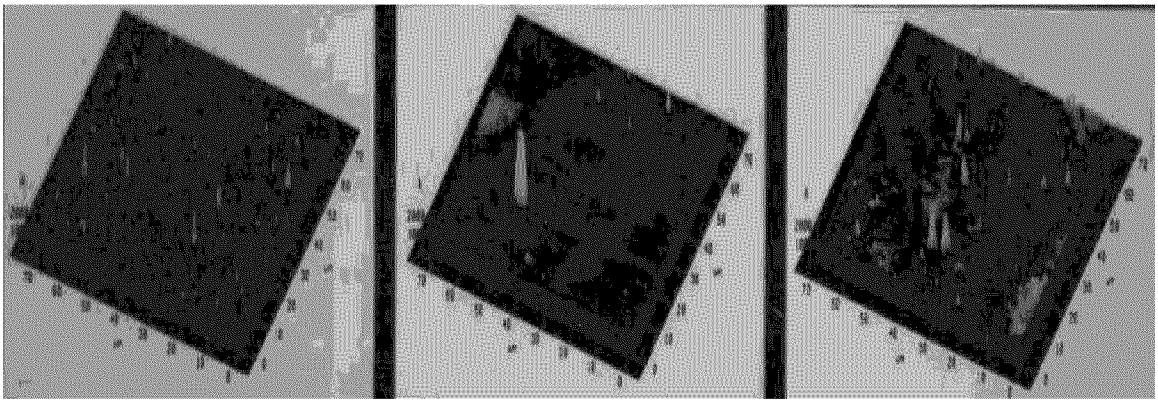


Figure 1.1.5. Effect of filler loading on surface roughness of hydrosilylation cured silicone coatings.

Left) 5% filler, rms roughness = 14 nanometers

Center) 10% filler, rms roughness = 17 nanometers

Right) 16% filler, rms roughness = 19 nanometers

Variation of the filler loading from 5 to 16% led to a systematic increase in the pseudobarnacle attachment strength (Figure 1.1.6, df = 35, p = 0.000). This result is consistent with the result obtained on condensation curable silicones. Unexpectedly, the ratio of crosslinker hydride to linear hydride had no effect on pseudobarnacle adhesion values (Figure 1.1.7, df = 35, p =0.447). The fact that these surfaces have identical critical surface tensions yet exhibit different release implies that other factors beside surface energy are important in defining performance. Bausch and Tonge have suggested that the rheological properties of both the glue and the coating as well as the kinetics of the release process must be considered[2].

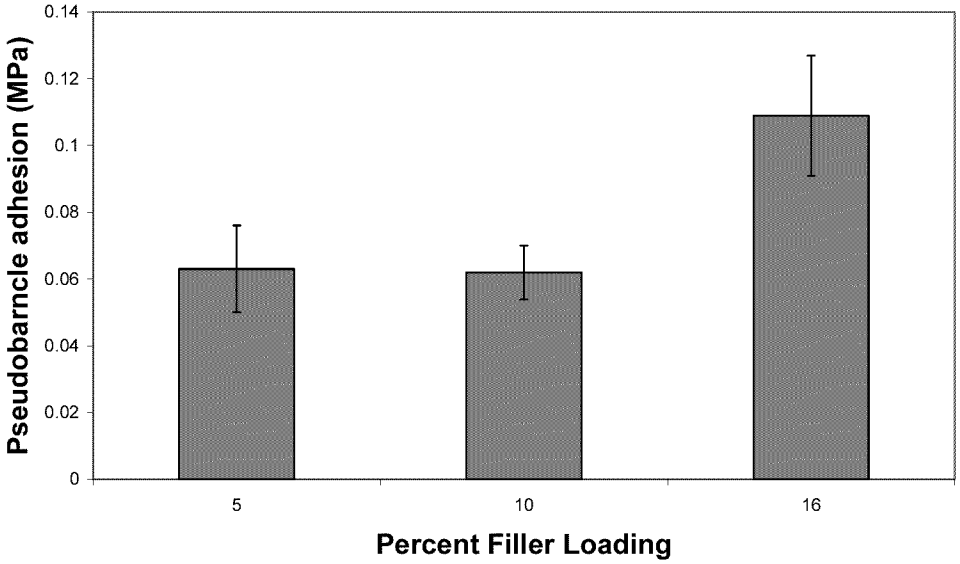


Figure 1.1.6. Effect of filler loading of hydrosilylation cured silicone coating on pseudobarnacle adhesion (df = 35, p= 0.000). Error bars represent one standard deviation.

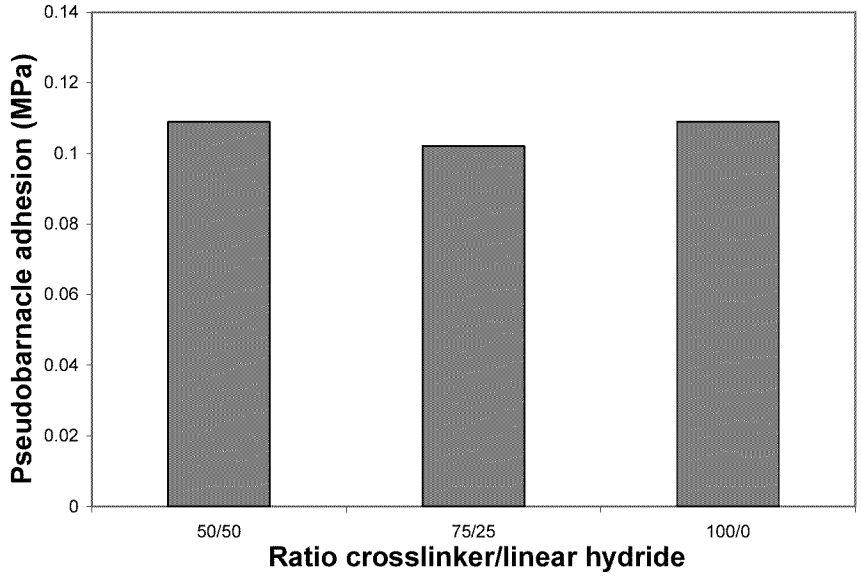


Figure 1.1.7. Effect of crosslink of hydrosilylation cured silicone coatings on pseudobarnacle adhesion (df = 35, p = 0.447). Error bars represent one standard deviation.

Kendall reported that the release performance of elastomers depends on both the surface energy and elastic properties[7]. The equation below was developed to describe the pull off force of a stud bonded to thin elastomeric glue:

$$P_c = \pi a^2 (2\omega_a K/t)^{1/2}$$

Where P_c, t, ω_a, K and a are the critical pull off force, thickness of the coating, work of adhesion, elastomer bulk modulus and contact radius, respectively. Singer has successfully applied the Kendall equation to silicone duplex coatings, where he demonstrated the thickness dependence of the pull off force[8]. According to the Kendall equation, the detachment force of pseudobarnacles from a silicone coating should correlate with the bulk modulus of the coating. As can be seen from Figure 1.1.8, the pseudobarnacle adhesion strength increases significantly with increasing bulk modulus ($R_{pearson}$ = 0.881, p = 0.48).

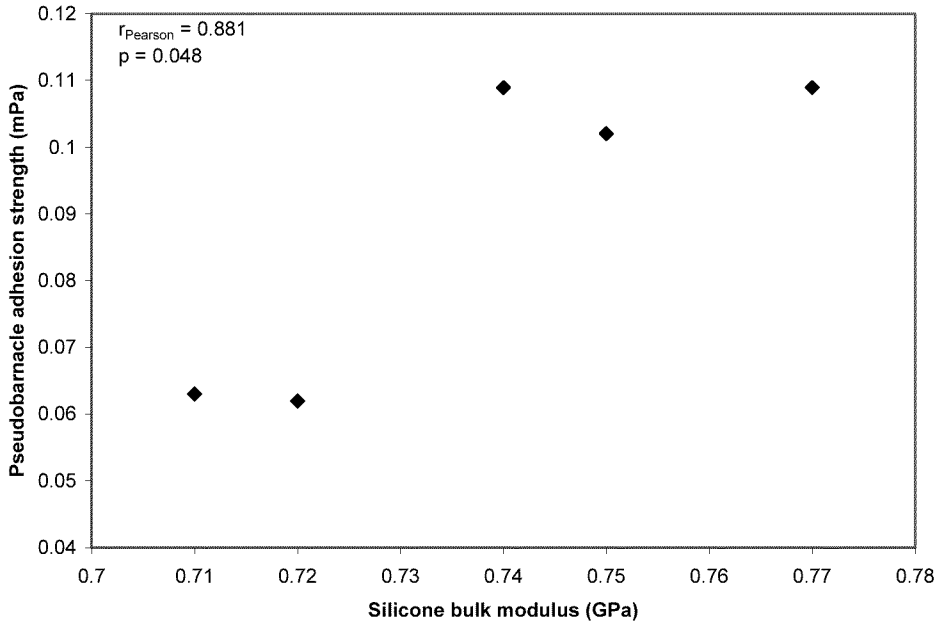


Figure 1.1.8. Correlation between calculated bulk modulus of hydrosilylation cured silicone and pseudobarnacle adhesion strength.

Gatenholm has reported that small amounts of uncrosslinked silicone from both hydrosilylation and condensation-cured silicones are transferred to the pseudobarnacles upon detachment from the surfaces[9]. We have examined the failure mode in our hydrosilylation cured systems using XPS (Table 1.1.3). Transfer of silicone to the pseudobarnacles is small at all filler loadings, at a constant crosslinker hydride to linear hydride ratio of 50/50. However, the amount of silicone on the pseudobarnacle increases as the crosslinker hydride to linear hydride ratio increases at constant filler loading. At 100% crosslinker hydride, the failure mode is certainly cohesive within the silicone since the amount of silicon present on the pseudobarnacle surface is equivalent to the atomic composition of the silicone (21%). This implies a change in fracture mechanism is a function of crosslink density.

Table 1.1.3. Effect of silicone architecture of hydrosilylation cured coatings on the failure mode in pseudobarnacle adhesion tests.

Filler loading	Crosslinker/linear hydride ratio	Pseudobarnacle adhesion strength (mPa)	% Si (XPS)
5	50/50	0.063+/- 0.013	6.7
10	50/50	0.062+/- 0.008	4.8
16	50/50	0.109+/- 0.018	8.6
16	75/25	0.102+/- 0.013	12.4
16	100/0	0.109+/- 0.017	21.8

Barnacle adhesion strength was also measured on the hydrosilylation cured model system coatings. Trends were similar for both barnacles and pseudobarnacles. Barnacle adhesion strength was lowest on coatings with low filler loading ($df = 17$, $p < 0.05$) which mirrors the trend found with psuedobarnacles (Figure 1.1.9). As found with pseudobarnacles, crosslink density had no effect on barnacle attachment strength ($df = 17$, $p > 0.05$; (Figure 1.1.10.).

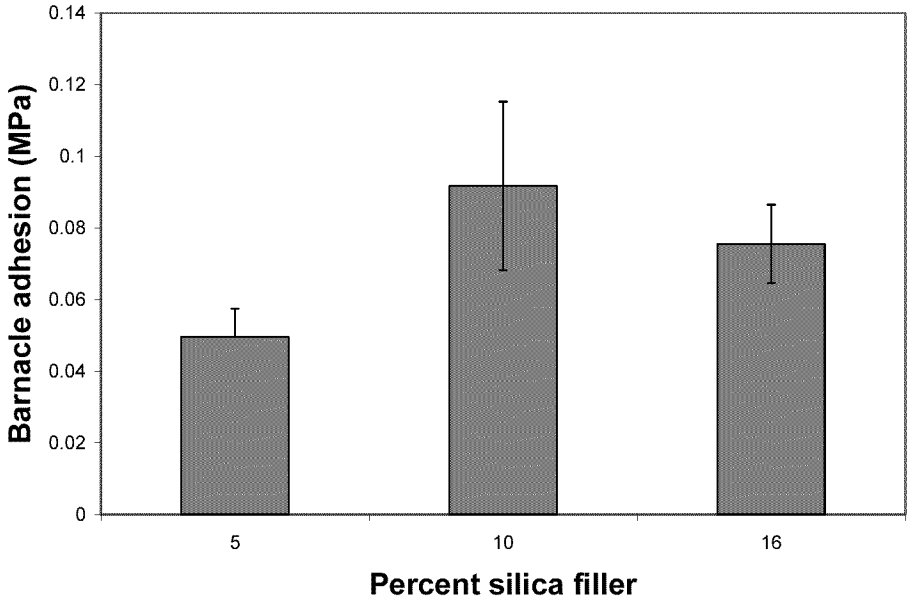


Figure 1.1.9. Effect of filler loading on barnacle attachment strength.

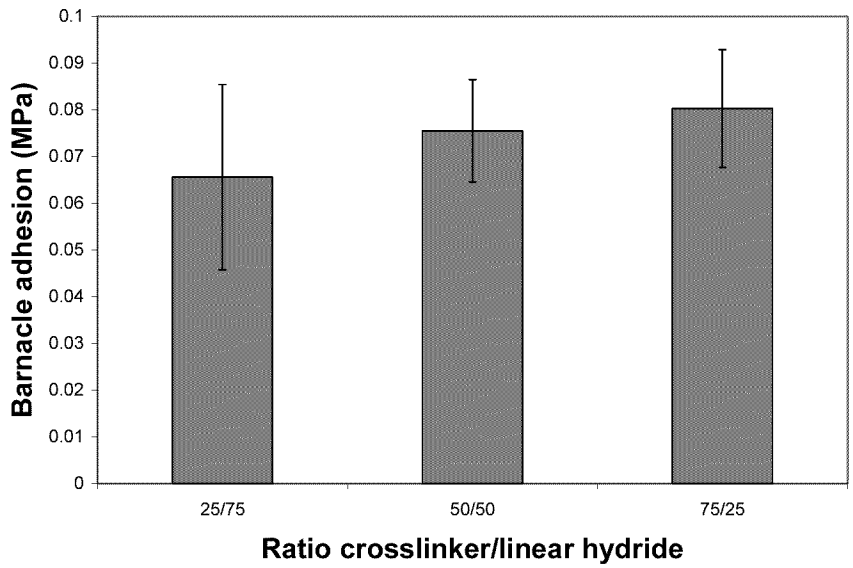


Figure 1.1.10. Effect of crosslink density on barnacle attachment strength.

Studies of model silicone coatings have provided data that suggest that coatings with lower filler loadings will have better fouling release properties than those with higher filler levels. This result is independent of filler type (silica or calcium carbonate). Unfortunately, the most durable coatings contain high filler loadings. Crosslink density had an insignificant effect on attachment strengths of pseudobarnacles, but did change the failure mechanism, suggesting that lower crosslink densities are preferred for durable coatings. These results suggest a trade-off between mechanical integrity of the coatings and foul-release performance.

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SECTION 1.2 SCREENING EXPERIMENTS

In the previous section, we reported the relationship between crosslink density and filler loading of silicone coatings and fouling release performance. We found an inverse correlation between foul-release performance and filler loading. However, physical properties were enhanced by addition of filler. Therefore, the best foul-release coatings had the lowest durability. One way to increase foul release performance without compromising properties is by incorporation of oil into the silicone coating. We therefore performed screening experiments in which oil was incorporated into the silicone coatings. The factors in the experimental design included: oil type, oil loading level, oil molecular weight, location of the oil, coating matrix type, filler level, oil encapsulation, and biocide enhancement. Of the numerous manipulations of oil type, location, loading, molecular weight, filler type, and biocidal enhancement, only two treatments reduced barnacle adhesion strength by practically significant levels [greater than 50%]. These reductions were mainly due to the effect of the oil type and it's interaction with the coating base.

INTRODUCTION

Incorporation of oil into foul release coatings has been shown to reduce organismal coverage and adhesion strength[1]. To date, no one has reported on the effect of oil composition on organismal adhesion. We therefore performed a number of design experiments in which we systematically varied the oil type, the oil level, and oil encapsulation (+/-). In addition, we examined the effect of supplementary filler types on performance to see if we could moderate oil release by their incorporation. The effect of biocides on barnacle adhesion strength was also probed. The complete screening matrix is given in Table 1.2.10. Further elaboration of the effect of tethering the oil to the coating matrix to inhibit depletion is provided in Appendix 1.

EXPERIMENTAL

Panel Preparation

Oils were obtained from either GE Silicones or Gelest (Tullytown, PA). GE Silicones provided base compositions. Aluminum panels were obtained from the Q-Panel Company. Sea-nine 211 was obtained from Rohm and Hass. Irgarol 1051 was obtained from Ciba-Geigy. Encapsulated oils were obtained from Microteck. Fillers were obtained from Aldrich Chemical Company.

One hundred and thirty silicone panels were painted on one side of 100 mm x 400 mm aluminum panels. The coating was based on the duplex technology developed by James Griffith at the Naval Research Laboratory (U.S. Patent 5,449,553). Topcoats were placed over a tiecoat of Wacker J501 silicone. Formulations were based on the following three silicone matrices RTV11®, silica filled base (*vida infra*) and RTV511. Oils were incorporated into the topcoat or tiecoat. Silicone oil additives were held to 10% by weight (unless otherwise specified).

FIT Panel Testing

Panels were attached to PVC frames and suspended from a fixed platform approximately 1 m below the water surface in the Indian River Lagoon, Florida. Panels were held within cages constructed of 25.4 mm mesh to prevent removal of attached organisms by predation.

Test coatings were initially exposed to fouling in January, 1997. Measurements of hard fouling (barnacle, oysters and tubeworms) and shear adhesion strength were taken as fouling permitted. When possible, at least 18 adhesion measurements were made per panel. The adhesion measurements were based on procedures outlined in ASTM D5618-94, "Standard Test Method for Measurement of Barnacle Adhesion Strength in Shear". Measurements were made on live individuals with basal areas ranging between 20 – 250 mm^2. A hand-held force gauge was used to apply a force parallel to the attachment plane of the organism at a rate of approximately 4.5 Ns^{-1} (1.8 cms^{-1}) until it was removed from the surface. The force required to detach an organism was recorded, and the individuals collected and taken to the laboratory. Attachment area was determined by one of two methods. Either diameter measurements were taken with digital calipers in four directions, the average diameter calculated, and the basal area calculated from $A = 4\pi D$. Or, the base of the individual was scanned and the image analyzed with SigmaScan® software. Pixel to area determination was based on a three-point calibration, and computations were validated by inclusion of an object of known dimension with each data set analyzed. Adhesive shear strength, τ, was calculated by dividing shear force, F, required to remove the organism by the surface area, A, of attachment ($\tau = F/A$).

Data Analyses

The adhesion strength data were statistically analyzed using analysis of variance (ANOVA). In most cases, a two-way ANOVA was performed, followed by Tukey's multiple pairwise comparison tests for significance. In some cases, a one-way ANOVA was performed. In all cases, α was set at 0.01. Data were transformed by the square root of the original value to meet homogeneity of variance and normality assumptions for the analyses. All results are presented as transformed adhesion strength data $(MPa)^{1/2}$. Results are the pooled data from all sampling dates.

RESULTS

Comparison of Oil Type and Oil Incorporation Site

Table 1.2.1 Comparison of oil type and oil incorporation site(tiecoat or topcoat).

Treatment	Coating Additive Description
None	Unmodified RTV11® or silica filled base
SF1147	Decylmethylsiloxane
DMSC15	Carbinol (hydroxyl) terminated polydimethylsiloxane
FMS123	Poly-3, 3, 3-trifluoropropylmethylsiloxane
PS406	Polydimethylsiloxane methacryloxypropyl T-structure branch points
PS563	Polydimethylsiloxane carboxypropyldimethyl terminated, 2000cs
PS835	80-90% Dimethyl (10-20%)-(hydroxyalkylene oxide) methylsiloxane

Seven coating treatments were compared to analyze the effects of oil type and oil location on barnacle adhesion strength (Table and Figure 1.2.1). The effects of additive type and additive location were both statistically significant ($p = 0.007$ and $p < 0.001$, respectively). A significant interaction ($p < 0.001$) was observed between additive type and the location of incorporation, and the strength of barnacle adhesion. Addition of DMSC15 to the RTV11® tiecoat resulted in a lower barnacle adhesion strength than all other oils, except when PS835 was present in the tiecoat of RTV11®, and when SF1147 was incorporated into the topcoat of the silica filled base. The barnacle adhesion strength with the additive SF1147 was lower than formulations with no additives (FMS123, PS406, PS563, and PS835) incorporated into the topcoats of RTV11® or the silica filled base. However, barnacle adhesion differed when SF1147 was present in the RTV11® tiecoat. Barnacle adhesion strength on panels with SF1147 in the RTV11® tiecoat was statistically indistinguishable from treatments incorporating the majority of additives (FMS123, PS406 and PS563). However, when the additive PS835 was incorporated, barnacle adhesion was significantly lower." No significant difference in barnacle adhesion was observed on coatings with no additive, or with the additives FMS123, PS406, PS563, and PS835 incorporated into the RTV11® topcoat and the silica filled base. The location of the oil matrix within additive types also affects barnacle adhesion strength. No differences were apparent for formulations with no additive, or with the additives FMS123 and PS406. However, addition of DMSC15 to the RTV11® tiecoat resulted in the lowest barnacle adhesion strength. Adhesion was significantly lower than when DMSC15 was added to the tiecoat or the topcoat of the silica filled base. Alternatively, barnacle adhesion strength with the additive PS563 was significantly lower when it was added to the tiecoat compared to addition in the topcoat of RTV11®. With the additive PS835, barnacle adhesion strength was also lower when additions were made to the tiecoat of RTV11®, and were significantly lower than additions to the topcoat of both RTV11® and the silica filled base. In contrast, additions of SF1147 produced the opposite effect on barnacle adhesion strength, revealing significantly higher values when the oil was added to the tiecoat of RTV11® compared to addition to the topcoat of either RTV11® or the silica filled base.

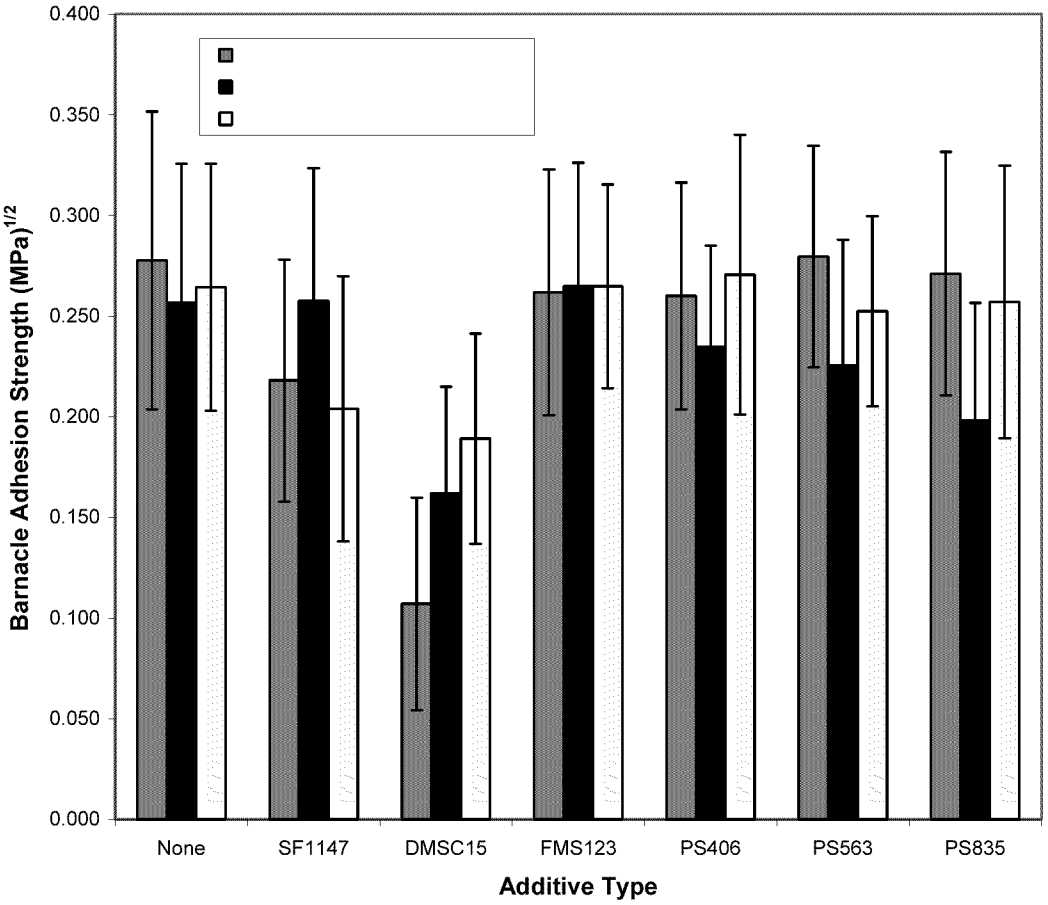


Figure 1.2.1 Comparison of barnacle adhesion strength to panels with various oil types added to several matrix locations of silicone coatings. Data are presented as transformed values [$(MPa)^{1/2}$]. Error bars represent one standard deviation.

Comparison of Matrix Type and Oil Type

Table 1.2.2 Comparison of matrix type and oil type (located in topcoat).

Treatment	Coating Additive Description
None	Unmodified Duplex RTV11® or RTV511
DBE224	Dimethylsiloxane-ethylene oxide block copolymer
DMSC15	Carbinol (hydroxyl) terminated polydimethylsiloxane
DMSC25	Carbinol (hydroxyl) terminated polydimethylsiloxane, 60% non-siloxane
SF1154	Polydiphenyldimethylpolysiloxane

The barnacle adhesion strength to two RTV silicone coatings with varying additive types was compared with a two way ANOVA. The main effect of oil type was found to be significant ($p <$

0.001). All coatings with additives were significantly lower in barnacle adhesion strength than unmodified coatings. Barnacle adhesion strength on DMSC15 modified coatings was significantly lower than on coatings with any other oil. The interaction effect of matrix and. oil type was also significant ($p < 0.001$). Barnacle adhesion strength did not differ between the RTV11® and RTV511 coating types in some instances (unmodified, DBE224 and DMSC15 coatings). However, adhesion strength was significantly lower on RTV11® than on RTV511 with addition of DMSC25, while it was significantly lower on RTV511 than RTV11® with the addition of SF1154 (Table 1.2.2 and Figure. 1.2.2).

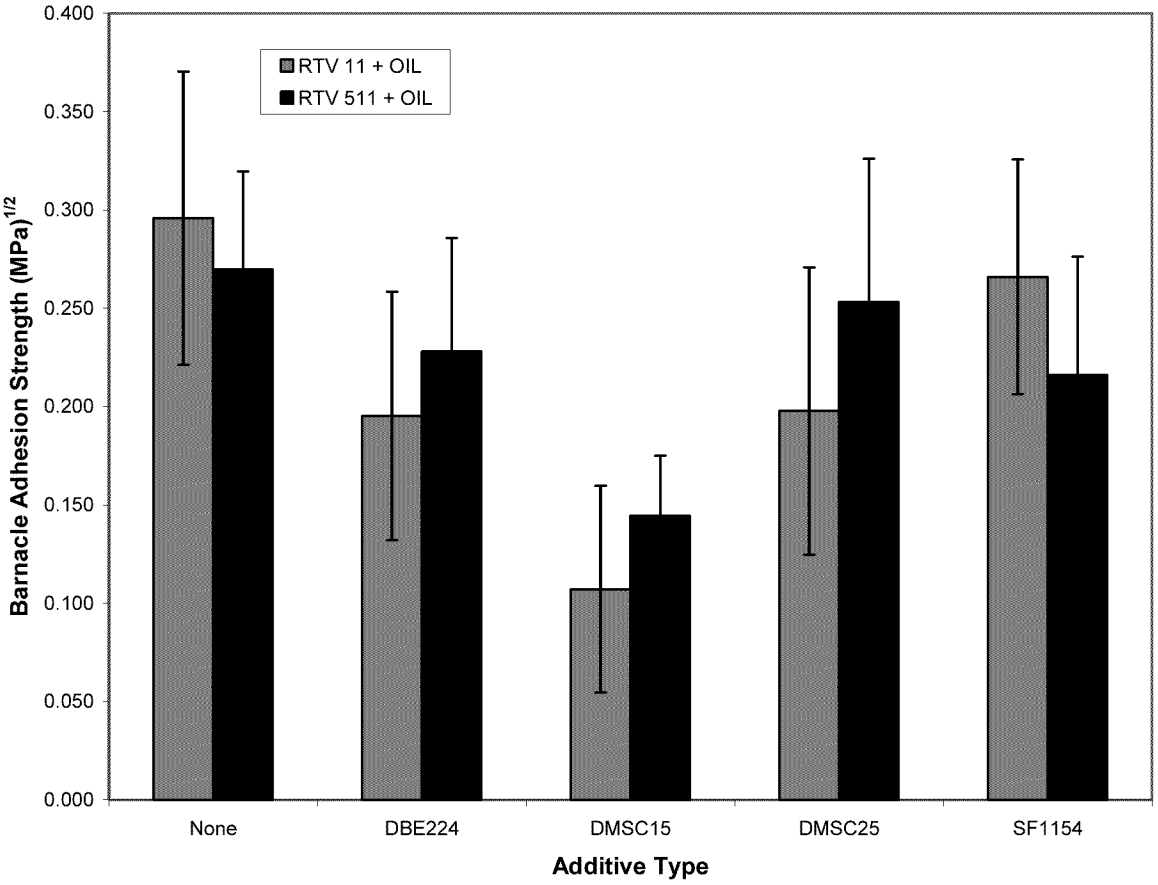


Figure 1.2.2 Comparison of barnacle adhesion strength to two different RTV silicone coatings with various oil types. Data are presented as transformed values [$(MPa)^{1/2}$]. Error bars represent one standard deviation.

Comparison of Oil Molecular Weight and Oil Incorporation Site

Table 1.2.3. Comparison of oil molecular weight and oil incorporation site (tiecoat or topcoat).

Treatment	**Coating Additive Description**
None	Unmodified Duplex RTV11® or Silica filled base
PDV0325	3.0-3.5% Diphenylsiloxane dimethylsiloxane copolymer, MW = 15,500
PDV0331	3.0-3.5% Diphenylsiloxane dimethylsiloxane copolymer, MW = 27,000
PDV0341	3.0-3.5% Diphenylsiloxane dimethylsiloxane copolymer, MW = 62,000

A polydimethyldiphenyl siloxane additive was selected to test the effect of changes in additive molecular weight on barnacle adhesion strength. The molar content of diphenylsiloxane was held constant in the treatments at 3.0 - 3.5%. Additives were placed in three matrix locations: topcoat of RTV11®, tiecoat of RTV11®, and the topcoat of silica filled base. A significant interaction was found among additive treatments and the site of incorporation. Additions of PDV0341 resulted in a lower barnacle adhesion strength when located in the tiecoat of RTV11® and the topcoat of silica filled base, than when present in the topcoat of RTV11® (Table 1.2.3 and Figure. 1.2.3). Within the topcoat of the silica filled base, the PDV0341 additive (the highest molecular weight treatment) showed significantly lower barnacle adhesion strength than the silica filled base coating without additive. No differences were observed when additives were present in the RTV11® topcoat.

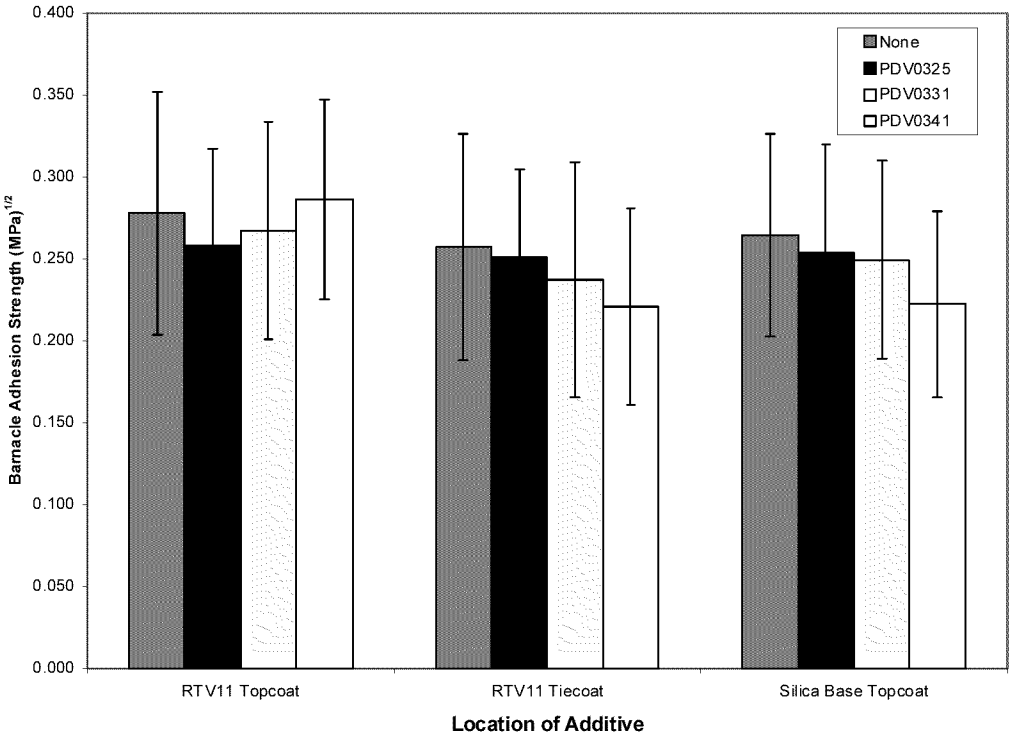


Figure 1.2.3. Comparison of barnacle adhesion strength for polydiphenyldimethylsiloxane oils of different molecular weights. Data are presented as transformed values [$(MPa)^{1/2}$]. Error bars represent one standard deviation.

Comparison of Loading Level and Oil Incorporation Site

Table 1.2.4 Comparison of oil loading level and oil incorporation site (tiecoat or topcoat).

Treatment	**Coating Additive Description**
None	Unmodified Duplex RTV11® or Silica filled base
10% SF1154	10% Diphenyldimethylpolysiloxane
20% SF1154	20% Diphenyldimethylpolysiloxane
30% SF1154	30% Diphenyldimethylpolysiloxane

Three loading levels (10, 20, and 30% by weight) of the SF1154 additive were incorporated within the topcoat of RTV11®, the tiecoat of RTV11®, and the topcoat of the silica filled base. Both the main effects of loading level and location were significant in a two-way ANOVA ($p = 0.006$ and $p < 0.001$, respectively); however, the interaction term was not. In pairwise comparisons, the 30% loading of SF1154 was found to produce barnacle adhesion strengths that were significantly lower than with unmodified coatings. In relation to location, additives to the

silica filled base topcoat had lower barnacle adhesion than additives to the RTV11® topcoat (Table 1.2.4 and Figure. 1.2.4).

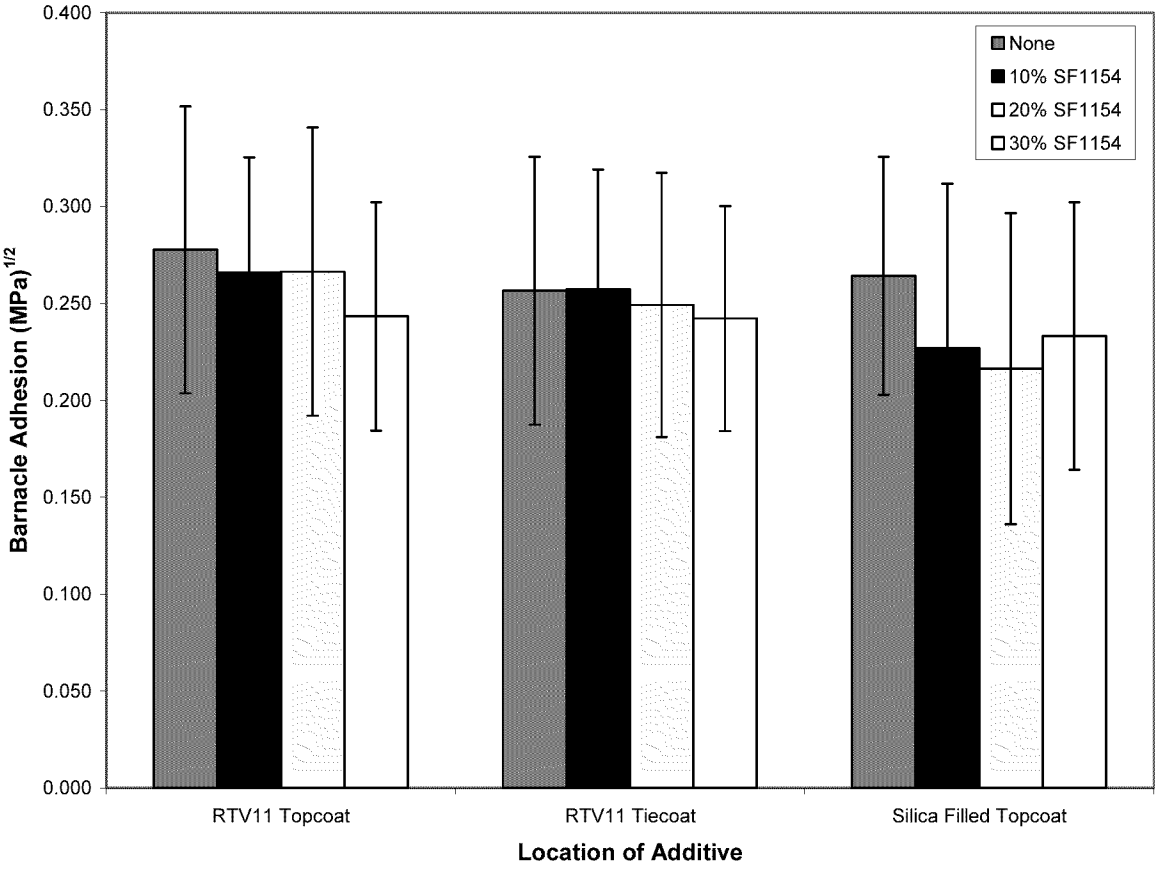


Figure 1.2.4 Comparison of barnacle adhesion strength to panels containing varying levels of oil loading (10, 20, and 30 % SF1154). Data are presented as transformed values [$(MPa)^{1/2}$]. Error bars represent one standard deviation.

Comparison of Filler Type and Base Composition

Table 1.2.5 Comparison of filler type and base composition.

Treatment	Coating Additive Description
None	Duplex RTV11® or Silica filled base plus 10% SF1154
Talc	Duplex RTV11® or Silica filled base plus 10% SF1154 + Talc filler
Resin	Duplex RTV11® or Silica filled base plus 10% SF1154 + Resin filler
Alumina	Duplex RTV11® or Silica filled base plus 10% SF1154 + Alumina filler

Graphite	Duplex RTV11® or Silica filled base plus 10% SF1154 + Graphite filler
Carbon Black	Duplex RTV11® or Silica filled base plus 10% SF1154 + Carbon black filler

The effect of five different filler types on the barnacle adhesion strength on RTV11® compositions and silica filled base containing 10% SF1154 in the topcoat were examined in a two-way ANOVA. The main effects of filler type and coating type were significant ($p < 0.001$). The interaction term was not significant. Pairwise comparisons indicated increased barnacle adhesion strength on coatings containing resin filler compared to coatings with no additional filler and talc filler. Barnacle adhesion strength was consistently lower on the silica filled base topcoat than the RTV11® topcoat (Table 1.2.5 and Figure. 1.2.5).

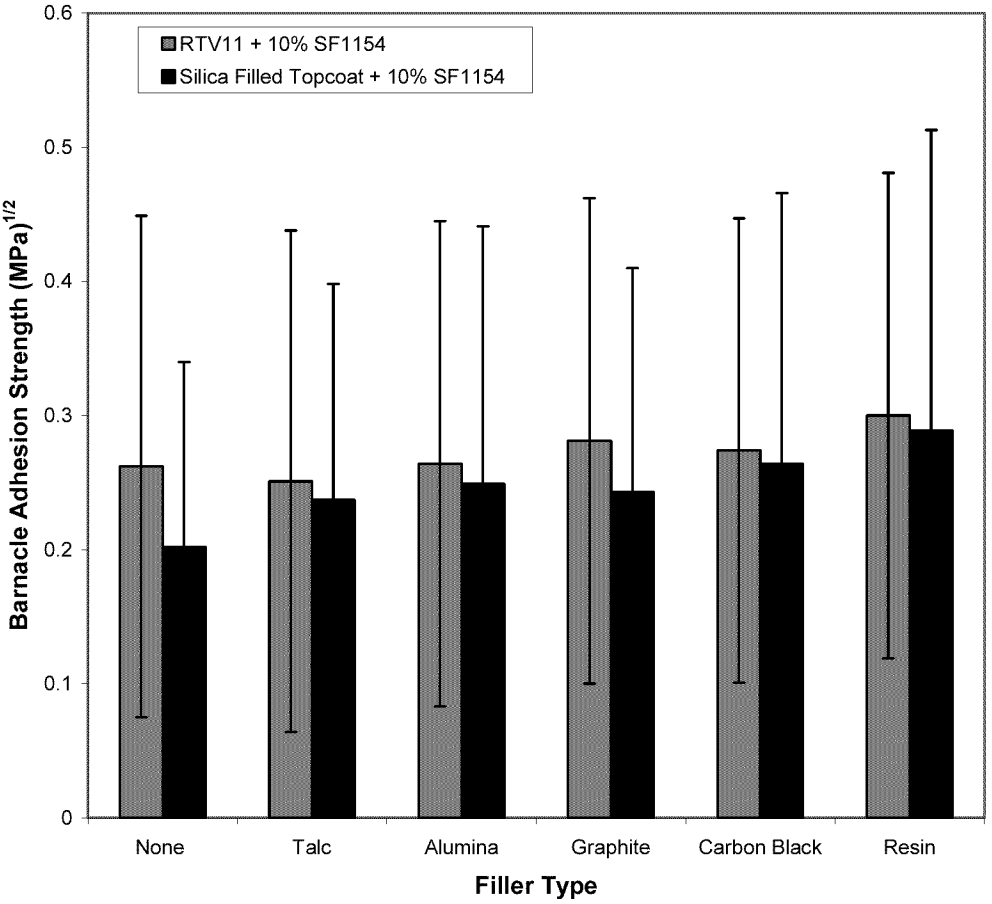


Figure 1.2.5 Comparison of barnacle adhesion strength to panels containing varying filler types in the topcoat of RTV11 and silica filled base. All topcoats contained 10% SF1154. Data are presented as transformed values [$(MPa)^{1/2}$]. Error bars represent one standard deviation.

Comparison of Encapsulant Type and Loading Level

Table 1.2.6 Comparison of encapsulant type and oil loading level.

Treatment	Coating Additive Description
None	Duplex RTV11® or Silica filled base plus SF1154 at 10, 20 or 30% by weight
A	Duplex RTV11® or Silica filled base plus SF1154 in A capsules
B	Duplex RTV11® or Silica filled base plus SF1154 in B capsules
C	Duplex RTV11® or Silica filled base plus SF1154 in C capsules
10	Duplex RTV11® or Silica filled base plus 10% SF1154
20	Duplex RTV11® or Silica filled base plus 20% SF1154
30	Duplex RTV11® or Silica filled base plus 30% SF1154

The effect of incorporating SF1154 oil in controlled-release capsules (in RTV11® coatings) on the adhesion strength of barnacles was analyzed with a two-way ANOVA (Table 1.2.6 and Figure 1.2.6). The main effects of capsule type and loading level were significant ($p < 0.001$ and $p = 0.003$, respectively). The capsule type and. loading level interaction was statistically significant ($p < 0.001$). Capsule A treatments did not differ from unencapsulated SF1154 in terms of barnacle adhesion strength. Capsule types B and C were higher in adhesion strength than capsule type A at the 30% and 10% SF1154 loading levels, respectively. No differences were seen among capsule types at the 20% loading level.

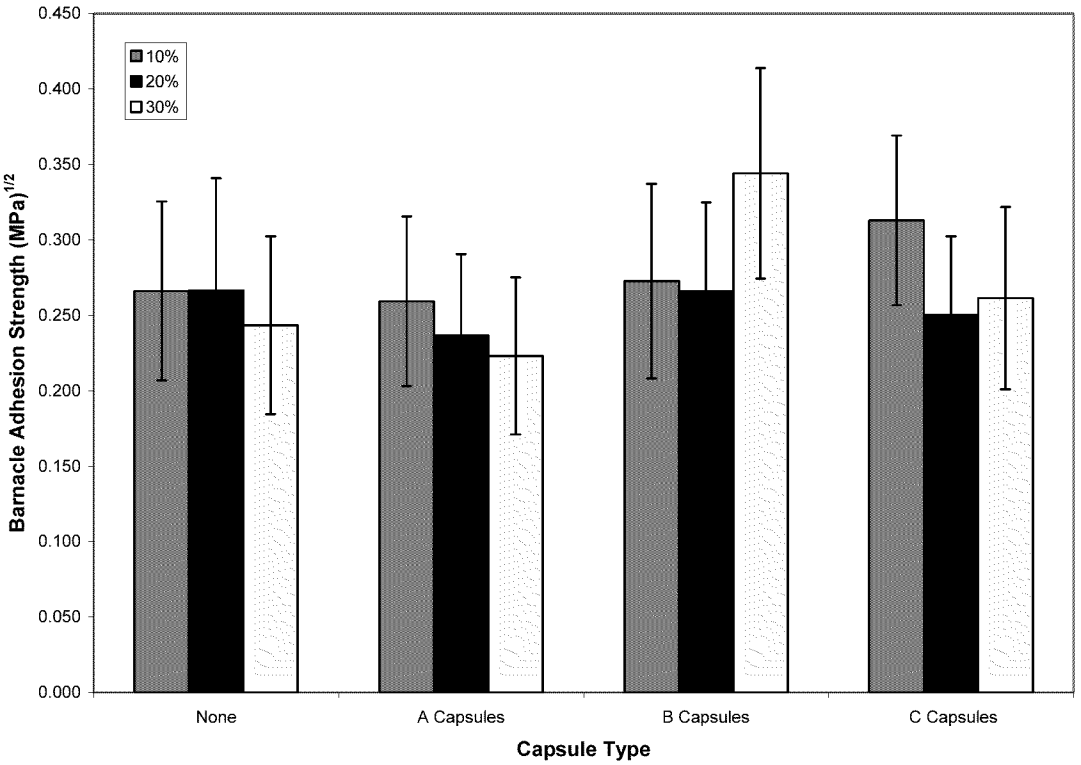


Figure 1.2.6 Comparison of barnacle adhesion strength to panels containing varying loading levels of encapsulated SF1154 in the topcoat of RTV11®. Data are presented as transformed values [$(MPa)^{1/2}$]. Error bars represent one standard deviation.

Effect of Additive Mixtures

Table 1.2.7 Comparison of mixtures of oils.

Treatment	**Coating Additive Description**
None	Unmodified Duplex RTV11®
SF1154	10% Diphenyldimethylpolysiloxane
DBE224	10% Dimethylsiloxane-ethylene oxide block copolymer
DMSC15	10% Carbinol (hydroxyl) terminated polydimethylsiloxane
SF1154 + DBE224	5% by weight of each oil type
SF1154 + DMSC15	5% by weight of each oil type

The effect of mixtures of oils on barnacle adhesion strength was analyzed with a one-way ANOVA. Comparisons were made among coatings with pure additions of SF1154, DBE224, and DMSC15, and equal mixtures of SF1154 and the other oils. The total content of oil was held to 10% by weight in all cases. A significant difference was seen among treatments ($p < 0.001$). A pairwise comparison test (Tukey's) of means revealed no significant difference between RTV11® and RTV11® + 10% SF1154. Coatings with additions of DBE 224 were significantly lower than these treatments. Barnacle adhesion strength on the 10% DMSC15 coating was still lower. Adhesion on the coating formulation containing a mixture of 5% DMSC15 + 5% SF1154 was intermediate between the DBE224 and DMSC15 treatments (Table 1.2.7 and Figure. 1.2.7).

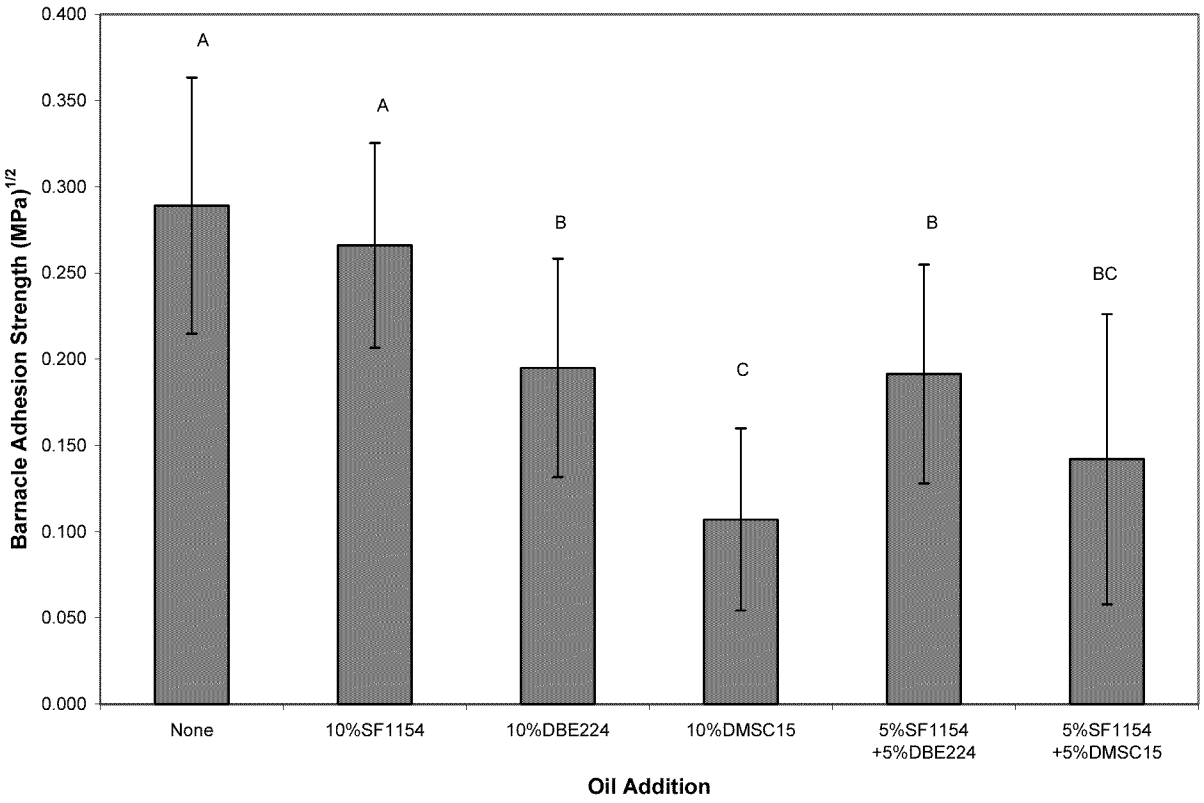


Figure 1.2.7 Comparison of barnacle adhesion strength to RTV11® coatings with mixtures of oils. Data are presented as transformed values [$(MPa)^{½}$]. Error bars represent one standard deviation.

Effect of Biocide Additives

Table 1.2.8 Comparison of biocide additives.

Treatment	**Coating Additive Description**
None	Unmodified Duplex RTV11®
Treatment A	10% DMSC15 in topcoat
Treatment B	10% DMSC15 in tiecoat
Treatment + Irgarol 1051	10% DMSC15 + 10% biocide by weight in topcoat or tiecoat
Treatment + Sea-Nine 211	10% DMSC15 + 10% biocide by weight in topcoat or tiecoat

The effect of addition of biocides to RTV11® coatings with oil treatment A (10% DMSC15 in the topcoat) or B (10% DMSC15 in the tiecoat) on barnacle and oyster adhesion strength was analyzed with a two-way ANOVA. A significant difference was seen for both the main effects, organism type and coating type ($p < 0.001$). A Tukey's pairwise comparison test of means

revealed a significant difference between barnacle and oyster adhesion strength. Oyster adhesion strength was higher than barnacle adhesion strength in all treatments (Table 1.2.8 and Figure. 1.2.8). Adhesion strength was higher on RTV11® than on all coatings with oil and biocide additions. Incorporation of biocides to coatings with 10% DMSC 15 did not differ from those containing DMSC 15 alone. Adhesion strengths of either organism did not change when additions were made to the topcoat *vs.* the tiecoat for each oil.

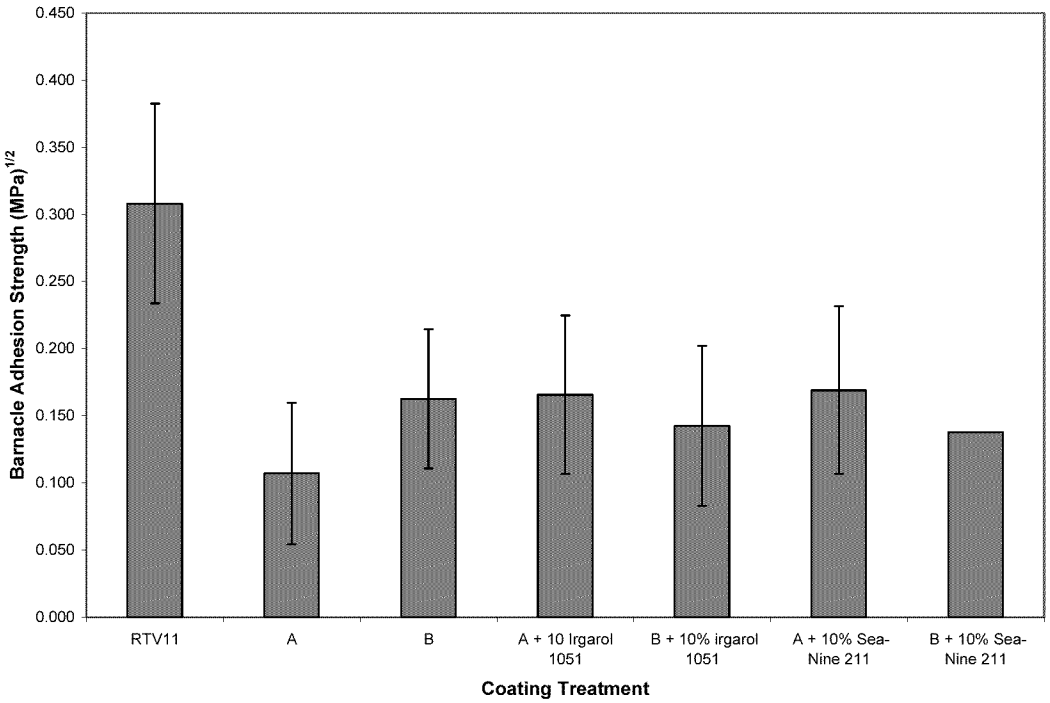


Figure 1.2.8 Comparison of adhesion strength of barnacles and oysters to RTV11® coatings with DMSC15 and biocides in the topcoat and the tiecoat. Data are presented as transformed values [$(MPa)^{1/2}$]. Error bars represent one standard deviation.

Effect of Oil Addition to Epoxy

Table1.2. 9 Comparison of oil addition to epoxy coatings.

Treatment	**Coating Additive Description**
None	Unmodified epoxy
SF1154	Epoxy + 10% Diphenyldimethylpolysiloxane
DMSC15	Epoxy + 10% Carbinol (hydroxyl) terminated polydimethylsiloxane

The effect of addition of oils to epoxy on barnacle adhesion was analyzed with a one-way ANOVA. A significant difference was seen among treatments ($p = 0.006$). A Tukey's pairwise comparison of means revealed a significant differences between epoxy and epoxy + 10% DMSC

15 (Table 1.2.9 and Figure. 1.2.9). Barnacle adhesion strength on all treatments was approximately an order of magnitude greater than on comparable treatments of RTV11®.

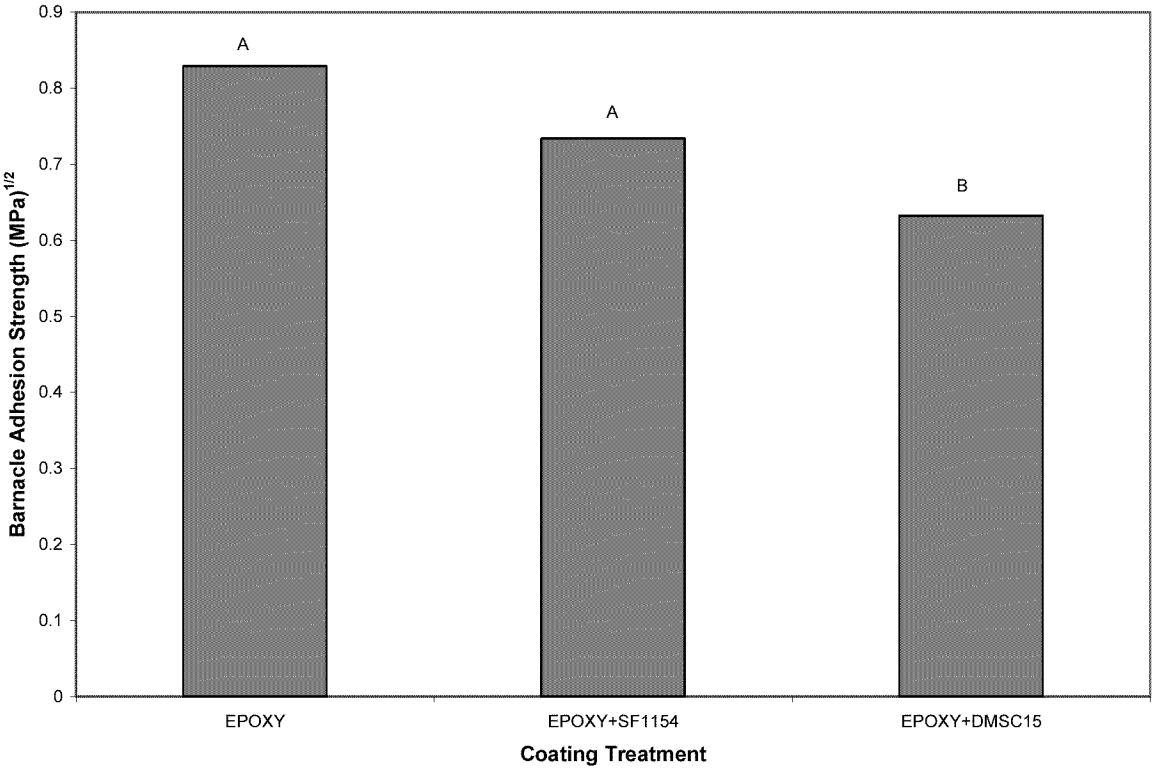


Figure 1.2.9 Comparison of barnacle adhesion strength to epoxy coatings with varying oil additions. Data are presented as transformed values [$(MPa)^{1/2}$]. Error bars represent one standard deviation.

DISCUSSION

Comparison of Oil Type and Oil Incorporation Site

The comparison of barnacle adhesion strength on 7 PDMS silicone formulations with varying silicone oil additives in 3 different silicone matrix locations revealed outstanding results for one specific oil type. Barnacle adhesion was reduced on coatings containing DMSC15, a carbinol-terminated polydimethylsiloxane, compared to unmodified coatings and coatings containing other oils. Most other formulations with oil additives did not differ in barnacle adhesion strength from the unmodified controls. Results for treatments that did show differences compared to the unmodified controls inconsistent based on the site of incorporation of the additive. For example, PS563 and PS835, both dimethylsiloxanes, showed reduced barnacle adhesion when incorporated into the tiecoat under the RTV11® topcoat. In contrast, SF1147, a decylmethylsiloxane, showed reduced barnacle adhesion strength when it was added to the topcoats of two different silicone matrices, RTV11® and the silica filled base.

Comparison of Matrix Type and Oil Type

Comparison of the barnacle adhesion strength to two RTV addition cured silicone coatings (RTV11® and RTV511) with four different additives reinforces the observation that barnacle adhesion strength is dependent upon oil type and the interaction of the oil with the bulk matrix. Some oils produce greater or lesser effects on barnacle adhesion than others, based on the inherent chemical properties of the oil. For example, DMSC15 and DMSC25 are both carbinol-terminated PDMS additives, but differ in viscosity, molecular weight, and the percent of non-siloxane components. In addition, oils may react differently in silicone matrices of slightly differing character. Thus, barnacle adhesion strength on two opposing silicone matrices varies according to additive type. For example, adhesion onRTV11® with DMSC25 is lower than when this oil is incorporated into RTV511; the reverse appears to be true when the oil is SF1154.

Comparison of Oil Molecular Weight and Location

Comparison of barnacle adhesion strength to coatings with additions of diphenyl-dimethyl siloxane oils of varying molecular weight into three silicone matrix locations (RTV11® topcoat, RTV11® tiecoat, and silica filled base) revealed lower adhesion on coatings with the higher molecular weight oil (PDV 0341). This is in contrast to results for the carbinol functional oil (DMSC) in RTV11® and RTV511. Differences in adhesion with respect to location of the oil were also noted. The additive, PDV0341, when present in the tiecoat with the RTV11® topcoat produced lower barnacle adhesion strength than when it was added directly to the RTV11®topcoat. It is suggested that physical properties other than molecular weight may combine to produce characteristic surface characteristics that affect biological adhesion.

Comparison of Loading Level and Location

Comparison of barnacle adhesion strength on coatings with three loading levels of the SF1154 additive showed reduced adhesion at the 30% level compared to unmodified RTV11® At this loading level, the location of the additive did not appear to affect barnacle adhesion. Within the silica filled base, reduced adhesion compared to the control was observed at the 10% and 20% levels. While addition of the SF1154 oil at all loading levels to the silica filled base showed 15 – 20% reductions in barnacle adhesion strength compared to the unmodified coating.

Comparison of Filler Type and Location

Addition of five different fillers (talc, resin, alumina, graphite and carbon black) to RTV11® and silica filled base coatings containing SF1154 revealed little difference in barnacle adhesion strength. Slight increases in the mean adhesion were observed in the silica filled base coatings compared to the control without extra filler incorporation. Barnacle adhesion on silica filled base coatings was consistently lower than on the RTV11® controls. In general, the type of additional filler additions had no significant effect on the adhesion strength of barnacles. Coatings with resin were the exception, exhibiting increased barnacle adhesion over the controls.

Comparison of Encapsulation Type and Loading Level

Encapsulation of the SF1154 additive showed no effect on barnacle adhesion strength. Unmodified RTV11® coatings, and coatings with capsule type A, did not differ in barnacle adhesion strength, and adhesion was lower than on coatings with capsule types B (at 30%

loading) and C (at 10% loading). Possible improved performance with the use of capsule A could was not established. Additional experiments studying the release rate of A encapsulated SF1154 may provide further information.

Effect of Additive Mixtures

Mixtures of two oils in RTV11® coatings produced a mean barnacle adhesion strength characteristic of the better performing additive compared to coatings with unmixed additives. Equal 5% mixtures of DBE224 and SF1154 exhibited the same barnacle adhesion strength as 10% DBE224 in RTV11®. Similarly, mixtures of 5% DMSC15 + 5% SF1154 exhibited barnacle adhesion strengths only slightly higher than 10% DMSC15 alone. In both cases, adhesion strength was significantly lower than on coatings of RTV11® + 10% SF1154 (which, in this case, did not differ statistically from unmodified RTV11®).

Effect of Biocide Additives

Additions of the commercial biocides, Irgarol 1051 and Sea-Nine 211 to RTV11® coatings with the oil additive DMSC15 provided no additional benefit in terms of adhesion strength of barnacles.

Effect of Oil Addition to Epoxy

Comparison of barnacle adhesion strength to epoxy coatings modified by oil addition revealed lower values on epoxy + DMSC15 than to epoxy + SF1154 and to unmodified epoxy; a rank order similar to that observed on RTV11® treatments. However, the scale of adhesion is an order of magnitude greater on epoxy than silicone. It should be noted that samples consisted of three barnacles per coating, since most barnacle baseplates failed before release from epoxy substrates.

References

1. Truby, K., Wood, C., Stein, J., Cella, J., Carpenter, J., Kavanagh, C., Swain, G., Wiebe, D., Lapota, D., Meyer, A., Holm, E., Wendt, D., Smith, C., and Montemarano, J., *Biofouling* ***15***,141 (2000).

Table 1.2.10 Screening panels

Acronym	Paint Name	Date Started	Mean MPa	SD MPa	Sample
2061AC	RTV11® +10% type A caps (SF1154)	1/22/97	0.070	0.030	33
2061BC	RTV11® +10% type B caps (SF1154)	1/22/97	0.078	0.035	50
2061CC	RTV11® +10% type C caps (SF1154)	1/22/97	0.101	0.035	31
2062AC	RTV11® +20% type A caps (SF1154)	1/22/97	0.059	0.025	50
2062BC	RTV11® +20% type B caps (SF1154)	1/22/97	0.074	0.031	41
2062CC	RTV11® +20% type C caps (SF1154)	1/22/97	0.065	0.025	31
2063AC	RTV11® +30% type A caps (SF1154)	1/22/97	0.053	0.023	50
2063BC	RTV11® +30% type B caps (SF1154)	1/22/97	0.123	0.047	32

2063CC	RTV11® +30% type C caps (SF1154)	1/22/97	0.073	0.031	27
C180-73-1A	RTV11®	1/22/97	0.075	0.036	44
C180-73-1B	RTV11®	1/22/97	0.082	0.041	70
C180-73-2A	RTV11® then extract w/ tolulene-3days	1/22/97	0.106	0.045	54
C180-73-2B	RTV11® then extract w/ tolulene-3days	1/22/97	0.083	0.039	44
C180-73-3A	RTV11® then extract w/ tolulene+SF1154	1/22/97	0.041	0.026	29
C180-73-3B	RTV11® then extract w/ tolulene+SF1154	1/22/97	0.044	0.020	53
C180-73-4A	RTV11® +10% SF1154	1/22/97	0.041	0.031	56
C180-73-4B	RTV11® +10% SF1154	1/22/97	0.045	0.022	69
C180-73-5A	RTV11® +10% SF1154-extract. tolulene	1/22/97	0.112	0.039	45
C180-73-5B	RTV11® +10% SF1154-extract. tolulene	1/22/97	0.096	0.042	62
C180-73-6A	RTV11® +10% SF1154-extract. tolulene+	1/22/97	0.054	0.031	37
C180-73-6B	RTV11® +10% SF1154-extract. tolulene+	1/22/97	0.066	0.033	55
C336-6710D	RTV11® +10% PS406	1/22/97	0.071	0.029	56
C336-6711D	RTV11® +20% SF1154	1/22/97	0.076	0.040	53
C336-6712D	RTV11® +30% SF1154	1/22/97	0.063	0.029	64
C336-6713D	RTV11® +10% PDV0331	1/22/97	0.076	0.035	59
C336-6714D	RTV11® +10% PDV0325	1/22/97	0.070	0.031	59
C336-6717D	Silica filled base	1/22/97	0.074	0.033	56
C336-6718D	Silica filled base +10% FMS123	1/22/97	0.073	0.027	48
C336-6719D	Silica filled base +10% DMSC15	1/22/97	0.037	0.022	18
C336-671D	RTV11®	1/22/97	0.082	0.041	43
C336-6721D	Silica filled base +10% SF1147	1/22/97	0.046	0.026	53
C336-6722D	Silica filled base +10% PDV0341	1/22/97	0.052	0.025	49
C336-6723D	Silica filled base +10% SF1154	1/22/97	0.059	0.042	61
C336-6724D	Silica filled base +10% PS835	1/22/97	0.071	0.036	43
C336-6725D	Silica filled base +10% PS563	1/22/97	0.066	0.023	49
C336-6726D	Silica filled base +10% PS406	1/22/97	0.078	0.039	29
C336-6727D	Silica filled base +20% SF1154	1/22/97	0.053	0.033	56
C336-6728D	Silica filled base +30% SF1154	1/22/97	0.059	0.035	50
C336-6729D	Silica filled base +10% PDV0331	1/22/97	0.066	0.031	37
C336-672D	RTV11® +10% FMS123	1/22/97	0.072	0.033	47
C336-6730D	Silica filled base +10% PDV0325	1/22/97	0.068	0.034	53
C336-673D	RTV11® +10% DMSC15	1/22/97	0.014	0.012	40
C336-674D	RTV11® +10% DBE224	1/22/97	0.042	0.026	42
C336-675D	RTV11® +10% SF1147	1/22/97	0.051	0.028	57
C336-676D	RTV11® +10% PDV0341	1/22/97	0.085	0.035	58
C336-677D	RTV11® +10% SF1154	1/22/97	0.074	0.032	55
C336-678D	RTV11® +10% PS835	1/22/97	0.077	0.034	49
C336-679D	RTV11® +10%PS563	1/22/97	0.081	0.030	56
C336-691D	RTV11®	1/22/97	0.071	0.035	53
C336-6931D	RTV11® +10% FMS 123 in J501	1/22/97	0.074	0.031	56

C336-6932D	RTV11® +10% DMSC15 in J501	1/22/97	0.029	0.016	47
C336-6933D	RTV11® +10% DBE224 in J501	1/22/97	0.006	0.006	12
C336-6934D	RTV11® +10% SF1147 in J501	1/22/97	0.071	0.034	60
C336-6935D	RTV11® +10% PDV0341 in J501	1/22/97	0.052	0.026	51
C336-6936D	RTV11® +10% SF1154 in J501	1/22/97	0.070	0.030	33
C336-6937D	RTV11® +10% PS835 in J501	1/22/97	0.043	0.022	39
C336-6938D	RTV11® +10% PS563 in J501	1/22/97	0.055	0.027	53
C336-6939D	RTV11® +10% PS406 in J501	1/22/97	0.058	0.024	52
C336-6940D	RTV11® +20% SF1154 in J501	1/22/97	0.067	0.034	39
C336-6941D	RTV11® +30% SF1154 in J501	1/22/97	0.062	0.026	37
C336-6942D	RTV11® +10% PDV0331 in J501	1/22/97	0.061	0.031	53
C336-6943D	RTV11® +10% PDV0325 in J501	1/22/97	0.066	0.026	59
C336-7245D	RTV11® +10% SF1154 + 10%talc	1/22/97	0.063	0.035	50
C336-7246D	RTV11® +10% SF1154 + 10%kaolin	1/22/97	0.070	0.030	31
C336-7247D	RTV11® +10% SF1154 +10%macro resin	1/22/97	0.091	0.034	46
C336-7248D	RTV11® +10% SF1154 +10%alumina	1/22/97	0.070	0.033	31
C336-7249D	RTV11® +10% SF1154 +10%graphite	1/22/97	0.079	0.034	37
C336-7250D	RTV11® +10% SF1154 +10%carbon black	1/22/97	0.075	0.030	28
KC220A3	RTV11® +10%3-aminopropyl tris(trimethylsiloxy)silane	1/22/97	0.184	0.068	30
KC220B3	RTV11® +10% phenyltris(trimethylsiloxy)silane	1/22/97	0.065	0.031	50
C180-79-1	RTV11® +5%S F1154 +5%MCRC13	3/25/97	0.063	0.023	23
C180-79-10	RTV511 +10% DBE224	3/25/97	0.055	0.026	12
C180-79-11	RTV511 +10% SF96(350)	3/25/97	0.054	0.037	18
C180-79-12	RTV11® +10%V(O)(Acetylacetonate)2	3/25/97	0.140	0.056	21
C180-79-13	RTV11®	3/25/97	0.097	0.044	36
C180-79-14	RTV511 +10% DMSC25	3/25/97	0.069	0.037	27
C180-79-15	RTV11® +10% DBLC31	3/25/97	0.095	0.037	30
C180-79-16	RTV511	3/25/97	0.075	0.025	39
C180-79-17	RTV511 +10% SF1154	3/25/97	0.050	0.025	23
C180-79-18	RTV511 +10% DMSC15	3/25/97	0.022	0.009	6
C180-79-2	RTV11® +5% SF1154 +5%DBE224	3/25/97	0.040	0.024	20
C180-79-3	RTV11® +10% DMSC25	3/25/97	0.044	0.030	35
C180-79-4	RTV11® +10% MCRC15	3/25/97	0.050	0.025	25
C180-79-5	RTV11® +5% DMSC15 +5% SF1154	3/25/97	0.027	0.023	4
C180-79-6	RTV11® +10% CMS222	3/25/97	0.055	0.038	33
C180-79-7	RTV11® +10% C180-78-3	3/25/97	0.132	0.042	38
C180-79-8	RTV11® +10% trimethoxypropyltrimethylammonium chloride	3/25/97	0.119	0.053	30

C180-79-9	RTV11® +10%C-439-1	3/25/97	0.046	0.027	25
C336-8451C	Silica filled base +10% SF1154 +10 %talc	3/25/97	0.056	0.027	21
C336-8452C	Silica filled base +10% SF1154 +10% neutral alumina	3/25/97	0.062	0.037	25
C336-8454C	Silica filled base +10% SF1154 +10% graphite	3/25/97	0.059	0.028	25
C336-8455C	Silica filled base +10% SF1154 +10% carbon black	3/25/97	0.070	0.042	21
C336-8456C	Silica filled base	3/25/97	0.041	0.019	33
C336-8457C	Silica filled base +10% SF1154 +10% Amberchrom resin	3/25/97	0.084	0.051	24
C180-86-1C	RTV11® +2.5%TINUVIN770	5/2/97	0.076	0.037	28
C180-86-2C	RTV11® +2.5% Irganox 1076	5/2/97	0.076	0.043	55
C180-9311C	RTV511 +10% DMSC15 C caps /J501	5/2/97	0.043	0.020	33
C180-9312C	Silica filled base +10% DMSC15 C caps /J501	5/2/97	0.045	0.027	9
C180-9313C	RTV11® +10% DMSC15 C caps /J501	5/2/97	0.044	0.019	28
C180-9314C	RTV11®	5/2/97	0.100	0.040	41
C180-9315C	Silica filled base +10% DMSC15 B caps /J501	5/2/97	0.036	0.018	16
C180-93-1C	Silica filled base +10% DMSC15 in J501	5/2/97	0.013	0.006	7
C180-93-2C	Silica filled base +10% DMSC25 in J501	5/2/97	0.055	0.026	12
C180-93-3C	Silica filled base +10% SF1154 in J501	5/2/97	0.043	0.020	19
C180-93-4C	Silica filled base +10% DBE224 in J501	5/2/97	0.036	0.017	12
C180-93-5C	RTV511 +10% SF96(350) in J501	5/2/97	0.064	0.029	20
C180-93-6C	Silica filled base +10% PS563 in J501	5/2/97	0.062	0.024	19
C180-93-7C	RTV11® +10% DMSC15 in J501	5/2/97	0.029	0.019	19
C180-93-8C	RTV511 +10% DMSC15 B caps /J501	5/2/97	0.054	0.021	16
C180-93-9C	RTV11® +10% DMSC15 B caps /J501	5/2/97	0.052	0.025	28
C193-106C	RTV11® +10% DMSC15/J501+ irgarol 1051	5/2/97	0.023	0.016	8
C193-107C	RTV11® +10% DMSC15/J501+ C9211	5/2/97	0.019	0.000	1
C193-108C	RTV11® +10% DMSC15+ irgarol 1051	5/2/97	0.031	0.020	18
C193-109C	RTV11® +10% DMSC15+ C9211	5/2/97	0.032	0.019	4
C180-1161C	Epoxy/J501/RTV11®	7/18/97	0.073	0.031	22
C180-1162C	Epoxy/J501/RTV11®+10% DC5772	7/18/97	0.295	0.192	5
C180-1163C	Epoxy/J501/RTV11®+10% DC5772 +10% DMSC15	7/18/97	0.105	0.037	25
C180-1164C	Epoxy/J501/RTV11®+10% bound polydimethyldiphenylsiloxane	7/18/97	0.059	0.024	4
C180-1165C	Epoxy/J501/RTV11®+10% tethered plydimethyldiphenylsiloxane	7/18/97	0.101	0.037	31
C180-1203C	Epoxy/J501/RTV11®+ 10%tethered carbinol	7/18/97	0.091	0.036	8

C180-122-3	RTV11® +10% SF1154 gel caps	8/15/97	0.059	0.033	17
C180-122-4	RTV11® +10% SF1154 +10%SF1154 gel caps	8/15/97	0.038	0.011	10
C180-122-5	RTV11® +10% SF1154 gel caps in J501	8/15/97	0.063	0.031	17
C180-122-6	RTV11® +10% DMSC15 caps	8/15/97	0.083	0.045	24
C180-122-7	RTV1®1	8/15/97	0.078	0.033	35
C180-123-3	RTV11® + Capsicum	9/10/97	0.068	0.025	13
C180-123-4	RTV11® + Capsicum +E	9/10/97	0.087	0.039	26
C180-126-1	RTV11®	10/18/97	0.076	0.027	17
C180-126-2	RTV11®+10% DMSC15 +10% DMSC15 type C caps	10/18/97	0.040	0.017	12
C5071-1	RTV11® +0% DMSC15	4/17/98	0.108	0.042	18
C5071-2	RTV11® +2% DMSC15	4/17/98	0.050	0.033	18
C5071-3	RTV11® +4% DMSC15	4/17/98	0.027	0.023	19
C5071-4	RTV11® +6% DMSC15	4/17/98	0.034	0.018	23
C5071-5	RTV11® +8% DMSC15	4/17/98	0.026	0.017	18
C5071-6	RTV11® +10% DMSC15	4/17/98	0.026	0.017	18
C5073-1	AMERON EPOXY	5/6/98	0.688	0.053	3
C5073-2	AMERON + SF1154	5/6/98	0.540	0.054	3
C5073-3	AMERON + DMSC15	5/6/98	0.397	0.001	2

SECTION 1.3 SUMMARY OF FIRST DOWNSELECTION PANEL PERFORMANCE

We examined the adhesion of six fouling organisms, the barnacle, Balanus eburneus, the gastropod mollusc, Crepidula fornicata, the bivalve molluscs, Crassostrea virginica and Ostrea sandvichensis, and the serpulid tubeworms, Hydroides dianthus and H. elegans, to twelve silicone fouling release surfaces. Removal stress (adhesion strength) varied among the fouling species and among the surfaces. Principal component analysis of the removal stress data revealed the fouling species fell into two distinct groups, one comprising the bivalve molluscs and tubeworms, and the other the barnacle and gastropod mollusc. Adhesion of these groups was not obviously related to any of the surface physical or chemical properties measured for the silicone materials, including critical surface tension. None of the silicone treatments generated a minimum in removal stress for all the organisms tested, although several surfaces did produce low adhesion strengths for both groups of species.

INTRODUCTION

Based on the screening panel data discussed above, the 153 coating formulations were downselected to 13 (Table 1.3.1). These coatings were primarily chosen based on quantitative barnacle adhesion performance. The RTV11® coating was included as a control. Coating 2 was employed into the ESTCP program. Excellent fouling release performance was seen on coatings 4-8. Coating 12 was included to explore the possibility of using the tiecoat as a reservoir for the oil, thereby enhancing the effective lifetime of the coating. Coatings 10 and 11 employed a similar principle: the oil could be hydrolyzed very slowly from the surface. An organic biocide was incorporated into coating 13 and, thus, it was not used in this data analysis. Test panels of each coating were deployed at Miami Marine Research and Testing Station, University of Hawaii, FIT, SUNY Buffalo, and 2 Massachusetts sites. Here we describe the overall performance of the first downselect panels in worldwide exposure conditions.

Table 1.3.1. Downselected topcoat formulations.

Series	Description
1	RTV11® standard
2	RTV11® + 10% SF1154
3	Silica filled base + 10% SF1154
4	RTV11® + 10% DBE224
5	RTV11® + 10% DMSC15
6	Silica filled base + 10% DMSC15
7	Silica filled base + 10% SF1147
8	RTV11® + SF1147
9	RTV11® + 5% DBE224 + 5% SF1154
10	RTV11® + 10% Ablative carbinol oil
11	RTV11® + 10% Ablative phenyl oil
12	(J-501 + 10% CMS222) / RTV11®
13	(J-501 + 10% SEA-9-211)/ RTV11® + 10% DMSC15

EXPERIMENTAL

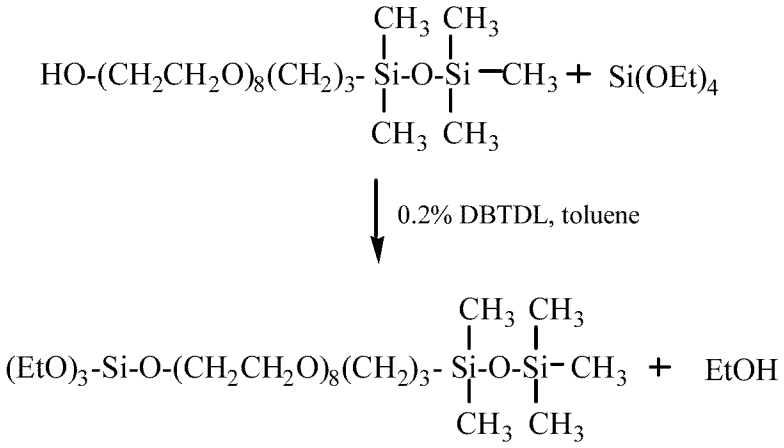
Panel Preparation

Surfaces were based on the duplex fouling-release coating system developed by Griffith at the Naval Research Laboratories[1]. This coating system consists of an epoxy anticorrosive layer (Amerlock 400FD), mistcoat (Epon-Versamide) to enhance the adhesion of the tiecoat to the epoxy, overcoated with a toughening layer (tiecoat) of silicone-styrene butylacrylate copolymer (Wacker Silgan J501), followed by a silicone top coat. The silicone topcoats were generated from two different polydimethylsiloxane elastomer bases (RTV11® and a silica filled based variously modified by addition of silicone oils (Table I.3.1). All base elastomers were obtained from General Electric Silicones. A silica filled master batch was prepared according to literature methods (U.S. Patent 5,906,893). To 40 g of the resultant master batch was added 53 g of silanol-terminated polydimethylsiloxane (MW = 40,000, 1.3 millimoles), 6 g propylsilicate (0.23 moles) and 1 g of silanol terminated polydimethylsiloxane (MW = 500, 2 millimoles). To 100 g of the above mixture was added 10 g of the appropriate oil. The oil-amended coating was catalyzed with 0.9 g dibutyltindilaurate (1.3 millimoles). RTV11® was amended with the appropriate quantity of oil and catalyzed with 0.5% dibutyltindilaurate.

The duplex system was applied to 25.4 cm x 30.5 cm steel panels using standard airless spray equipment.

Synthesis of Ablative Carbinol Oil

The ablative monocarbinol oil was synthesized by reacting tetraethyl orthosilicate with a monocarbinol terminated polydimethylsiloxane (MCR-C13 obtained from Gelest) of 580 molecular weight in the presence of 0.2 mole% dibutyltin dilaurate (DBTDL) to give 1.3 Kg of triethoxy-terminated polydimethylsiloxane as shown below in Scheme 1.3.1. This material was successfully crosslinked into the RTV11® network at 10 wt% with 0.07 wt% dibutyltin dilaurate.

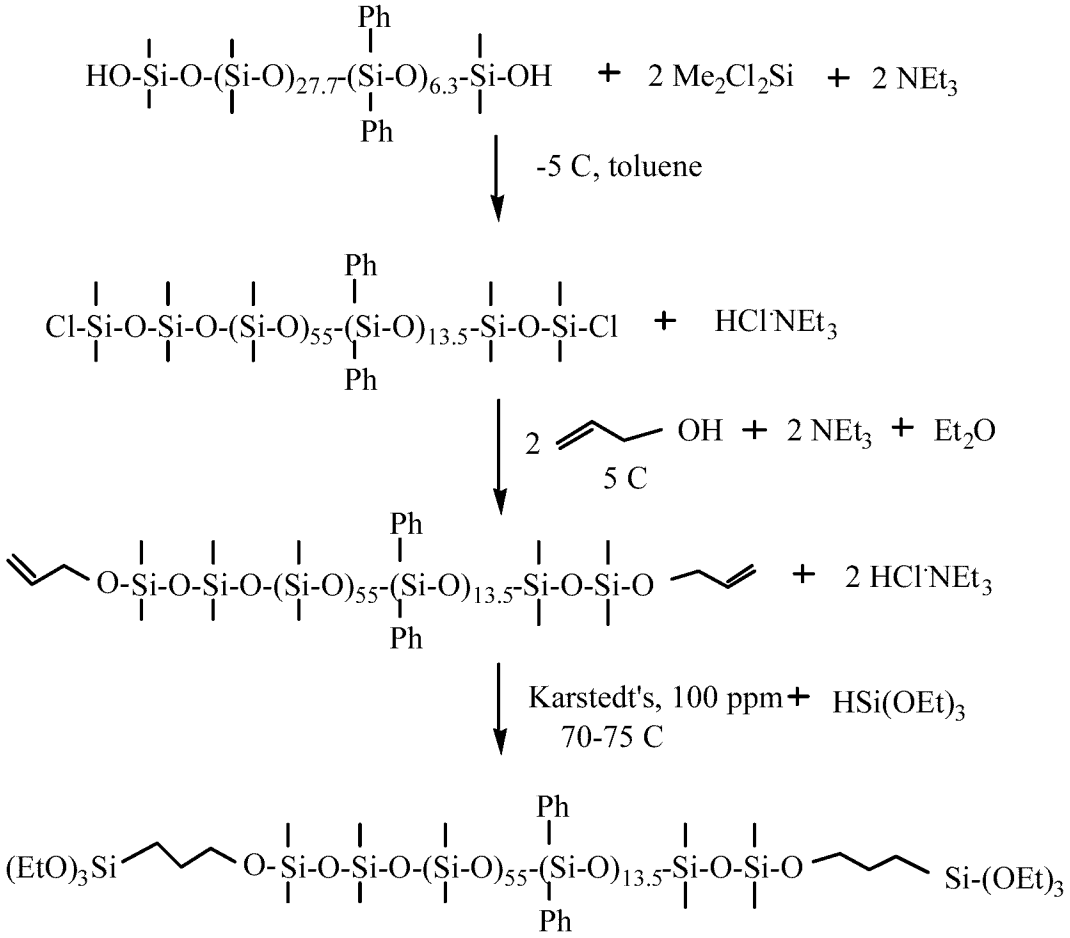


Scheme1.3.1 Preparation of ablative carbinol oil

Synthesis of Ablative Polydiphenyldimethylsiloxane Oil

The synthesis of an ablative dimethylsiloxane-diphenylsiloxane copolymer was prepared in three steps as shown below in Scheme 1.3.2. The starting material, a silanol terminated diphenylsiloxane-dimethylsiloxane copolymer comprising 16 mole% diphenylsiloxane, was obtained from Gelest. After ^{29}Si NMR characterization, the silanol endgroups of the ~3,300 molecular weight polymer were capped with dimethyldichlorosilane at -5°C with triethylamine to give the chlorosilane derivative. The chlorosilane derivative was subsequently reacted with allyl alcohol and triethylamine to give the bis-allyl terminated dimethyldiphenyl siloxane copolymer. Hydrosilation with triethoxysilane and Karstedt's catalyst at 70-75°C gave 120 g of the triethoxy-terminated dimethylsiloxane-diphenylsiloxane copolymer.

Unfortunately, some chain extension occurred in the first step and the molecular weight doubled from 3,300 to approximately 7,000. This was possibly due to the method of monomer addition, the presence of residual water, or the rate of the second addition of dimethylchlorosilane possibly being faster than the first. The latter possibility is unlikely since a 3-fold excess of Me_2Cl_2Si was used.



=Scheme 1.3.2 Synthesis of polydimethyldiphenylsiloxane oil

The two intermediates and final product were characterized by ^{1}H NMR and have been submitted for ^{29}Si NMR and/or ^{13}C NMR spectroscopy. This oil was successfully crosslinked into the RTV11® network at 10 wt% with 0.25 wt% dibutyltindilaurate.

Field Exposure Sites

Two panels of each of the twelve experimental surfaces were immersed at four test sites: two sites at the head of the Narragansett Bay, Massachusetts (NE1, NE2); the Florida Institute of Technology's exposure and testing platform in the Indian River lagoon Florida; Miami Marine Research and Testing site in Biscayne Bay, Florida, and the University of Hawaii's exposure site on Ford Island in Pearl Harbor, Hawaii.

Massachusetts test sites

Both test sites in Massachusetts are located in temperate estuaries, with water temperatures ranging from 4°C in the winter to 24°C in the summer, and salinities from 25°/oo to 31 °/oo [2]. Fouling at these sites is strongly seasonal, with most recruitment occurring during the spring and summer. Common fouling organisms include encrusting bryozoans, tunicates, sponges, and the gastropod *Crepidula fornicata*.

Florida Institute of Technology (FIT)

The test platform in Florida is located in an estuary, where salinities range from 20°/oo to 36 °/oo depending on the season and occurrence of rainfall. Mean water temperature varies from approximately 20°C in the winter to 30°C in the summer, and tidal currents and wave action are minimal[3]. Settlement of fouling organisms, and species structure of the fouling community, is affected by season of the year[4]. Common fouling organisms include the barnacles *Balanus eburneus* and *B. improvisus*, the oyster *Crassostrea virginica*, the serpulid tubeworm *Hydroides dianthus*, and encrusting bryozoans.

University of Hawaii

The University of Hawaii's exposure site is characterized by relatively constant water temperature (24°C to 27°C) and salinity (34-35°/oo)[2]. The location experiences little current or wave action. The fouling community is extremely diverse and exhibits no strong seasonality[5]. Important fouling organisms include the serpulid tubeworms *Hydroides elegans* and *Salmacina dysteri*, the oyster *Ostrea sandvichensis*, and several species of sponges, colonial tunicates, and encrusting bryozoans.

Measurement of Physical Properties

We quantified twelve physical properties of the silicone test surfaces, including surface tension (critical surface tension, acid and base components of polarity, and dispersion, polar and summed [dispersion and polar] components), a qualitative rating of the instability of various fluids (polar, methylene iodide, and naphthalenes) contacting the surfaces, and abrasion resistance as measured by depth of wear after $2x10^4$, $5x10^4$, and $9x10^4$ strokes of a rotating brush. Surface tension values were determined from contact angle measurements for selected diagnostic fluids, using a Ramé-Hart NRL100 contact-angle goniometer[7, 8]. Dispersion and polar components of critical surface tension were calculated using Kaelble's paired contact angle method[9]. The test for abrasion resistance employed a rotating brush device consisting of a rotor equipped with four nylon bristle brushes mounted at equidistant locations around the perimeter[6]. Rotation of the

rotor at 67 rpm yielded approximately 250 brush strokes per minute across the surface of a 3.8 cm x 3.8 cm sample coupon of the silicone treatment of interest. The coupon was loaded with a mass of 290 g, normal to the direction of the brush stroke. Depth of wear of the silicone surfaces, relative to two reference points outside of the brush path, was measured using a Starrett depth gauge (Model 25-441)[6,7]. All measurements were carried out at the University at Buffalo's Industry/University Center for Biosurfaces.

Adhesion of Fouling Organisms in Shear

We measured the shear force (removal stress) required to detach fouling organisms from the silicone test surfaces, following the standard methodology described in ASTM D5618 and Swain & Schultz[4]. At the Hawaii test site, procedures for estimating basal area were modified slightly to allow measurement of removal stress for tubeworms[5]. At the Florida test site, basal areas of fouling organisms were measured directly from scanned images. All forces measured were pooled across sampling dates, panel faces, and replicate panels before analysis. No tests for temporal variation in removal stress were conducted.

Statistical Analysis

Removal stresses were heteroscedastic in all but one case (*Crepidula fornicata* from site NE2). Transformation (log [x+1]) did not improve the homogeneity of variances. Consequently, we used the non-parametric Kruskal-Wallis test (*H* statistic) to examine differences in removal stress among surface treatments. Separate tests were conducted for each organism measured at each site. Spearman rank correlation coefficients were calculated to compare removal stresses between organisms and between sites. All correlation calculations were based on the mean removal stress for a particular organism on a particular surface treatment.

We used principal component analysis (PCA) to produce groupings of surface treatments in terms of both their physical properties and their effects on the adhesion of fouling organisms. PCA reduces the size of multivariate data sets by taking the original, correlated, variables (for example, removal stresses of the individual fouling organisms, or various measures of surface tension) and generating linear combinations of these variables (the principal components) that are uncorrelated. The uncorrelated principal components measure distinct characteristics (or 'dimensions') of the original data[9]. PCA may be a useful technique for identifying surface treatments to which several types of fouling organisms adhere poorly, or groups of surface physical properties that are characteristic of treatments for which removal stress is low. All statistical analyses were conducted using SAS (SAS Institute Incorporated, 1989).

RESULTS AND DISCUSSION

The removal stresses for six species of fouling organisms were collected from the downselected coatings: the gastropod mollusc *Crepidula fornicata* at sites NE1 and NE2 in Massachusetts; the barnacle *Balanus eburneus*, bivalve mollusc *Crassostrea virginica*, and serpulid polychaete *Hydroides dianthus* at the Florida exposure site; and the bivalve mollusc *Ostrea sandvichensis* and serpulid polychaete *Hydroides elegans* at the site in Pearl Harbor, Hawaii. *C. fornicata* failed to settle on all of the surface treatments; data were only collected for surfaces 1-2 and 5-9 at site NE1, and surfaces 1-4 and 6-11 at site NE2. All other species occurred on all of the surface treatments.

Massachusetts Test Sites (NE1 and NE2)

The removal stresses measured for *Crepidula fornicata* were very low, ranging from a mean of 0.009 MPa (RTV11® + 5% DBE224 + 5% SF1154, NE1) to 0.042 MPa (silica filled base + SF1154, NE2). At both sites, there were significant differences among the silicone treatments in the shear stress required to remove *C. fornicata* from the panel surface (NE1, H = 62.56, df = 6, P < 0.0001; NE2, H = 36.15, df = 9, P < 0.0001). Mean removal stresses at the two sites were not correlated (r_{Sp} = 0.6, n = 6, P = 0.21), although a positive trend was apparent that may have been rendered significant if individuals of *C. fornicata* had been available for testing on additional surface treatments (Figure 1.3.1).

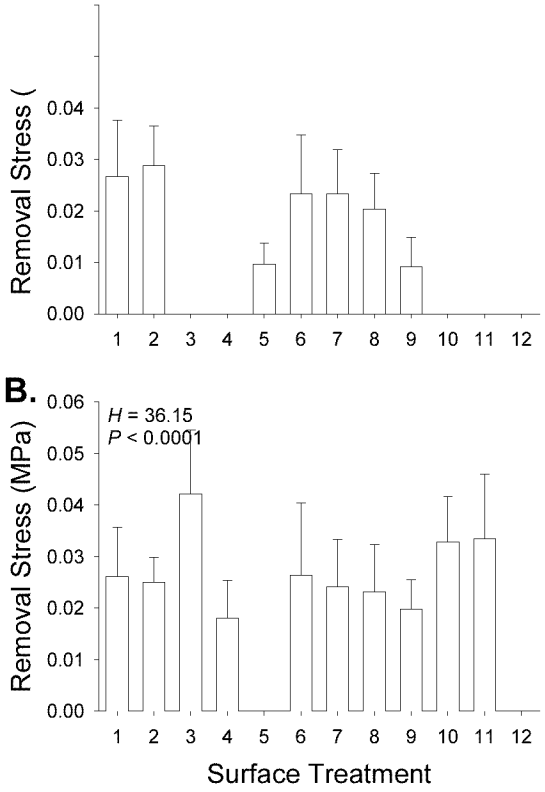


Figure 1.3.1 Mean values of shear stress required to remove the gastropod mollusc, *Crepidula fornicata* from test surfaces exposed at the Massachusetts test sites NE1 (**A.**) and NE2 (**B.**). Error bars = SDs; H = value of the Kruskal-Wallis test statistic for effect of surface treatment on removal stress; P = probability > H.

FIT Test Site

There was a significant effect of the topcoat formulation on removal stress for all of the species examined at the Florida site (*Balanus eburneus*, H = 745.73; *Crassostrea virginica*, H = 90.07; *Hydroides dianthus*, H = 303.79; df = 11 and P < 0.0001 in all cases). The shear stress required to remove the barnacle *B. eburneus* (Figure 1.3.2) was generally lower than that required to

detach either oysters *C. virginica* (Figure 1.3.3) or tubeworms *H. dianthus* (Figure 1.3.4). Mean removal stresses for *B. eburneus* ranged from 0.024 MPa (RTV11® + 10% DMSC15) to 0.088 MPa (RTV11® + 10% ablative phenyl oil); for *C. virginica* the range was from 0.033 MPa (RTV11® + 10% SF1147) to 0.195 MPa (Silica filled base + 10% SF1154), and for *H. dianthus* the range was 0.04 MPa (RTV11® + 10% SF1147) to 0.276 MPa (RTV11® + 5% DBE224 + 5% SF1154). Mean removal stresses for the three species were uncorrelated.

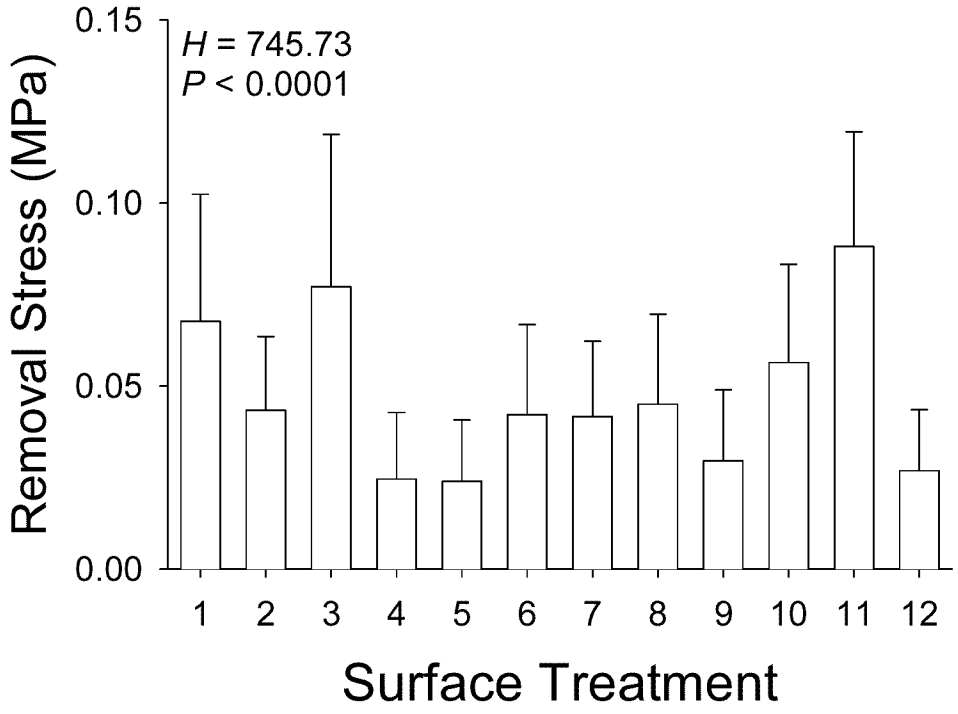


Figure 1.3.2 Mean values of shear stress required to remove the barnacle, *Balanus eburneus* from test surfaces exposed at the Florida test site. Error bars = SDs; H = value of the Kruskal-Wallis test statistic for effect of surface treatment on removal stress; P = probability > H.

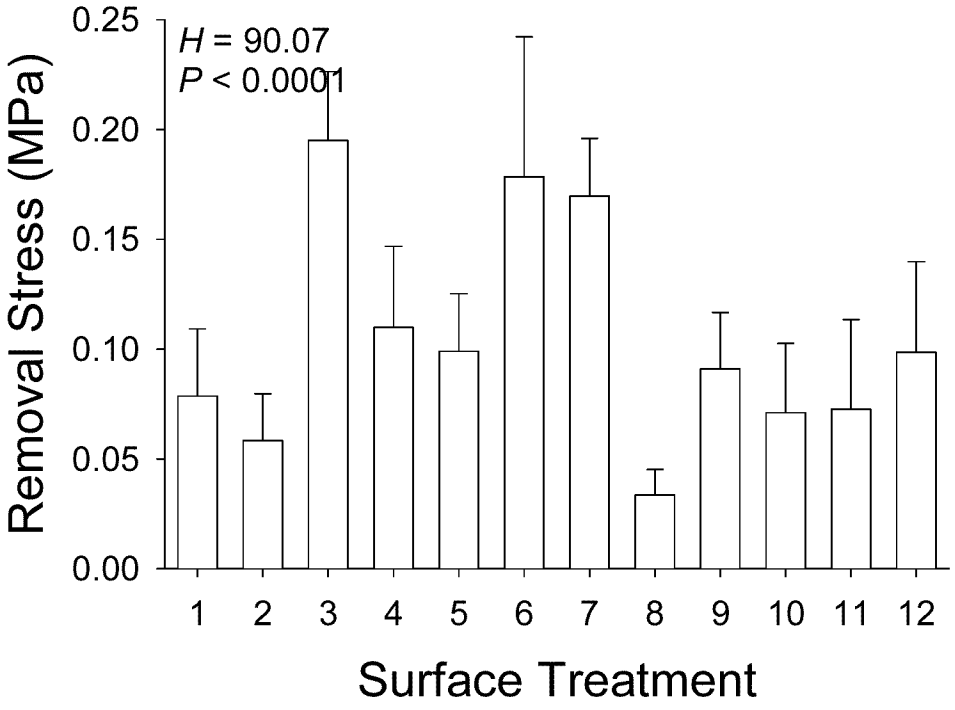


Figure 1.3.3. Mean values of shear stress required to remove the bivalve mollusc, *Crassostrea virginica* from test surfaces exposed at the Florida test site. Error bars = SDs; H = value of the Kruskal-Wallis test statistic for effect of surface treatment on removal stress; P = probability > H.

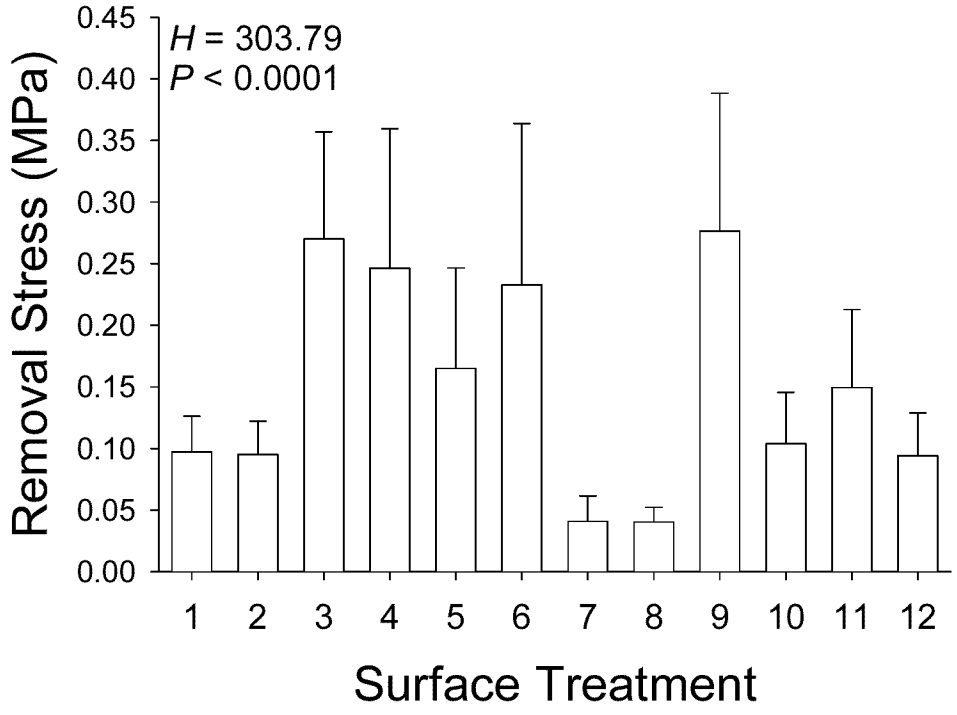


Figure 1.3.4 Mean values of shear stress required to remove the serpulid tubeworm, *Hydroides dianthus* from test surfaces exposed at the Florida test site. Error bars = SDs; H = value of the Kruskal-Wallis test statistic for effect of surface treatment on removal stress; P = probability > H.

University of Hawaii

Removal stresses measured for oysters *Ostrea sandvichensis* (Figure 1.3.5) and tubeworms *Hydroides elegans* (Figure 1.3.6) in Hawaii were also strongly affected by the silicone surfaces (*O. sandvichensis*, H = 106.99; *H. elegans*, H = 114.08; df = 11 and P < 0.0001 in both cases). Mean shear stresses required to remove *O. sandvichensis* were lowest on RTV11® + 10% SF1147 (0.079 MPa) and highest on silica filled base + 10% DMSC15 (0.354 MPa), while for *H. elegans* the range in mean values was from 0.074 MPa (silica filled base + 10% SF1147) to 0.269 MPa (silica filled base + 10% SF1154). Mean removal stresses were positively correlated for these two species (r_{Sp} = 0.89, n = 12, P = 0.0001;Figure 1.3.7).

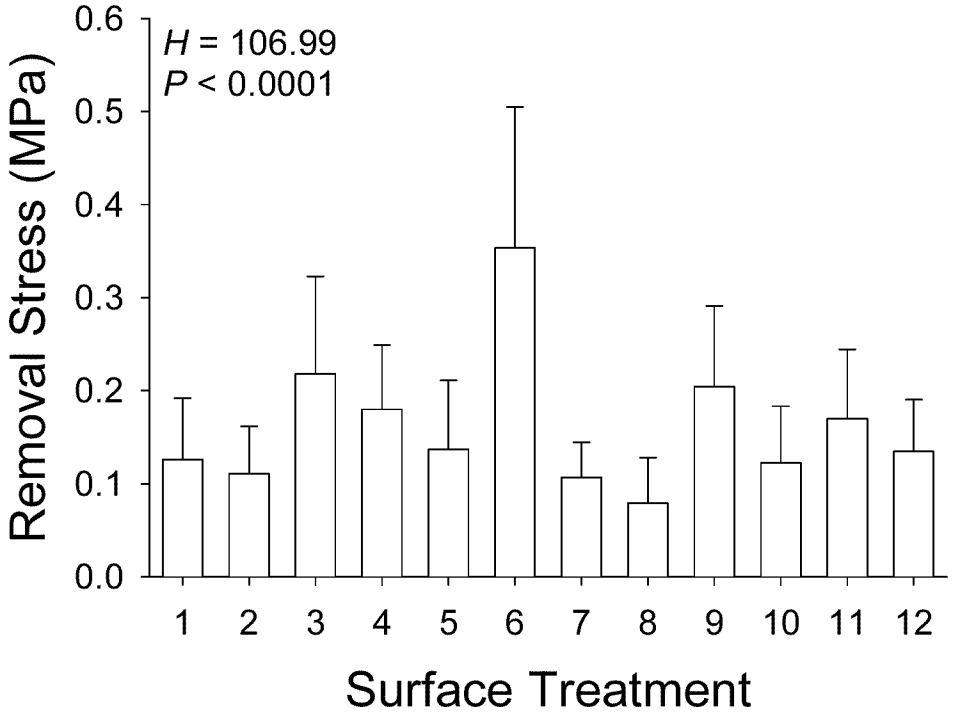


Figure 1.3.5 Mean values of shear stress required to remove the bivalve mollusc, *Ostrea sandvichensis* from test surfaces exposed at the Hawaii test site. Error bars = SDs; H = value of the Kruskal-Wallis test statistic for effect of surface treatment on removal stress; P = probability > H.

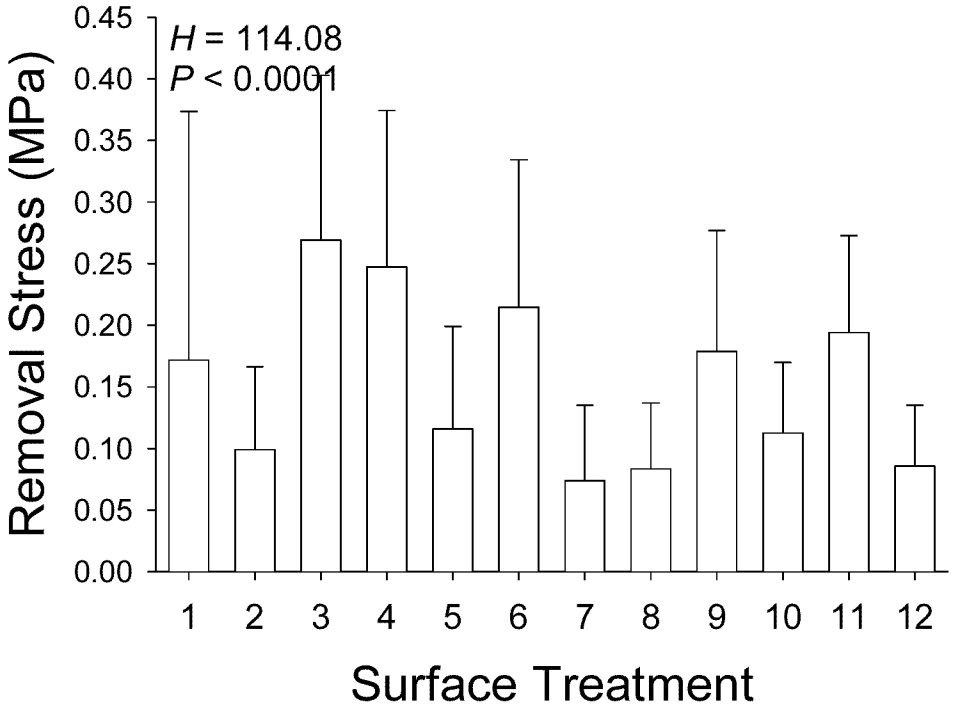


Figure 1.3.6. Mean values of shear stress required to remove the serpulid tubeworm, *Hydroides elegans* from test surfaces exposed at the Hawaii test site. Error bars = SDs; H = value of the Kruskal-Wallis test statistic for effect of surface treatment on removal stress; P = probability > H

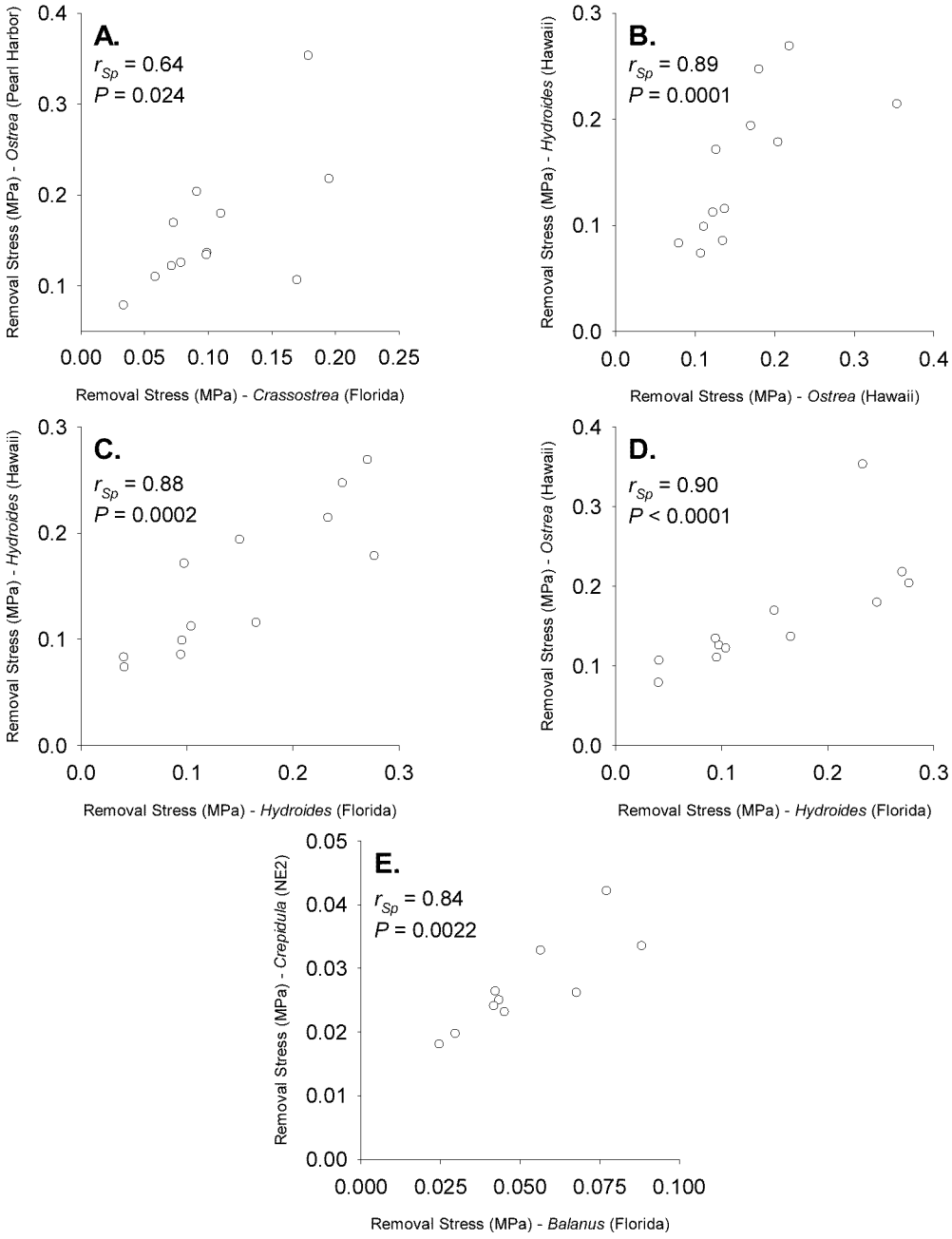


Figure 1.3.7. Correlations between mean removal stresses measured for different fouling organisms at the various field sites. Only comparisons producing significant ($\underline{P} < 0.05$) Spearman rank correlations are shown. $\underline{r_{Sp}}$ = Spearman's rank correlation coefficient; $\underline{P}$ = probability > $|\underline{r_{Sp}}|$.

Comparisons Among Sites and Principal Component Analysis of Removal Stress

Comparisons among the sites, of the mean removal stresses measured for each site's characteristic fouling species, yielded few significant correlations. The shear stress required to remove *Crassostrea virginica* in Florida was positively correlated with that required to remove *Ostrea sandvichensis* in Hawaii (r_{Sp} = 0.64, n = 12, P = 0.024; Figure 1.3.7A). Mean removal stresses for *Hydroides dianthus* in Florida were positively correlated with mean removal stresses for both *H. elegans* (r_{Sp} = 0.88, n = 12, P = 0.0002; Figure 1.3.7C) and *O. sandvichensis* (r_{Sp} = 0.90, n = 12, P < 0.0001; Figure 1.3.7D). Mean removal stresses measured for *Balanus eburneus* and *Crepidula fornicata* from site NE2 were also positively correlated (r_{Sp} = 0.84, n = 10, P = 0.0022; Figure 1.3.7E).

We conducted a principal component analysis (PCA) using the mean removal stresses for all species for which measurements were available for every surface treatment (*Balanus eburneus, Crassostrea virginica, Hydroides dianthus, Ostrea sandvichensis, Hydroides elegans*). The first two principal components produced by the analysis accounted for approximately 81.1% of the variance in the shear stress data, and reflected the correlations between mean removal stresses described above. The first component accounted for 59.5% of the variance, and was positively correlated to the shear stress required to remove the oysters and tubeworms (Table 1.3.2). The second principal component accounted for 21.6% of the variance and was positively correlated to mean removal stresses measured for *B. eburneus* (Table 1.3.2). The remaining three principal components were uncorrelated to the mean removal stresses characteristic of any of the fouling species.

Table 1.3.2. Spearman rank correlations between the mean shear stresses required to remove particular fouling species from the surface treatments, and the principal components. Only significant correlations (P < 0.05) are listed, n = 12 in all cases. Mean shear stresses to remove *Crepidula fornicata* from surface treatments at the NE2 site were significantly correlated to the second principal component (r_{Sp} = 0.75, n=10), but were not used in the calculation of the principal components themselves.

Principal Component	**1**	**2**
Balanus eburneus		0.96
Hydroides dianthus	0.89	
Crassostrea virginica	0.70	
Hydroides elegans	0.92	
Ostrea sandvichensis	0.94	

A graph of the principal component scores for each of the surface treatments (Figure 1.3.8) indicated that no treatment represented a minimum in removal stress for all the fouling species tested. Surface treatments occurring in the lower left quadrant of the graph, however, do represent materials for which adhesion of both classes of fouling organisms (as identified by PCA) were poor.

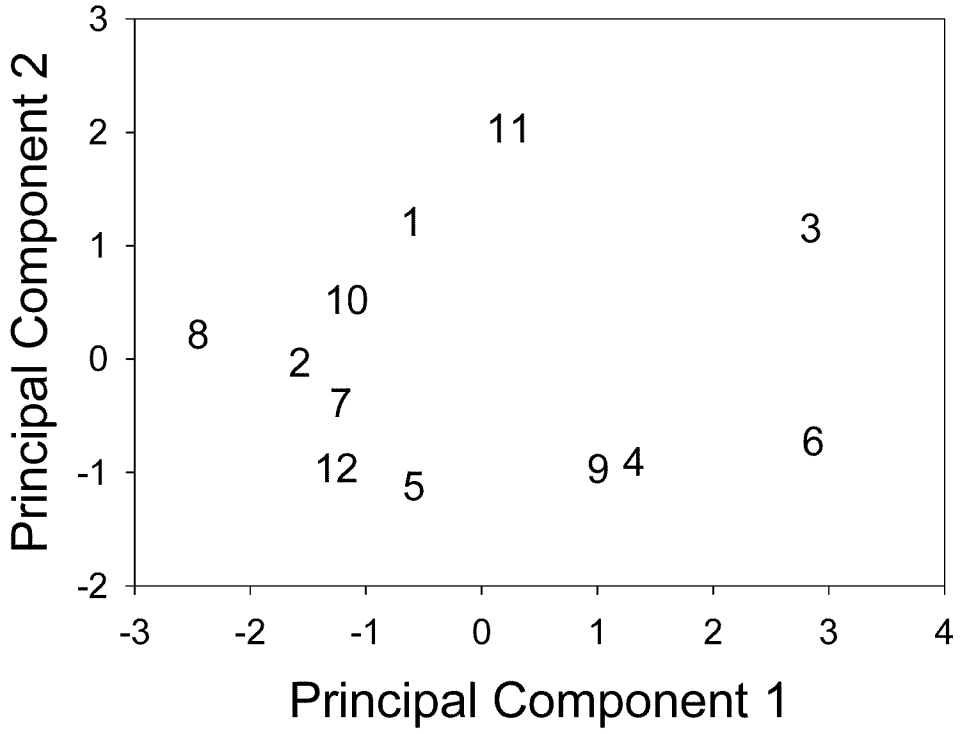


FIGURE 1.3.8 Clustering of the silicone surface treatments by their first two principal component scores, calculated from mean values of removal stress for the five fouling organisms (*Balanus eburneus, Crassostrea virginica, Hydroides dianthus, Ostrea sandvichensis, Hydroides elegans*) for which data were available for every surface treatment. Principal component 1 is positively correlated with the removal stress observed for the bivalve molluscs and the tubeworms, while principal component 2 is positively correlated with the removal stress for the barnacle *Balanus eburneus* (Table 1.3.2). Surface treatments occurring in the lower left quadrant of the graph produce low removal stresses (poor adhesion strength) for both classes of fouling organisms identified by the PCA.

Effects of Physical Properties of the Treatments on Removal Stress

We quantified twelve physical properties, characteristic of the silicone surface treatments before they were exposed, including surface tension and its components, the instability of various diagnostic fluids when applied to the surface of the treated panels, and abrasion resistance. The treatments displayed critical surface tensions between 20.5 $mN \cdot m^{-1}$ (RTV11® + 10% ablative carbinol oil) and 27.5 $mN \cdot m^{-1}$ (silica filled base + 10% DMSC15), within the range of critical surface tensions (20 - 30 $mN \cdot m^{-1}$) previously determined to yield low adhesion[10]. Critical surface tension was unrelated to either of the principal components derived from the mean values for removal stress (Figure 1.3.9).

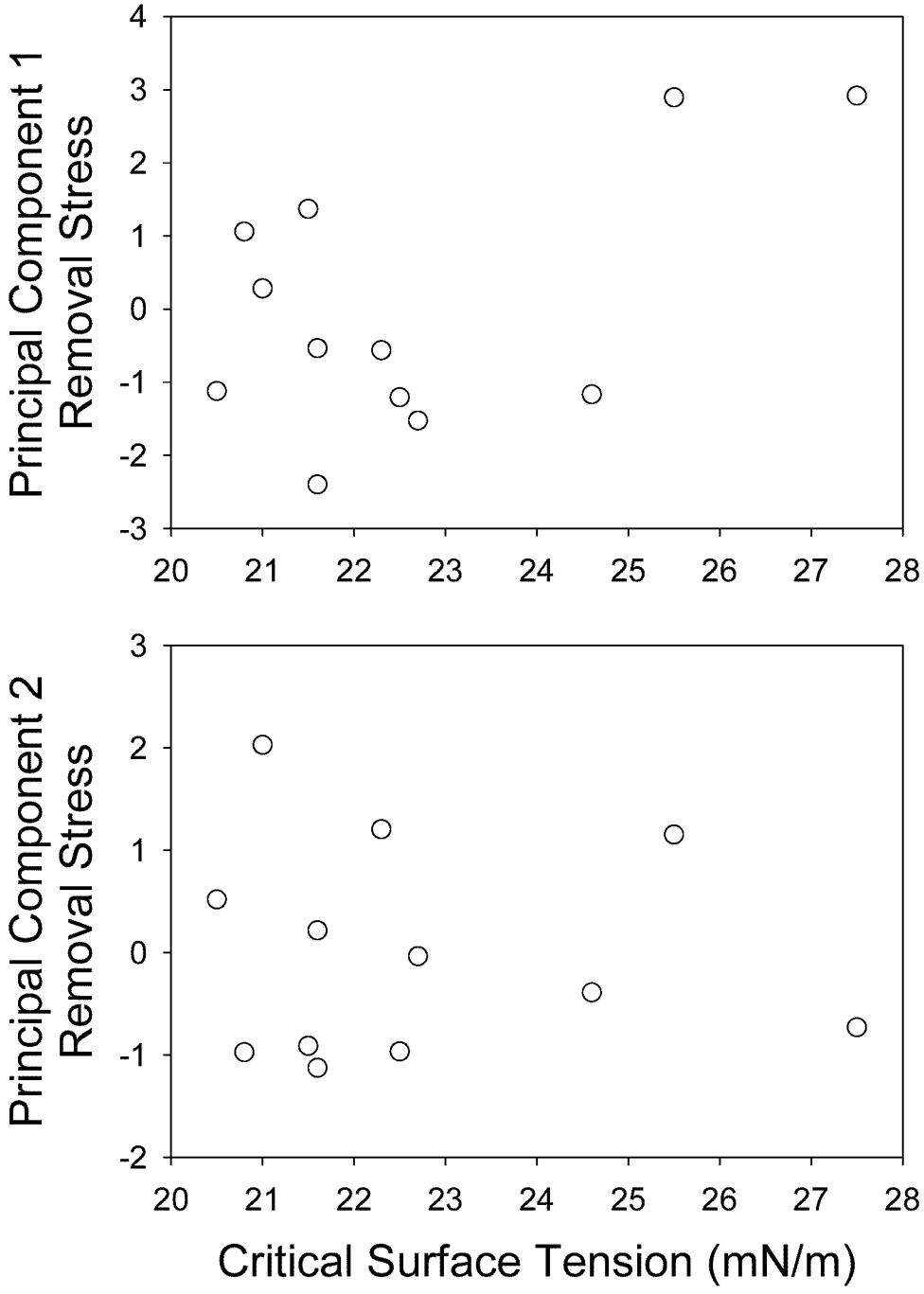


Figure 1.3.9 Relationship between the first two principal components calculated from mean values of removal stress, and the critical surface tension of the surface treatments.

We used a second PCA to generate principal components describing the characteristic physical properties of the silicone surfaces. The first four principal components produced by the analysis accounted for approximately 88% of the variation in the 12-dimensional data set of physical properties. The first principal component, accounting for 39.6% of the variance, was positively correlated to the polar and summed (dispersion and polar) components of surface tension, and to the depth of wear resulting from $2x10^4$ and $5x10^4$ brushstrokes (Table 1.3.3). The second principal component explained 27.5% of the variance in the data set, and was positively correlated with the base component of polarity and the polar component of surface tension, and with the qualitative rating of the instability of polar fluids (Table 1.3.3). The third principal component (13.1% of variance) reflected a relationship between the acid component of polarity and the dispersion component of surface tension, while the fourth principal component (7.8% of variance) represented the instability of naphthalenes (Table 1.3.3). Critical surface tension was not correlated to any of the first four principal components, although the rank correlation to the first principal component was nearly significant ($r_{Sp} = 0.57$, $P = 0.051$). The remaining principal components were not correlated to any of the surface properties.

Table 1.3.3 Spearman rank correlations between the physical properties of the silicone surfaces, and the principal components calculated from those properties. Only significant correlations (P □ 0.05) are listed, n = 12 in all cases. Critical surface tension was uncorrelated to the principal components by this criterion, although the rank correlation to the first principal component was nearly significant ($r_{Sp} = 0.57$, $P = 0.051$).

Principal Component	**1**	**2**	**3**	**4**
Surface Tension				
Critical Surface Tension (γ^c)				
Acid Component (γ^a)			-0.58	
Base Component (γ^b)		0.69		
Dispersion Component (γ^d)			0.69	
Polar Component (γ^p)	0.72	0.64		
Sum (γ)	0.82			
Fluid Instability				
Polar Fluids		0.96		
CH_2I_2				
Naphthalenes				0.61
Abrasion Resistance				
Post 2 x 10^4 brushstrokes	0.78			
Post 5 x 10^4 brushstrokes	0.77			
Post 9 x 10^4 brushstrokes				

In order to examine relationships between the adhesion of the fouling organisms and the surface properties of the silicone treatments, we plotted the principal component scores derived from the mean values for removal stress against the scores derived from the physical properties (Figure 1.3.10). The shear stress required to remove barnacles appeared to exhibit a threshold, with removal stress decreasing rapidly for high values of the acid component of polarity and low

values of the dispersion component of surface tension (Figure 1.3.10F). We observed no similar, or otherwise readily apparent, relationships between removal stress and the surfaces' physical properties.

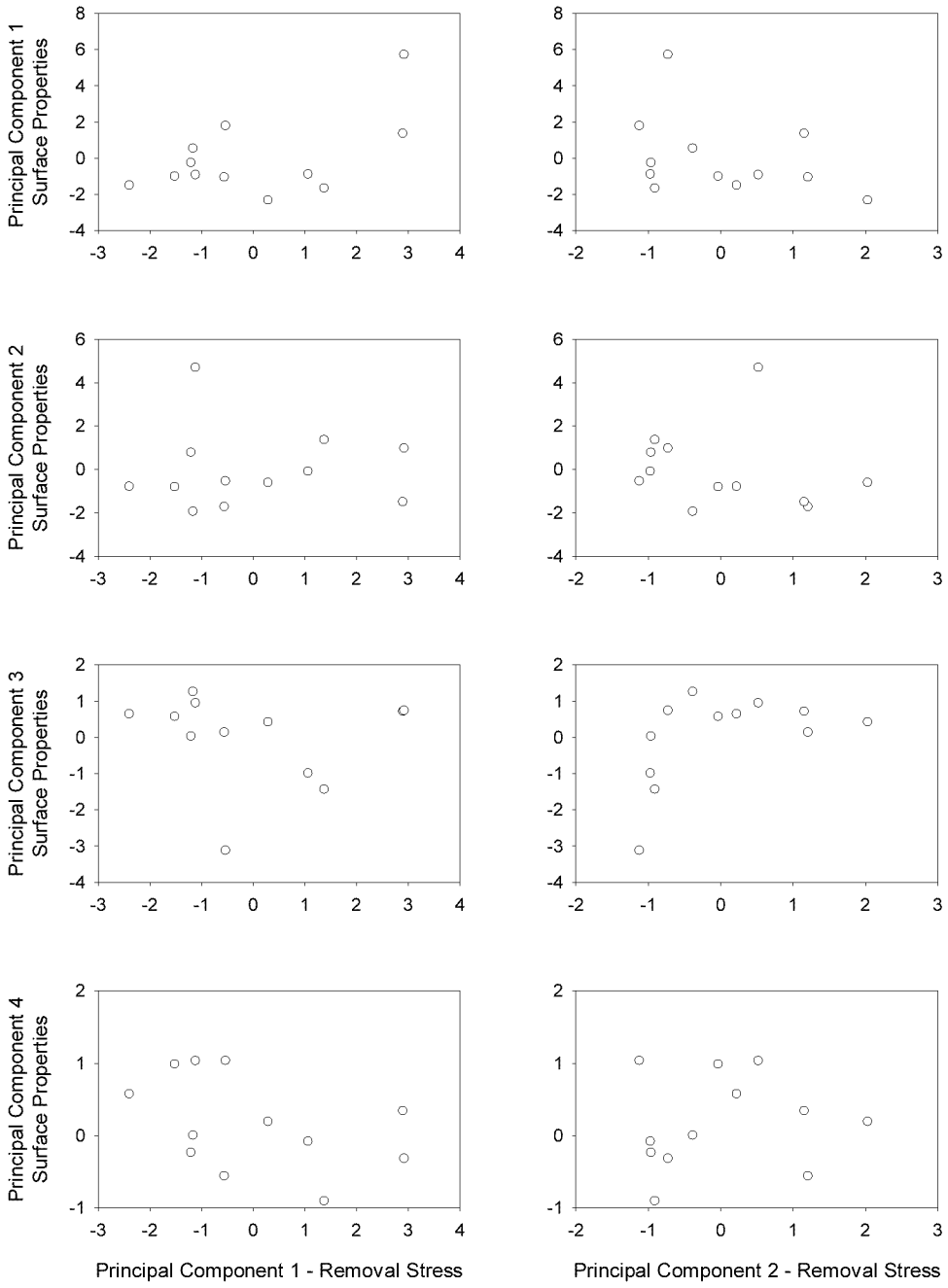


Figure 1.3.10 Relationship between the first two principal components calculated from mean values of removal stress, and the first four principal components calculated from the physical properties of the surface treatments.

The experimental silicone surfaces varied in their ability to prevent the strong adhesion of six different fouling species. As observed in other studies, the magnitude of the force required to remove an individual fouler also varied across species[11]. *Crepidula fornicata* (Figure 1.3.1) consistently required the lowest shear stress for detachment from the surface of a panel, followed by *Balanus eburneus* (Figure 1.3.2), the bivalve molluscs (Figures 1.3.3 and 1.3.5) and serpulid tubeworms (Figures 1.3.4 and 1.3.6)

In order for a fouling-release coating to be globally effective, it must prevent strong adhesion by a diversity of fouling organisms that may manifest a diversity of adhesion mechanisms[12]. If differences in the magnitude of removal stress among fouling species were consistent across surface treatments, development of a globally-effective fouling release material would potentially be relatively straightforward - the surface that produced the lowest value of removal stress for any one fouling species would produce the lowest value for all of them. Our data, however, showed that, while removal stress varied among species and among surface treatments (for all species tested), removal stress did not vary across surface treatments in the same way for all species. Correlations between the mean removal stresses, and the results of the principal component analysis on removal stress values, indicated that the fouling species we examined fell into two independent groups (Table 1.3.2). One group consisted of the bivalves *Crassostrea virginica* and *Ostrea sandvichensis*, and the tubeworms *Hydroides dianthus* and *H. elegans* (Table 1.3.2, Figure 1.3.7A-D). The second group included the barnacle *Balanus eburneus* (Table 1.3.2); *Crepidula fornicata* may also fall into this group as mean removal stresses for this gastropod (at site NE2) were correlated to removal stresses for barnacles and to the second principal component derived from the shear stress data (Table 1.3.2 and Figure 1.3.7E).

Our observation of two distinct classes of fouling organisms, defined by their ability to adhere to the silicone surface treatments, suggests the existence of at least two, unique or uncorrelated, surface physical or chemical properties affecting organismal adhesion. The identity of these properties is not apparent. Critical surface tension is an important determinant of the ability of a surface to reduce adhesio.[12]. Effective fouling release materials present critical surface tensions between 20-30 $mN \cdot m^{-1}$ [10]. All of the materials we tested fell within this range, and removal stress was not obviously related to critical surface tension (Figure 1.3.9). In addition, plots of the principal components defined by removal stress, against the principal components defined by the twelve physical properties of the surfaces measured before exposure (Figure 1.3.10), suggested that none of these properties fully explained the patterns in adhesion that we observed. Recent studies have shown that a surface's elastic modulus[12] and thickness[13] can also affect the ease with which objects affixed to the surface may be removed. For the range in thickness displayed by our silicone test materials, however, thickness has no effect on the shear stress required to remove barnacles.

Given that a myriad of adhesion mechanisms are likely to exist among the diverse group of organisms that occur as fouling, it is perhaps not surprising that none of the surfaces represented in this study generated a minimum in removal stress for <u>all</u> the fouling organisms tested (Figure 1.3.8). Several surfaces, however, did produce low values of removal stress for both the groups of fouling organisms defined in the principal component analysis. An effective fouling release surface may not need to represent an adhesion minimum for all fouling species if removal

stresses are reduced to the extent that sloughing of attached organisms, or self-cleaning, occurs at reasonable operating speeds.

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SECTION 1.4 OIL-BASE TYPE INTERACTIONS AND FINAL DOWNSELECTION

The downselection series discussed in Section 1.3 was further evaluated to determine the effect of the compositional variables of oil type and base type on organismal adhesion values. We have found that not only are the main effects important in determining the organismal response, but the interaction term (oil type crossed with coating type) is highly significant for all organisms studied except oysters at the University of Hawaii test site which is significant at the 90% confidence level. Using the Teguchi method, we downselected to the best performing composition.

INTRODUCTION

In section 1.1 we reported on the effect of crosslink density and filler loading of silicone coatings on their fouling release properties. We found an inverse correlation between foul release performance and filler loading. However, physical properties were enhanced by addition of filler. Therefore, the best foul release coatings had the lowest durability. In sections 1.2 and 1.3, we examined the main effect of oil incorporation on foul release performance. We found in some cases, oil had a beneficial effect. Here, we describe the effect of the oil type (polydimethyldiphenylsiloxane, hydrophilic silicone or organic compatible silicone) and silicone coating type (calcium carbonate filled versus silica filled)) on macrofouling attachment strength at two different sites (Indian River Lagoon, Melbourne, Florida and Ford Island, Oahu, Hawaii). We also describe our downselection procedure.

EXPERIMENTAL

Coatings were prepared and deployed as described in Section 1.3.

Coverage

The cumulative coverage at the University of Hawaii was monitored according to the standard method for testing of antifouling panels in shallow submergence (ASTM D3623). The panels were inspected quarterly.

Statistical Analysis

Statistical analyses were preformed using Minitab and Design Expert. ANOVA analysis and linear regression models were employed to evaluate the data. A Taguchi inner outer array was used to determine the optimum coating. All data was normalized by adding one to the data followed by taking the natural log of the sum for use in ANOVA and linear regression analyses.

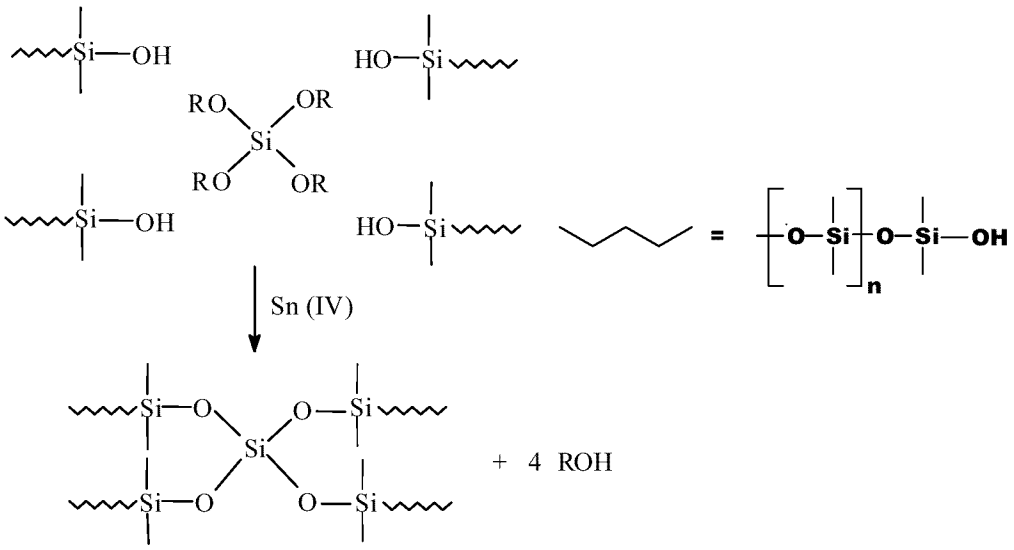
RESULTS AND DISCUSSION

Coverage

A statistical Design of Experiments (DOE) was performed to elucidate the effect of compositional variables on macrofouling attachment strength and coverage. The robust design incorporated two silicone base systems and three silicone oil types. Silicone bases were comprised of either a silica filler or RTV11® and oil types comprised polydimethyldiphenylsiloxanes (SF1154), hydrophilic siloxanes (DMSC15) or organic

compatible siloxanes (SF1147). Both silicone coatings were crosslinked via condensation in which telechelic silanol polymers were reacted with tetraalkoxysilanes using dibutyltindilaurate as the catalyst in the presence of either silica or calcium carbonate fillers. Fillers are necessary for mechanical integrity because of the inherent weakness of silicone coatings. Oils were incorporated at 10-wt% prior to addition of the catalyst. A general scheme for preparation of the coatings is given in Scheme 1.4.1.

Coverage assays were performed at the University of Hawaii after 12 months exposure. Substantial differences in macrofouling coverage were seen on the different coatings (Figure 1.4.1). The benefit of oil incorporation on coverage was a function of the oil type and coating system. For example, RTV11® had similar coverage to that of RTV11® amended with SF1154 oil, but a higher degree of coverage than that found for RTV11® amended with either the DMSC15 or SF1147. In general, fouling was present in greater quantities on coating systems containing silica filler than on RTV11®; however, the effect of oil was dependent upon the coating system into which it had been incorporated. Whereas the RTV11® coating system with DMSC15 oil exhibited little fouling, the comparable silica filled system was heavily fouled with oysters. Thus, the main effects of oil type and coating system were important in determining the efficacy of the coatings, but more significantly, there is an interaction between the coating and the oil type that dictated the degree of fouling accumulation.



Scheme 1.4.1. Generalized scheme of crosslinking of silicone foul release coating

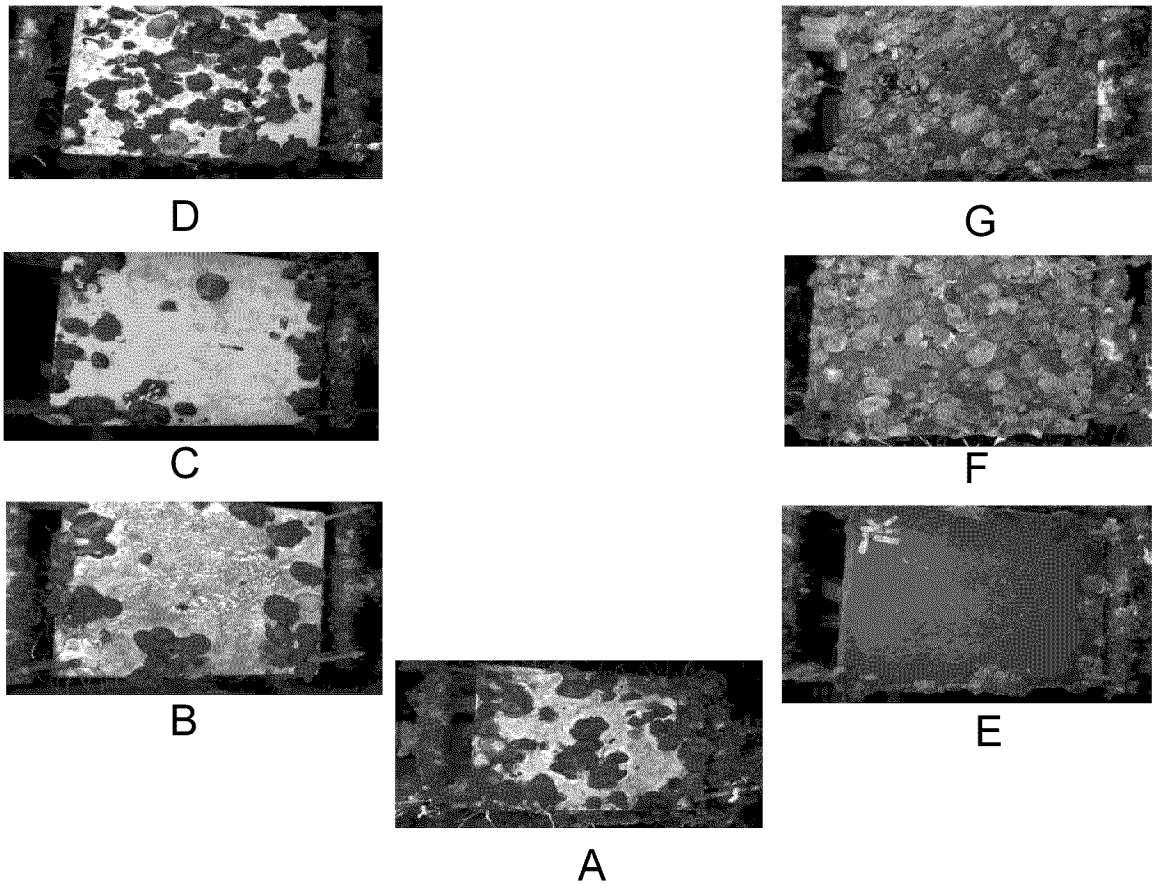


Figure 1.14.1. Effect of model silicone coating and oil type on macrofouling coverage at University of Hawaii.
A) RTV11®; B) RTV11® with SF1147; C) RTV11® with DMSC15; D) RTV11® with SF1154; E) Silica filled model system with SF1147; F) Silica filled model system with DMSC15, G) Silica filled model system with SF1154

Barnacle Attachment at FIT

Attachment strengths of macrofouling organismsat the FIT site were determined on the six oil-amended coatings using a force gauge (barnacles, tubeworms and oysters) and the University of Hawaii (oysters and tubeworms). A check of gage reproducibility and repeatability was performed on the force gauge using standard weights rather than barnacles. The study employed two operators, four weights and ten measurements per each weight per each operator. The force gauge had a total standard deviation for reproducibility and repeatability of 0.007 with a repeatability standard deviation of 0.005 and reproducibility standard deviation of 0.005.

In order to distinguish between the means of the organismal adhesion strengths, large populations of organisms were sampled over a 1.8-year timeframe. For example, 1328 *Balanus eburneus* measurements were performed on the six coatings to ensure that the means had small 95% confidence intervals so that we could statistically distinguish coating performance differences. An analysis of variance (ANOVA) provided a p value of 0.000 with an F factor of 67.12 (Table 1.4.1; Figure 1.4.2).

Table 1.4.1. ANOVA analysis for barnacle adhesion strength (*balanus eberneus*) on the six coatings at FIT

Source	DF	SS	MS	F	P
Acronym	5	0.226581	0.045316	80.98	0.000
Error	1323	0.740326	0.000560		
Total	1328	0.966908			

Individual 95% CIs For Mean Based on Pooled StDev

Level	N	Mean	StDev	---------+---------+---------+-------
2	219	0.04241	0.01938	(-*)
3	213	0.07339	0.03789	(-*-)
5	91	0.02371	0.01633	(--*--)
6	138	0.04116	0.02340	(--*-)
7	299	0.04055	0.01960	(*-)
8	369	0.04157	0.01955	(-*)

Pooled StDev = 0.02366 ---------+---------+---------+------- 0.032 0.048 0.064

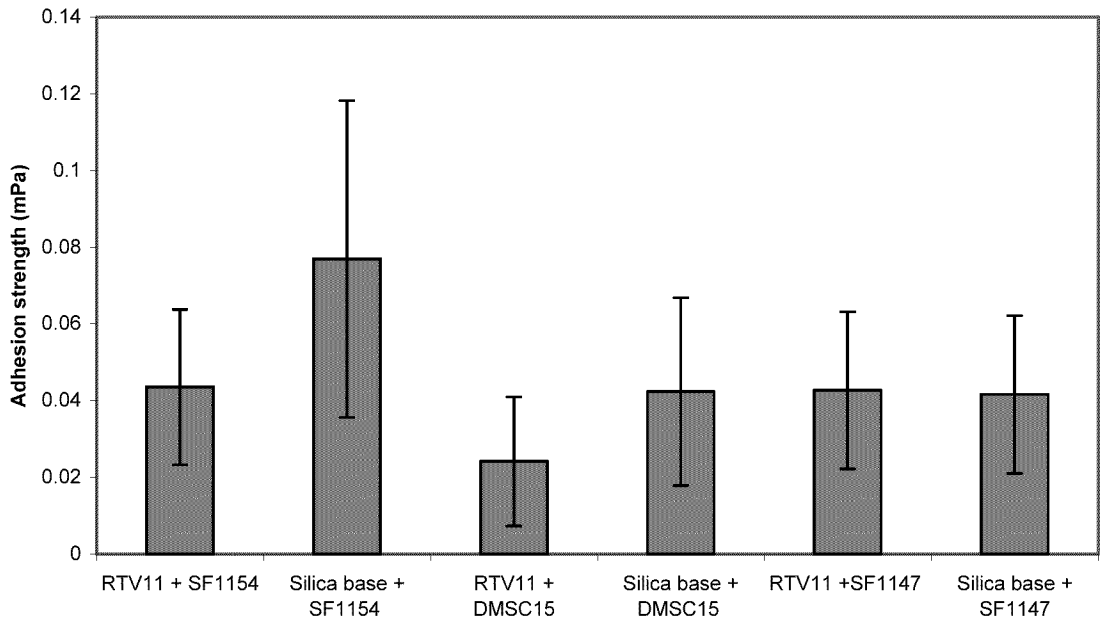


Figure 1.4.2. Mean barnacle (*balanus eberneus*) adhesion strengths for the six coatings at FIT.

Linear regression analysis was performed to determine whether the coating composition or oil type as well as the interaction term of coating composition with oil type were significant factors in determining barnacle adhesion strengths. Both main effects and the interaction term were statistically significant (Figure 1.4.3, Table 1.4.2). Thus, not only was the barnacle attachment strength a function of which model coating was employed as well as which oil was used, it was

also dependent upon which oil was incorporated into which silicone coating. Attachment strengths were generally lower in RTV11® than in the silica filled base. Although DMSC15 oil provided the lowest attachment strength in the RTV11® system, its performance in the silica filled system was comparable to SF1147. The highest attachment strength was obtained on the silica filled coating systems amended with SF1154.

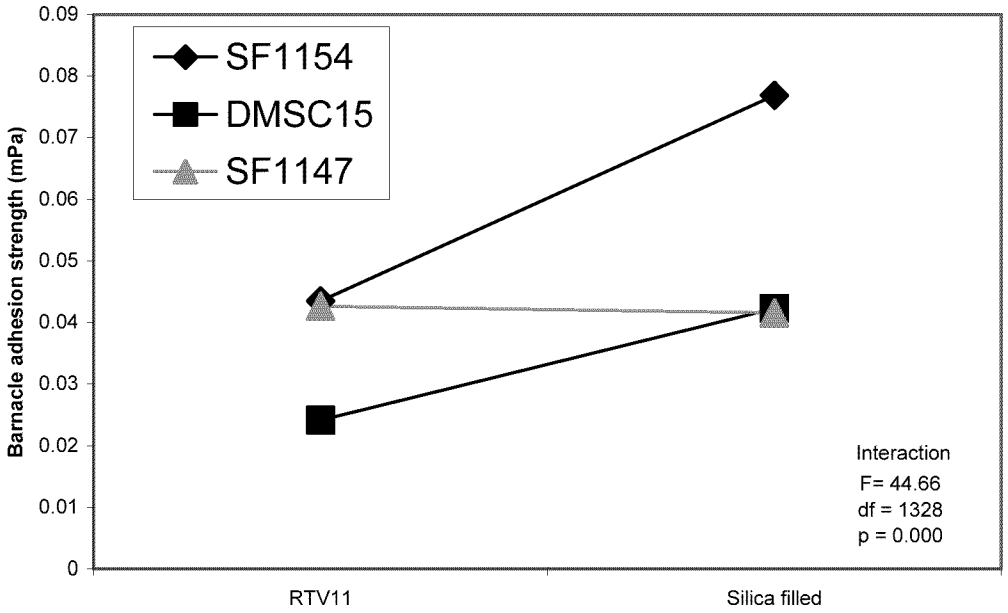


Figure 1.4.2. Interaction plot of barnacle (*balanus eberneus*) adhesion strength vs. coating type at FIT.

Table 1.4.2. Linear regression model for barnacle adhesion strength (*balanus eberneus*) vs. coating type and oil type at FIT.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Oil	2	39.451	45.862	22.931	101.97	0.000
Coating Type	1	15.938	25.174	25.174	111.94	0.000
Oil*Coating Type	2	20.084	20.084	10.042	44.66	0.000
Error	1323	297.518	297.518	0.225		
Total	1328	372.991				

Photographs of the basal plates of barnacles (***b****alanus improvisus*) removed from three different coatings are shown in Figure 1.4.3. It is evident that the morphology of the basal plate is dependent upon the surface from which it was removed. The barnacle basal plate removed from the oil-amended coating was smooth; whereas the basal plate of the barnacle removed from the RTV11® coating has a ringed tree-like structure. Detachment from the copper coated PVC was difficult and resulted in partial fracture within the plate.

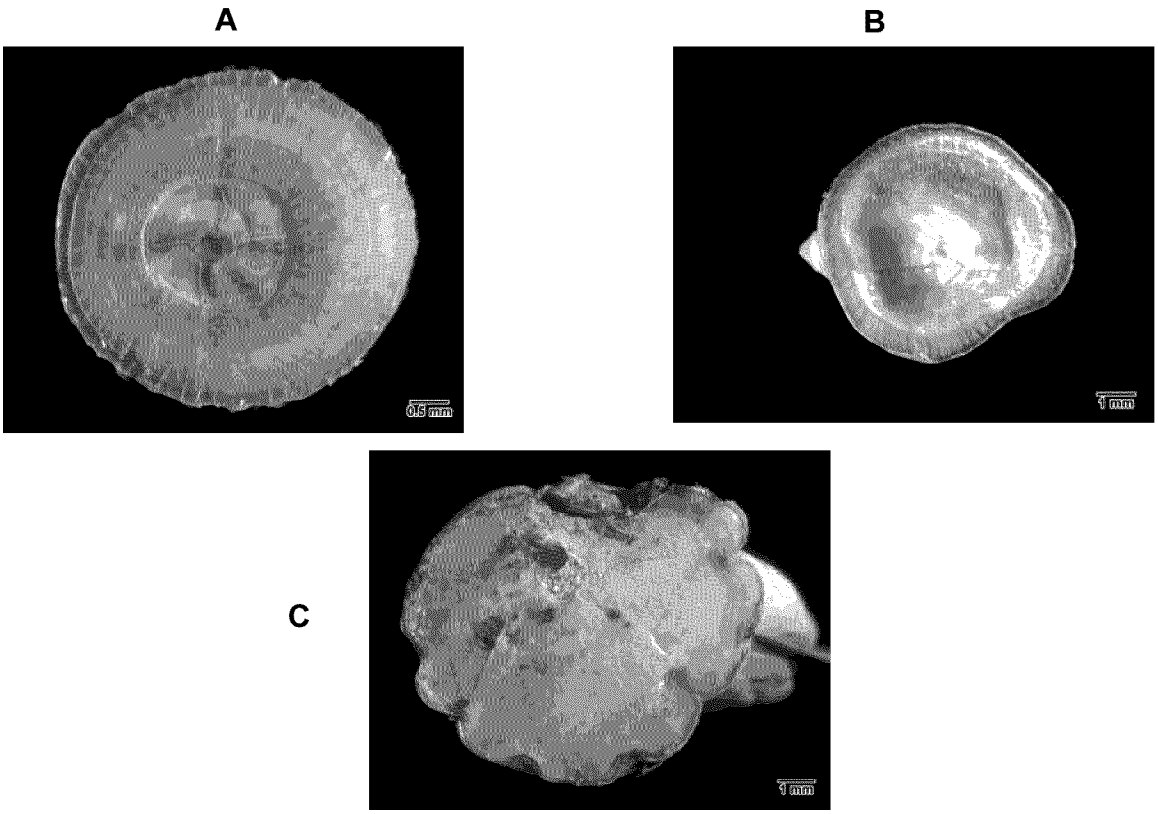


Figure 1.4.3. Barnacle (*balanus improvisus*) basal plates removed from different surfaces at FIT A) RTV11®B) RTV11® with DMSC15 C) Copper coated PVC.

Oyster and Tubeworm Attachment Strengths at FIT

Linear regression analyses of the adhesion strengths of tubeworms and oysters at FIT indicate that both main effects of silicone coating type and oil type are significant (Figures 1.4.4, 1.4.5; Tables 5, 6). Interaction plots for both organisms show a significant dependence on the cross-term of coating type and oil type. As noted previously, the response of the coatings to tubeworms and oysters is quite similar and very different than that of barnacles. The RTV11® coatings always had lower adhesion values compared with silica coatings. For tubeworms and oysters, the RTV11® coating amended with ALTSF1147 had the lowest response; whereas the RTV11® coating containing DMSC15 had the lowest response against barnacles. For both organisms, the silica filled systems amended with SF1154 exhibited the worst performance.

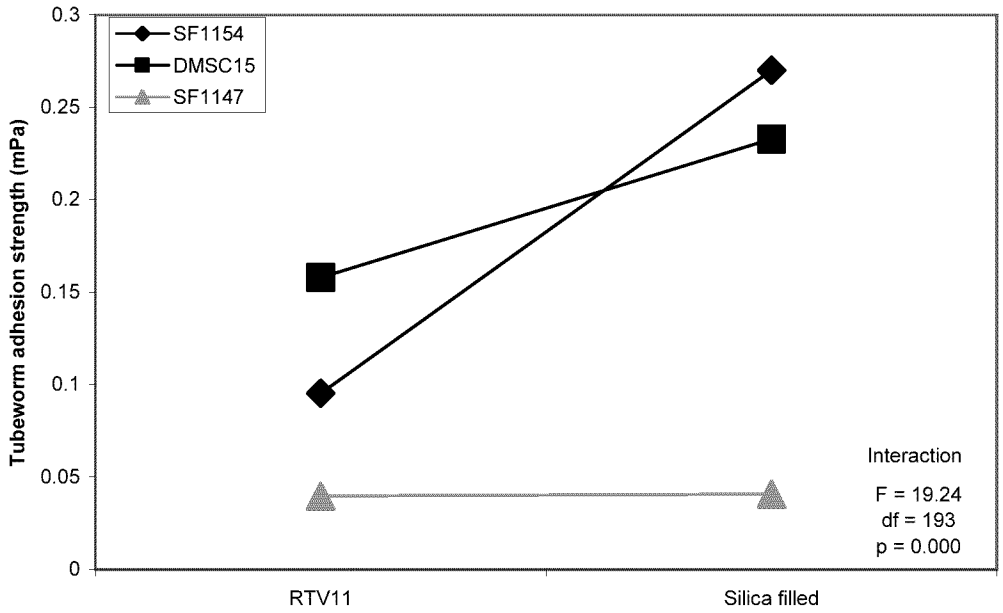


Figure 1.4.4. Interaction plot of tubeworm adhesion strength vs. coating type at FIT.

Table 1.4.3. Linear regression model for tubeworm adhesion strength vs. coating type and oil type at FIT.

Source	DF	Seq. SS	Adj. SS	Adj MS	F	P
Oil	2	76.931	74.774	37.387	241.68	0.000
Coating type	1	5.771	7.741	7.741	50.04	0.000
Oil*Coating type	2	5.953	5.953	2.976	19.24	0.000
Error	188	29.083	29.083	0.155		
Total	193	117.738				

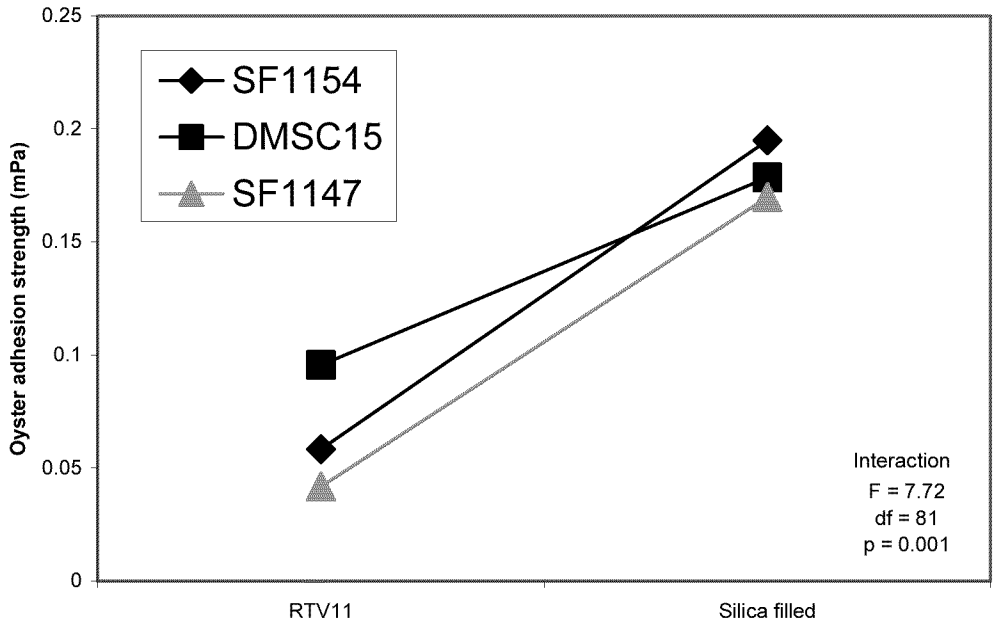


Figure 1.4.5. Interaction plot of oyster adhesion strength vs. coating type at FIT.

Table 1.4.4. Linear regression model for oyster adhesion strength vs. coating type and oil type at FIT.

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
Oil	2	0.9888	0.5359	0.2680	3.72	0.029
Coating Type	1	9.4661	5.6175	5.6175	77.89	0.000
Oil*Coating Type	2	1.1132	1.1132	0.5566	7.72	0.001
Error	76	5.4813	5.4813	0.0721		
Total	81	17.0493				

Oyster and Tubeworm Attachment Strengths at University of Hawaii

Performance of the coatings against tubeworms and oysters in Hawaii showed again that RTV11® systems performed better than silica filled coatings. SF1147 in either coating exhibited the lowest adhesion values. With both organisms, the main effects were significant. However, the interaction term of oil type crossed with coating type was only significant for tubeworms at the 95% confidence level (Figures 1.4.6 and 1.4.7; Tables 1.4.5 and 1.4.6). Interaction plots were similar for both organisms.

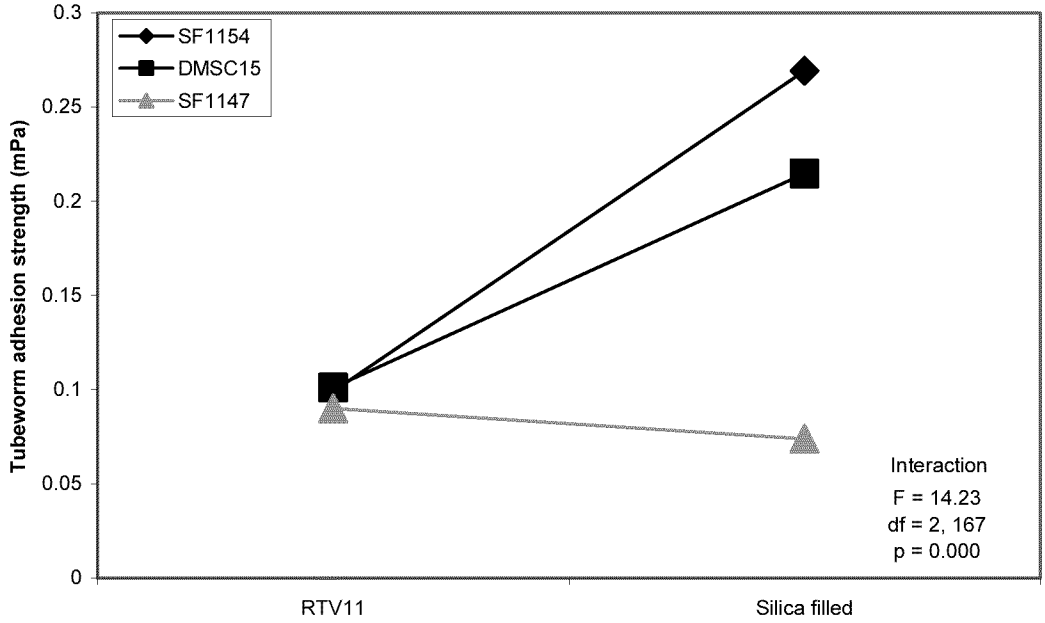


Figure 1.4.6. Interaction plot of tubeworm adhesion strength vs. coating type at University of Hawaii.

Table 1.4.5. Linear regression model for tubeworm adhesion strength (*Hydroides elegans*) vs. coating type and oil type at University of Hawaii.

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
Oil	2	12.1003	14.2154	7.1077	16.75	0.000
Coating Type	1	8.1777	9.7972	9.7972	23.08	0.000
Oil*Coating Type	2	12.0800	12.0800	6.0400	14.23	0.000
Error	162	68.7524	68.7524	0.4244		
Total	167	101.1104				

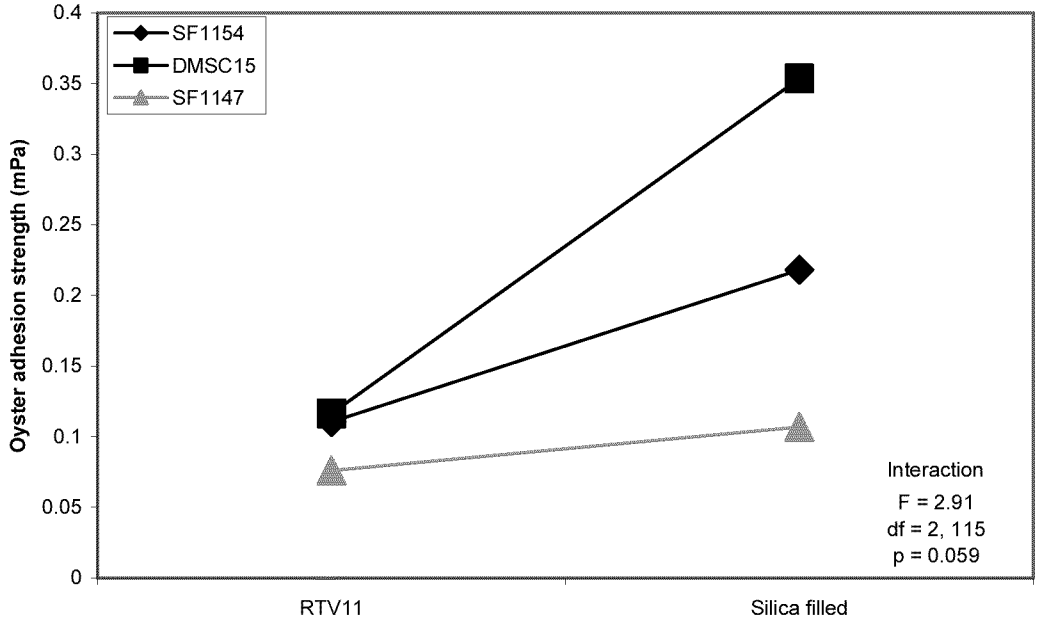


Figure 1.4.7. Interaction plot of oyster adhesion strength vs. coating type at University of Hawaii.

Table 1.4.6 Linear regression model for oyster adhesion strength vs. coating type and oil type at University of Hawaill.

Source	DF	Seq. SS	Adj. SS	Adj. MS	F	P
Oil	2	10.6671	6.8606	3.4303	13.59	0.000
Coating Type	1	13.2648	10.3216	10.3216	40.88	0.000
Oil*Coating Type	2	1.4699	1.4699	0.7349	2.91	0.059
Error	110	27.7725	5.4813	0.0721		
Total	115	53.1742				

Downselected Composition

The composition of the optimal coating with respect to attachment strengths of macrofouling organisms was determined using a Teguchi inner-outer array design analysis of the data. The inner array contained the control factors of oil type and coating type in a full factorial design. The outer array contained the noise factors for organism type and site in a full factorial design. The average of the averages of adhesion values were calculated as well as the average of the averages of the standard deviation (Table 1.4.7). Using this method of analysis the best performance against all organisms at both sites was exhibited by the RTV11® coating amended with SF1147.

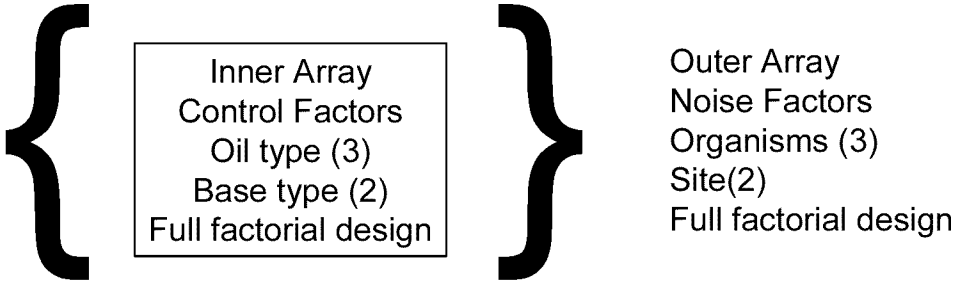
Other attributes of the downselected topcoat (RTV11® + 10% SF1147) are described in later sections. These include:

- Good hydrodynamic performance (Task 2)

- Durable, compatible with tiecoat, repairable, easy to apply (Task 2)
- Toxicity and oil exudates rate within acceptable limits (Task 3)
- Manufacturable- all off the shelf products.

Based upon the above considerations, we have chosen RTV11® + 10% SF1147 as our best performing topcoat.

Table 1.4.7 Teguchi analysis of optimal composition.



panel #	Matrix/Base	Oil	Overall average (mPa)	Overall Standard deviation
2	Calcium carbonate filled	SF1154	0.081	0.021
3	Silica filled	SF1154	0.206	0.043
5	Calcium carbonate filled	DMSC15	0.099	0.027
6	Silica filled	DMSC15	0.204	0.052
7	Silica base	SF1147	0.086	0.017
8	Calcium carbonate filled	SF1147	0.058	0.021

TASK 2. OPTIMIZATION OF PHYSICAL AND APPLICATION PROPERTIES OF THE FOULING COATING SYSTEM

SECTION 2.1 PHYSICAL PROPERTY OPTIMIZATION

The coating systems that were designed during this program were evaluated for physical properties, system (interfacial) adhesion, and recoatability. A requirement of the program was to develop a coating system in which the properties were not compromised by oil inclusion. The final downselected coating (Amerlock 400FD epoxy; SEA210A/SCM501C; RTV11® + SF1147) was evaluated for abrasion resistance using a modified crockmeter before and after 4 months of water immersion. No measurable damage was evident after 1000 abrasion cycles. The system adhesion of the final fouling release coating showed cohesive interfacial failure in peel mode after water immersion 542 ± 17 N/m). The GE repair and recoat package was validated under wet and dry conditions before and after water exposure over all layers of the final downselected fouling release coating system.

INTRODUCTION

Physical properties of the fouling release coatings developed in Task 1 were measured. As the coatings were modified, the physical properties were evaluated to ensure that they were not compromised. Adhesion of the coating system was evaluated using wet and dry peel adhesion methods. A repair and recoat package was developed and tested for adhesion over all layers of the final downselect coating (Amerlock 400FD epoxy; SEA210A/SCM501C; RTV11® + SF1147).

EXPERIMENTAL

Preparation of Samples for Physical Property Testing

The topcoat formulations were comprised of the silicone base, an oil, and catalyst (for example; RTV11® + 10% SF1147 + 0.4% dibutyltindilaurate). The topcoat formulation was thoroughly mixed and poured into Teflon molds (10.1 cm x 12.7 x 0.2 cm). To ensure a uniform thickness, the excess material was removed using a straight edge. After 24 hours at room temperature, the coatings were removed from the molds. The sheets were allowed to cure at ambient temperature for 6 additional days.

Evaluation of Tensile Properties and Tear Sstrength of the Tiecoat and Topcoat

The tensile strength of the coating was determined using the American Society for Testing and Materials method for vulcanized rubber and thermoplastic elastomers (ASTM D412-98). The tensile specimens were cut using a dumbbell die C cutter. The thickness of the test area of each tensile specimen was measured using an Ames Testing Machine, Inc. micrometer. The tear strength of the topcoat material was evaluated using ASTM method D624-98 developed for conventional vulcanized rubber and thermoplastic elastomers. Specimens were cut using a dumbbell die B cutter. The samples were nicked using an H.W.Wallace Tear Test Nicking Cutter Machine model S6/3/6. Tensile properties and tear strength were measured using a Model 4202 Instron.

Tensile Modulus

The dynamic tensile moduli of the silicone elastomers were measured using a Rheometrics Solids Analyzer Model RSA II. Test specimens having nominal dimensions of 1.5 mm x 10 mm x 25 mm were cut from sheets of the silicone. The measurements were performed in tension using the film fixtures. This geometry was found to provide the most reliable data of the various options available. All measurements were performed at room temperature over a frequency range from 0.1 to 100 rad/s with applied strain amplitude of 0.5%.

Abrasion Resistance

Panels for the abrasion resistance testing were prepared using the same method described in Task 1. The coatings consisted of a metal substrate, Amerlock 400 FD epoxy, SEA210A/SCM501C (tiecoat), and RTV11® + oil (topcoat). The abrasion test was performed using an AATCC model CM5 crockmeter modified with a glass stylus. A panel was secured under the stylus and the stylus was cycled 1000 times, after which time the panel was visually inspected for damage. The depth of the abrasion was measured by preparing an epoxy (Buehler Epo-Mix) mold of the scratch. The epoxy was allowed to cure for 24 hours at ambient temperature prior to depth profiling using a Dektak II.

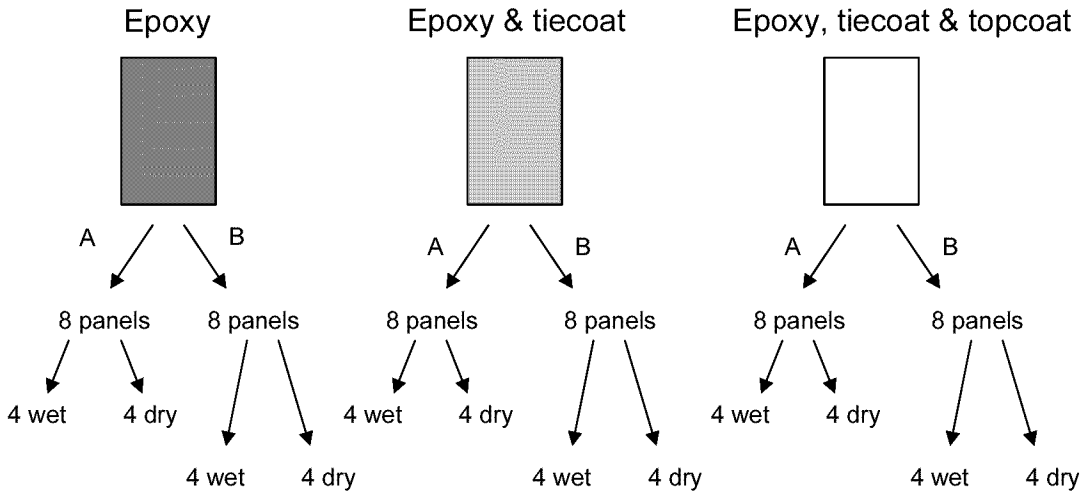
90^{o} Peel Adhesion

Peel adhesion samples were tested using modified ASTM method D429-99 for adhesion to rigid substrates. The coatings were applied to a grit blasted steel plate (15.2 cm x 5.1 cm). After blasting, the steel coupons were wiped with isopropanol and allowed to dry. Coupons were placed on contact paper and both sides were coated with Amerlock 400 FD. The next day the tiecoat was applied over the cured epoxy. A sheet of Osnaburg cloth was brushed with tiecoat and incorporated into the tiecoat layer. After 24 hours, the topcoat was applied.

The coating system was cured at ambient temperature for 7 days after which time the coupons were separated and removed from the contact paper. A set of coupons was immersed for a month in a 38 L aquarium tank with a filled with Milli-Q water. The water was filtered through an activated carbon fish tank filter and the tank contained a bubble aeration system. During coupon incubation, 7.5 L of water were changed once a week. For both dry and wet coupons, a 2.5 cm wide strip was cut in the sample using a 15.2 cm by 2.5 cm template. Each wet coupon was kept immersed until it was tested. Immediately prior to testing, the coupon was wiped dry and cut. The coupon was placed in the peel apparatus and peeled on a 4505 Instron tester. According to the specifications in ASTM D429-99.

Recoat and repair Validation

A test protocol was developed to evaluate the performance of the GE repair/recoat package under wet and dry testing conditions. In addition, the effect of water immersion prior to application of the recoat and repair system was evaluated (Figure 2.1.1). Peel adhesion data were obtained on all possible combinations.



A- Samples were painted, allowed to cure for 21 days and then the repair/recoat system was applied
B- Samples were painted, allowed to cure for 16 day and then were immersed in MilliQ water for 72 hours. The panels were removed from the water, allowed to dry overnight, and then the repair/recoat system was applied.

Figure 2.1.1. Recoat/repair evaluation procedure.

All peel adhesion samples were tested as follows:

1) Surfaces were wiped with naphtha and allowed to air-dry.
2) Repair/recoat package was applied to the surface.
3) Osnaburg cloth was incorporated into the GE repair/recoat package.
4) The repair/recoat package was allowed to cure overnight.
5) The GE topcoat was applied.
6) The same procedure as described for the 90° testing peel testing was followed.

RESULTS

Topcoat Testing

Tensile and tear physical properties of topcoats

Physical property measurements were performed on downselected topcoat formulations and the RTV11® control (Table 2.1.1). Results of measurements on the other topcoat formulations can be found in Appendix 2.A.

Table 2.1.1. Physical properties of fouling release topcoat formulations

Downselect Number	Composition	Tensile Stress (MPa)	Tensile Elongation at Break (%)	Die B tear Maximum Stress (MPa)
1	RTV11®	2.130 ± 0.372	228 ± 42	0.159 ± 0.007
5	RTV11® + 10% DMSC15	1.503 ± 0.965	140	0.172 ± 0.024
8	RTV11® + SF1147	1.703 ± 0.331	186 ±10	0.131 ± 0.006

Tensile modulus of topcoats

The tensile modulus was measured on the downselected topcoats amended with oils and the RTV11® control (Table 2.1.2). The storage modulus of the final downselected composition was equivalent to RTV11®. The storage modulus was dramatically decreased upon inclusion of DMSC15 into the coating. Tensile moduli data on other topcoats can be found in Appendix 2.A.

Table 2.1.2. Tensile moduli for oil amended foul release coatings

DS Number	Composition	Storage Modulus (MPa)	Loss Modulus (MPa)	tan δ
1	RTV11	1.44	0.0182	0.01
5	RTV11 + 10%DMSC15	0.42	0.0100	0.01858
8	RTV11 + 10 %SF1147	1.47	0.0086	0.00592

Coating System Testing

Many tiecoat systems were evaluated during the course of the program. The tiecoat development was initially necessitated because of application failures of the mist coat/Silgan J501 system. A mistcoat elimination/Silgan J501 system was developed that performed well in peel adhesion tests and was subsequently applied to a boat at FIT. Approximately midway through the program, Silgan J501 became commercially unavailable. The use of a commercially available tiecoat was explored. System adhesion was adequate as demonstrated in both field applications and laboratory experiments; however, the tiecoat inhibited topcoat cure. We therefore developed a tiecoat technology based on the SEA210A/SCM501C system that had been previously developed as a repair and recoat package.

System adhesion

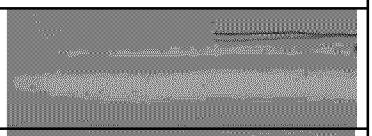
90° peel adhesion samples were prepared with the GE SEA/SCM tiecoat and the following topcoats: RTV11, RTV11 + 10% DMSC15, or RTV11 + 10% SF1147. These samples were tested under dry and wet conditions. Both dry and wet samples failed cohesively within the tiecoat (dry; RTV11- 666 ± 35 N/m, RTV11 + 10% DMSC15- 580 ± 64 N/m, RTV11 + 10% SF1147- 913 ± 55 N/m; wet; RTV11- 538 ± 33 N/m, RTV11 + 10% DMSC15- 400 ± 34 N/m, and RTV11 + 10% SF1147- 540 ± 18 N/m). This data confirmed that the SEA/SCM tiecoat could be used with all three topcoats. Other peel adhesion evaluations can be found in Appendix 2.B.

Abrasion resistance

The abrasion resistance of coatings comprised of RTV11® and 10% oil were evaluated using a modified crockmeter with a glass stylus for 1000 cycles. The abrasion test was used to observe "durability" of the coating systems. The coating containing the DMSC15 oil showed the most damage and the deepest scratch (Table 2.1. 3). A large scratch through the tiecoat was easily observed. The RTV11® control showed little damage and a few 35 μm deep scratches. The coating containing SF1147 oil showed no measurable scratches. A coating containing RTV11® + SF1147 oil was immersed in water for 4

months and followed by abrasion testing. No deterioration in abrasion resistance was seen.

Table.2.1.3. Abrasion damage on fouling release coatings.

Coating System (DS#)	**Abrasion Damage**	**Visual Survey**
Epoxy/ SEA210A/SCM501C/ RTV11® (1)	Over 4 mm scan with 1 scratch of 35 μm by 0.1 mm	
Epoxy/ SEA210A/SCM501C/ RTV11®+10% DMSC15 (5)	Over 6 mm scan entire scratch > 55 μm	
Epoxy/ SEA210A/SCM501C/ RTV11® +10% SF1147 (8)	No measurable change in depth over 6 mm scan	
Epoxy/ SEA210A/SCM501C/ RTV11® +10% SF1147 (8) post immersion	No measurable change in depth over 6 mm scan	

A total of 86 panels with the mist coat/Silgan J501 tiecoat were also evaluated for abrasion resistance. Results are provided in Appendix 2.C.

Recoat and repair package

All recoated samples tested under dry conditions gave good interfacial adhesion regardless of prior water exposure before the application of the repair/recoat package (Figure 2.1.1). Recoated samples exposed to water for 30 days and tested while still wet, demonstrated good interfacial adhesion to all layers with the exception of epoxy which had been immersed in water prior to overcoating. The adhesion of the repair/recoat package may be improved by roughening of the epoxy surface in addition to the solvent cleaning.

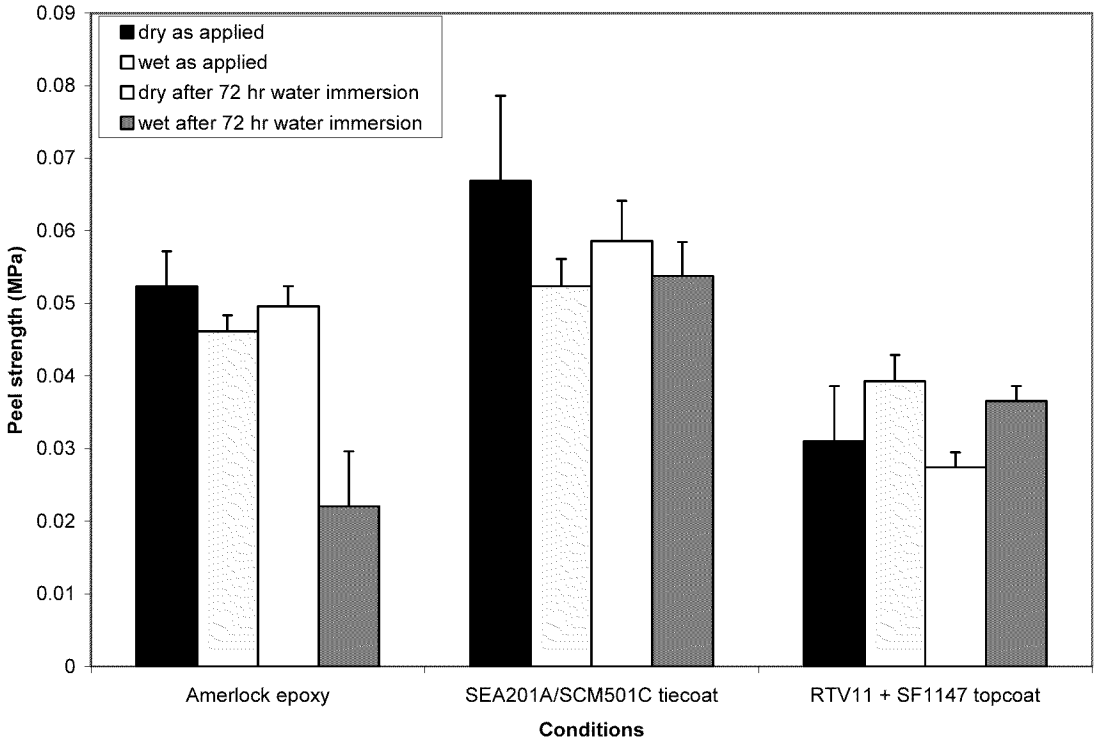


Figure 2.1.1. Adhesion results of repair and recoat system over all layers of the GE fouling release coating.

SECTION 2.1.2 CLEANABLITY OF FOUL-RELEASE COATINGS

Comprehensive contact angle analyses with 12 diagnostic fluids were performed on the RTV11® control, RTV11® + DMSC15 and RTV11® + SF1147 downselected panels both pre and post exposure to freshwater, brackish water, and seawater over periods ranging from 9 month to nearly 4 years. Composite contact angle data plots were similar within each panel data set before and after water immersion. Results of the contact angle experiments demonstrated surface activity of the oil-amended coatings both before and after long-term exposure.

INTRODUCTION

Foul release coatings must have effective lifetimes greater than 5 years. This implies that the surface characteristics of the coating should not degrade over time. Comprehensive contact angle measurements can be employed as a diagnostic tool to monitor changes in surface properties over time. Here we report results of contact angle measurements on pre and post water immersion for RTV11®, RTV11® + DMSC15 and RTV11® + SF1147. Pre exposure contact angles of all evaluated coatings are provided in Appendix 2.D.

EXPERIMENTAL

Contact angle measurements were performed according to literature methods[1]. The diagnostic liquids employed in the contact angle measurements are given in Table 2.1.2.1.

Table 2.1.2.1. Diagnostic liquids employed in comprehensive contact angle analyses.

Liquid	**$\gamma^{l/v}$ (Surface Tension in mN/m)**
water	72.4
glycerol	64.8
formamide	58.9
thiodiglycol	53.5
methylene iodide	49.0
1-bromonaphthalene	45.0
1-methylnaphthalene	39.3
dicyclohexyl	32.7
n-hexadecane	27.6
n-tridecane	26.0
n-decane	23.8
n-octane	21.6

The "advanced" angle technique was utilized throughout the study, whereby the contact angles were measured on each side of the profile of the applied sessile droplet, and again after a second droplet of the same liquid was placed on top of the first, thus advancing the leading edge of the droplet over the surface. All droplets were applied with a freshly flamed platinum wire; the wire was freshly flamed each time another droplet was

retrieved from the liquids' containers. These measures were key in the minimization of degradation of the liquids.

Each liquid was placed on a different spot of the sample surface and measurements of the contact angles of each droplet were made within one minute of applying the droplet. The results presented here are in the form of "Zisman plots" [2], where the cosine of the average contact angle for each diagnostic fluid is plotted against the liquid/vapor surface tension, $\gamma^{l/v}$, of that fluid (i.e. $\gamma^{l/v}$ prior to placement on the sample surface). Although estimates of the coating "critical surface tension"[2], components of surface free energy (e.g. polar and dispersion forces [3]; and acid and base polar components [4] can be made from these measurements, the nonequilibrium natures of several of the fluids on these samples strongly warns against placing much emphasis on critical surface tensions and surface energies.

Observations of droplet stability (or lack of stability) on the sample surface were recorded for each fluid. Unstable conditions due to surface activity were noted by droplet "creep" (decrease in contact angle one minute or less after application), or by droplet "kickback" on the platinum wire when the 2nd droplet was brought into contact with the droplet of fluid already on the surface. Observations of swelling were made based on a large increase in apparent contact angle when the 2nd droplet was placed on top of the first droplet and visible signs of coating swelling when the fluid was wicked from the surface.

Pre-exposure panels were received from GE, and post-immersion panels were received from Hawaii, Florida, and Massachusetts. A description of the immersion sites can be found in Task 1. Once received in the laboratory in Buffalo, fouling-free areas of the coated panels were identified by visible inspection. These areas were cleaned a second time, using a water-wet cleanroom wipe and moderate hand pressure, which removed loose dust or debris that may have fallen on the panel during storage or shipping, as well as most microscopic organisms and biological films. Any excess water remaining on the cleaned areas was soaked off the panel with a fresh cleanroom wipe. Comprehensive contact angle analyses were not performed until at least one hour after the wiping procedure. Coated panels were stored under ambient laboratory conditions throughout the study.

RESULTS

The contact angle data are presented from two points of view: first, as measured "apparent" contact angles, regardless of any observed instabilities and, second, in terms of observations of nonequilibrium behavior of the carefully selected fluids on the coatings.

Using the apparent contact angle, composite contact angle data plots are shown in Figures 2.1.2.1-3. On average, the post-exposure RTV11® standard coatings, cleaned of fouling, gave contact angles similar to those on the pre-exposure coating (Figure 2.1.2.1). Average water and glycerol contact angles on RTV11®-coated panels from the New York

and Hawaii sites were lower than on other panels characterized in the RTV11® sample set.

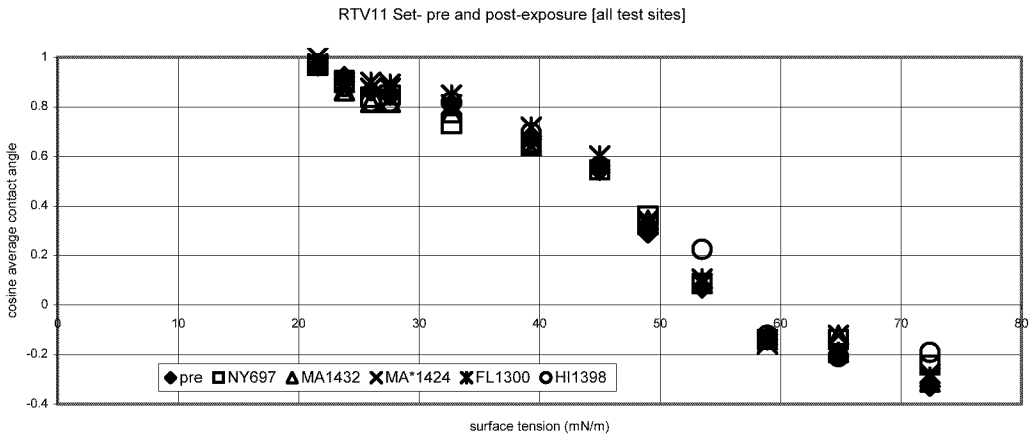


Figure 2.1.2.1. Average pre- and post-exposure contact angle data for the RTV11® standard coating. The symbol key indicates pre-exposure data and field site immersion duration (e.g. FL1300 = Florida site, 1300 days). The MA* site had more consistent and higher salinities than the MA site.

Effects of the "hydrophilic" DMSC15 oil in the RTV11® + DMSC15 sample set (Figure 2.1.2.2) are clear. The more polar diagnostic fluids (water, glycerol, formamide, thiodiglycol) had significantly lower contact angles on DMSC15-containing coatings than on coatings without this particular oil (Figures 2.1.2.1, and 2.1.2.3). For the RTV11® set, however, the average observed contact angles on cleaned, post-exposure RTV11® + DMSC15 coatings were very similar to contact angles of droplets on the DMSC15-containing coating prior to immersion.

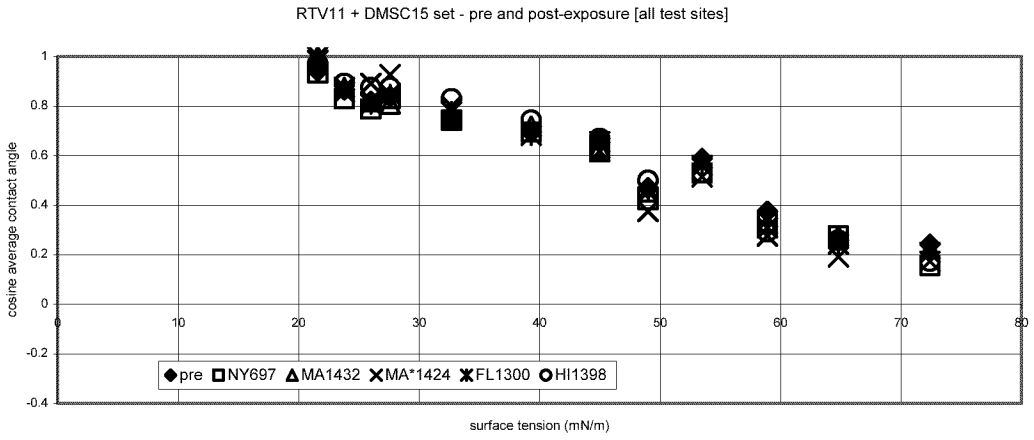


Figure 2.1.2.2. Average pre- and post-exposure contact angle data for the RTV11® coating amended with 10 wt% DMSC15 oil

In Figure 2.1.2.3 (RTV11® with SF1147 oil), the only significant departures from the pre-exposure coating and most of the post-exposure coatings occurred with several fluids on panels from the higher salinity Massachusetts site. Most of the contact angles measured on the RTV11 + SF1147 set were similar to results obtained for the RTV11® standard samples (compare Figure 2.1.2.3 with Figure 2.1.2.1).

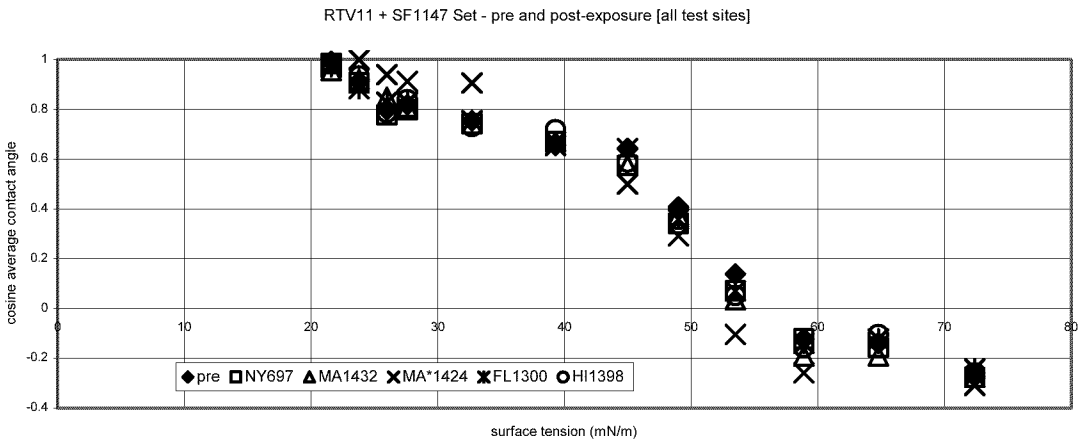


Figure 2.1.2.3. Average pre- and post-exposure contact angle data for the RTV11® coating amended with 10 wt% SF1147 oil.

Surface activity, indicated by droplet creep and/or droplet "kickback", of pre- and post-exposure DMSC15-amended RTV11® coatings was revealed by polar-force-dominated fluids (water, glycerol, formamide, thiodiglycol), as well as by bromonaphthalene, methylnaphthalene, and dicyclohexyl (Figure 2.1.2.2). However, the post-exposure RTV11® + DMSC15 coatings, also demonstrated surface activity in contact with two of the lower surface tension fluids, n-hexadecane and n-tridecane.

The surface-active responses of RTV11® standard and RTV11® with SF1147 oil were very similar (Table 2.1.2.2). Pre-exposure coatings of both types caused droplet creep and/or kickback when in contact with bromonaphthalene and methylnaphthalene. The pre-exposure RTV11 + SF1147 coating also caused instability of thiodiglycol. After long-term exposure, both coatings elicited interfacial instability of glycerol, thiodiglycol, dicyclohexyl, and n-hexadecane, as well as the two naphthalenes.

Table 2.1.2.2. Lowest liquid/vapor surface tension (mN/m) of diagnostic fluid displaced by droplet already on coating ("kickback").

Sample Set	Pre-Exposure Coating	Post-Exposure Coating*
RTV11® standard	39.3	27.6

RTV11® + DMSC15 oil	32.7	26.0
RTV11® + SF1147 oil	39.3	27.6

* for post-exposure sets, droplet kickback was observed on test panels from at least three of the five field sites.

Similarities in the apparent contact angles, without consideration of any observed instabilities on the pre- and post- water exposure panels indicated that the surface properties were largely unchanged. Small increases in surface activity were observed after water exposure of the coatings. The RTV11® and RTV11® + SF1147 had similar surface chemistries, whereas the response of the RTV11® + DMSC15 panel set was unique.

References

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2. Zisman, W. A. *Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution*; American Chemical Society: Los Angeles CA, 1963; Vol. 43, pp 1-52.
3. Kaelble, D. H. and Moacanin, J., *Polymer*, **18,** 475 (1977).
4. Van Oss, C. J., Chaudhury, M. K., and Good, R. J., *Langmuir*, **4**, 884 (1988).

SECTION 2.2 FIELD DEMONSTRATIONS

Field test were performed to evaluate coatings under real world conditions. Coatings were applied to bilge keel panels, flow channel panels, four small craft hulls and two submarines. Bilge keel and flow channel panels performed well with good fouling release. Some of the panels and submarine patches experienced delamination of the coating when Silgan J501 was used as the tiecoat. This was addressed by replacing the Silgan J501 with the SEA210A/SCM501C system for the final applications. RTV11® with 10% SF1147 topcoat was applied to two small research vessels; in one case over a commercial tiecoat and in the other case over the final downselected tiecoat, SEA210A/SCM501C.

Panel testing of the fouling release formulations using the through hull drag and fouling release meter revealed relationships between the Navy fouling rating and drag, as well as drag with coating condition. The panel drag increased with an increasing Navy fouling rating. The panel drag was also affected by the coating condition. RTV11® + 10% SF1147 panels in side-by-side tests with the commercial panels were shown to perform better based on fouling-release.

A 22 foot T-Craft power boat was coated with the RTV11® + 10% DMSC15 fouling release formulation in June of 1998, and has since been monitored for biofouling, hydrodynamic self cleaning and powering efficiency. It was found that during periods of low usage, the hull became fouled by both hard and soft organisms. The initial power trials demonstrated that a high percentage of the fouling was removed at high speed (24 knots) and that drag penalties were negligible.. After three years, the RTV11® + DMSC15 topcoat showed a decrease in the fouling release properties which was reflected by a reduction in performance as measured by subsequent power trials. The coating was still in good condition with no blistering, delamination or peeling. The boat was recoated in Augus tof 2000 with the final downselected system SEA210A/SCM501C tiecoat with RTV11® + SF1147 topcoat.

INTRODUCTION

A variety of field demonstrations and validation tests were undertaken during this program. The performance of the foul-release coatings was evaluated on the bilge keels of operational naval vessels. The fouling release capability was also measured in the Naval Research Laboratory's flow channel at Key West, Florida. The hydrodynamic cleanability of these coatings was evaluated using a though hull drag and fouling release meter. Test coatings were also applied as patches on Trident submarines and on small research vessels. These applications were an opportunity to explore the scalability and ease of application of the coating system, as well as assess the fouling release capability of the topcoat.

EXPERIMENTAL

Panel Preparation

Duplex system

Airless spray equipment was used for all applications. The surface of test panels was grit blasted to near white metal. An anticorrosive layer of Amerlock 400 was applied (5-7 mil wet film thickness (wft)) to both sides of the panels (Table 2.2.1). The next day, the mistcoat was formulated and applied. The mistcoat was prepared by mixing the Epon and the Versamid and allowing the mixture to react for 15-20 minutes. Butanol was added and the mixture stirred occasionally until the emulsion became clear(about 45-60 minutes). The mistcoat was applied at about 2-3 mils wft. This layer was allowed to cure until the mistcoat became tacky (approximately 30-60 minutes). The Silgan J501 tiecoat was applied (10-12 mil wft). The Silgan J501 was allowed to cure until it was tack-free (15-60 minutes) after which the topcoat was mixed and applied.

Table 2.2.1 Examples of the formulations for the duplex, mistcoat elimination, and final downselected coating systems.

System Layer	Duplex Coating System	Mistcoat Elimination System	Final Downselected System
Anticorrosive	19 l Amerlock 400 + 0.5 l lacquer thinner	19 l Amerlock 400 + 0.5 l lacquer thinner	19 l Amerlock 400 + 0.5 l lacquer thinner
Mistcoat or Mistcoat Elim	1.9 l Henkel Versamid + 1.9 l Shell Epon 828 + 3.8 l butanol	15.1 l Amerlock 400 + 1.9 l GE SCM501C	
Tiecoat	19 l Wacker Silgan J501 + 3.8 l GE SF69	19 l Wacker Silgan J501 + 3.8 l GE SF69	12.8 l GE SEA210A + 4.5 l R7 K27 Thinner K27 + 3.6 l VM&P Naphtha + 0.68 l GE SCM501C
Topcoat	19 l GE RTV11® + 1.9 l oil + 3 l VM&P Naphtha + 60 ml DBTDL	19 l GE RTV11® + 1.9 l oil + 3 l VM&P Naphtha + 60 ml DBTDL	19 l GE RTV11® + 1.9 l SF1147 + 3 l VM&P Naphtha + 60 ml DBTDL

Mistcoat elimination / Silgan J501

The surface of the metal was prepared and Amerlock epoxy applied as described above for the mistcoat system (Table 2.2.1). Next the mistcoat elimination layer was mixed which consisted of Amerlock 400 or 400FD epoxy and 20% GE SCM501C. This layer was applied at 12-14 mils wft. The Silgan J501 and the topcoat were applied as described above.

SEA210A/SCM501C tiecoat, and repair and recoat

The preparation of panels with the final downselected system involved surface preparation and Amerlock epoxy application as described in the mistcoat application above (Table 2.2.1). The tiecoat, comprised of SEA210/SCM501C and thinner, was applied directly to the epoxy. The topcoat could be applied as soon as the tiecoat was tack-free or any time up to 48 hours thereafter.

Topcoat bases

Topcoats comprised either RTV11® or a silica-filled base amended with oils and catalyzed with dibutyltindiluarate. Silica-filled masterbatches were prepared according to

literature methods (U.S. Patent 5,906,893). To 40 g of the resultant masterbatch was added 53 g of silanol terminated polydimethylsiloxane (MW = 40,000, 1.3 millimoles), 6 g propylsilicate (0.23 moles) and 1 g of silanol terminated polydimethylsiloxane (MW = 500, 2 millimoles). To 100 g of the above mixture was added 10 g of the appropriate oil. The oil-amended coating was catalyzed with 0.9 g dibutyltindilaurate (1.3 millimoles). The topcoat was applied at a wet film thickness of the 0.25-0.30 mm (10-12 mil). After 7 days of cure time, the panels were submitted to sites for exposure.

Navy Fouling and Paint Deterioration Rating

Shipboard test coating systems were evaluated using the fouling ratings (FR) and paint deterioration ratings (PDR) presented in the Naval Ships' Technical Manual (NSTM), Chapter 081. The FRs and PDRs are separate scales, each comprised of 11 ratings: 0 to 100. A rating (FR or PDR) of zero is the best performance; a rating (FR or PDR) of 100 is indicative of the worst condition. This evaluation method consisted of a narrative description and a photograph at each of the rating levels. The original FRs and PDRs were modified slightly to better accommodate silicone-based foul release coating systems. The narrative descriptions of both scales are shown in Tables 2.2.2 and 2.2.3.

Table 2.2.2. Proposed new Fouling Ratings (FR) descriptions.

FR	DESCRIPTIONS
	NO FOULING ON SUBSTRATE
0	A clean, foul–free surface
	SOFT FOULING ONLY (3 levels)
10	Continuous graduations of shades of green (incipient slime)
20	Slime as dark green patches with yellow or brown colored areas (advanced slime)
30	Grass as filaments up to 3 in. (76 mm) in length, projections up to ¼ in. (6.4 mm) in height; or a flat network of filaments, green, yellow, or brown in color
	HARD FOULING BUT NOT COMPLETE COVERAGE OF SUBSTRATE (3 levels)
40	Calcareous fouling on edges, welded seams, corners, or as discrete patches covering flat areas roughly 9 to 10 in. (229 to 254 mm) in diameter
50	Random and scattered tubeworms or barnacles (or both) on slightly curved or flat surfaces
60	Area distribution of tubeworms or barnacles, ¼ in. (6.4 mm) in diameter or less; fouling does not completely cover or blank out surface
	SUBSTRATE NOT VISIBLE; COMPLETE COVERAGE BY HARD FOULING (4 levels)
70	Tubeworms and barnacles completely cover surface in patches exceeding 9 to 10 in. (229 to 254 mm) in diameter. Tubeworms lying flat with radiating fringes of growth or barnacles ¼ in. (6.4 mm) in diameter or less
80	Tubeworms closely packed together and growing upright away from surface. Barnacles growing one on top of another. Calcareous shells appear clean or white in color
90	Dense growth of tubeworms with barnacles ¼ in. (6.4 mm) in diameter or greater. Calcareous shells brown in color or with slime or grass overlay
100	All forms of fouling present, particularly soft sedentary animals without calcareous covering (tunicates)

Table 2.2.3. New and old Paint Deterioration Ratings (PDRs).

PDR		New Description	Old Description
New	Old	NO PHYSICAL DAMAGE; COATING SYSTEM INTACT	
0	10	No physical damage; entire coating system intact	AF paint intact, red in color or with mottled pattern of light green or red
		INTERCOAT PHYSICAL DAMAGE; STEEL SUBSTRATE NOT EXPOSED	
10	20	Less than 10% of the area shows physical damage (abrasion, delamination, broken blisters, etc.) to topcoats exposing intact AC	AF paint missing from edges, corners, seams, welds, rivet or bolt heads to expose AC paint
	30		AF paint missing from slightly curved or flat areas to expose AC paint
20	40	From 10 to 50% of the area shows physical damage (abrasion, delamination, broken blisters, etc.) to topcoats exposing intact AC	AF paint missing from intact blisters to expose AC paint
	50		AF blisters ruptured to expose intact AC paint
30	60	More than 50% of the area shows physical damage (abrasion, delamination, broken blisters, etc.) to topcoats exposing intact AC	AF/AC paint missing or peeling to expose steel substrate, no corrosion present
		PHYSICAL DAMAGE DOWN TO EXPOSED STEEL SUBSTRATE	
40	70	Less than 10% of the area shows physical damage (abrasion, broken blisters, etc.) exposing steel substrate; corrosion may be present	AF/AC paint removed from edges, corners, seams, welds, rivet or bolt heads to expose steel substrate with corrosion present
50	80	From 10% to 50% of the area shows physical damage (abrasion, broken blisters, etc.) exposing steel substrate; corrosion may be present	Ruptured AF/AC blisters on slightly curved or flat surfaces with corrosion and corrosion stains present
60	90	Greater than 50% of the area shows physical damage (abrasion, broken blisters, etc.) exposing steel substrate, corrosion may be present	Area corrosion of steel substrate with no AF/AC paint cover because of peeling or abrasion damage
	100		Area corrosion showing visible surface evidence of pitting, scaling, and roughening of steel substrate

Bilge Keel Evaluation

The preparation of all panels is described above. A total of 4 test panels of each composition were fastened to the bilge keel of a Navy ship: 2 on the port side and 2 on the starboard side. Inspections were scheduled yearly, but were subject to ship availability.

Flow Channel Evaluation

Flow channel evaluation was performed at the Navy Research Laboratory, Key West facility (NRLKW). Panels were exposed in Biscayne Bay, Florida for 17 weeks (December 1998 to April 1999) in the horizontal face down configuration. After exposure, the panels were transported to NRLKW in fresh seawater collected at Biscayne Bay. Following arrival at the facility, the tank containing the panels was slowly flushed

overnight with natural seawater from Key West to preserve fouling organisms. The following morning, the panels were installed in the flow channel and dynamic testing initiated. Dynamic testing was performed using a flow of 37 km/hr and 55.5 km/hr. Coatings were evaluated for the removal of fouling.

Through Hull Drag and Fouling-Release Meter

An instrument was developed to measure the drag forces due to roughness and fouling, and the fouling-release on a standard 0.254 m x 0.305 m static immersion panel[1]. The instrument consisted of a floating-element drag meter, a pitot static tube, and a video camera (Figures 2.2.1 and 2.2.2).

The test panels were mounted on a portal-type floating-element force balance, which was built into the instrument box[2] (Figures 2.2.1 and 2.2.2). There was a 3 mm gap around the test panel. The force gage used 4 foil strain gages connected in a full bridge circuit that created a linear voltage response that was insensitive to moments. A pitot-static probe extended above the test section to measure the dynamic pressure that was used to determine the free stream flow velocity, using Bernoulli's equation. A video camera was mounted adjacent to the test section to record the condition of the fouling community and real-time fouling-release.

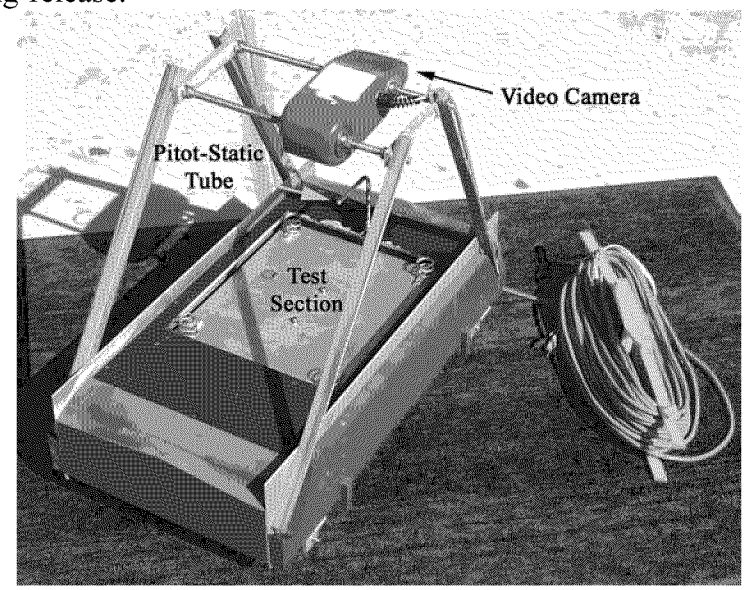


Figure 2.2.1. Through-hull drag and fouling-release meter

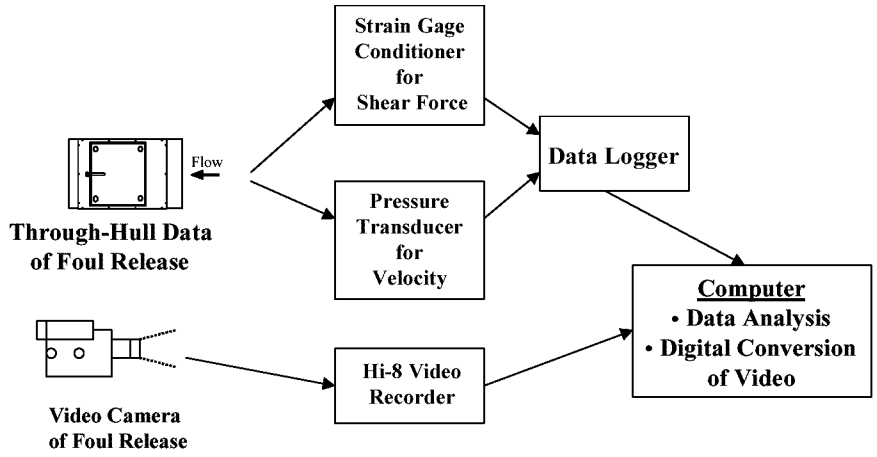


Figure 2.2.2. Schematic of through-hull drag and fouling-release testing system

The instrument was lowered into a wet-well, which was built into the deck of a 6.5 m powerboat (Figure 2.2.3). The front of the well was 3.2 m from the bow. The test section formed an integral part of the hull with minimal disturbance to the flow[3]. The system was capable of operation at velocities up to 12 m/s. The force gage measured the shear force due to the flow over the test surface at different velocities.
Instrumentation on the boat included a datalogger to record the drag forces on the panels and the free stream velocity. A digital video recorder provided real-time images of fouling-release with the force and velocity data overlaying the image. The instrument calibration was performed according to literature methods[3].

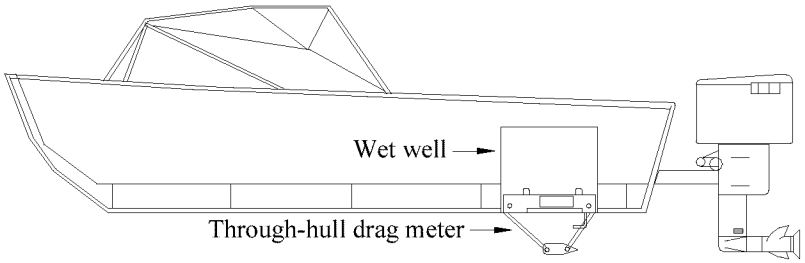


Figure 2.2.3. Longitudinal cross-section of powerboat with through-hull test system.

Panel evaluation using the through hull drag meter
The panels were exposed to fouling at the Florida Institute of Technology Static Immersion site in the Indian River Lagoon. The panels were caged to exclude fish and other organisms that have been shown to remove fouling[4]. The coatings were visually inspected for fouling and physical condition in accordance with ASTM D3623[1]. The fouling on the panels was rated using the U.S. Navy Ships' Technical Manual Rating for a ship's hull, which is used to determine the cleaning cycle of a copper-based antifoulant (Table 2.2.2). This method gave a fouling rating (FR) based on a description of the surface. The fouling-release properties were quantified by measuring the shear adhesion

strength of barnacles to the panels as described in Task 1.

The drag and fouling-release properties of each panel were measured using the through hull meter described above. Fouling was cleaned from one side of the panel and the panel mounted on to the force balance. Care was taken to ensure minimal disturbance of the fouling on the test side, and that the panel was flush with the instrument surface. The meter was then placed in the wet well and the instrumentation zeroed to confirm that all of the devices were working properly. The panel was tested at boat speeds of 2, 4, 6, 8, and 11 m/s for a period of one minute at each velocity, during which video, water velocity and drag were recorded. This provided data on fouling release and drag penalties. The test panel was run again at increasing velocities up to 11 m/s to observe changes in drag due to the loss of fouling that occurred during the first run. Finally, the panel was totally cleaned and reevaluated at increasing velocities up to 11 m/s. This provided data to compare between the drag forces of the fouled and hydrodynamically cleaned surfaces to the mechanically cleaned surface. The drag and velocity data were superimposed on the video to enable monitoring of fouling-release at each velocity. The seawater temperature and salinity were measured to determine density and kinematic viscosity.
It is important to note that testing was only undertaken under weather conditions of l less than 0.1 m chop and less than 2.5 m/s wind velocity, in order to minimize errors in flow around the hull.

T-Craft Power Trials

A T-Craft vessel stationed at FIT was painted with Amerlock 400, mistcoat or mistcoat elimination system, Silgan J501, and RTV11® + 10% DMSC15. The biofouling and physical condition data were obtained by analyzing underwater videos of the boat hull. The videos were taken in combination with a measuring tape. This enabled the exact location on the hull to be known. The video was made along the length of the hull for each of the four chines per side and the water line. Biofouling and physical condition were assessed for every 30.5 cm length of hull.

Four power trails were run to evaluate the hydrodynamic performance of the coating both with respect to fouling-release and drag, using the following procedure:

1. Fill fuel tanks to full capacity.
2. Perform underwater video inspection of the hull.
3. Run power trials, starting at about 2 knots. Maintain speed for 2 minutes. Monitor speed and rpm. Increase speed and repeat data collection up to speeds of about 22 knots.
4. Run the boat at top speed (up to 28 knots) for 20 minutes (self cleaning).
5. Perform underwater video inspection of the hull.
6. Run power trials, starting at about 2 knots. Maintain speed for 2 minutes. Monitor speed and rpm. Increase speed and repeat data collection up to speeds of about 22 knots.
7. Perform underwater video inspection of hull.
8. Take underwater hard fouling adhesion measurements.
9. Perform in-water cleaning of hull using a soft cloth.

10. Run power trials, starting at about 2 knots. Maintain speed for 2 minutes. Monitor speed and rpm. Increase speed and repeat data collection up to speeds of about 26 knots.
11. Analyze the boat power data to estimate performance.

RESULTS

Validation Applications

Coatings were applied to 4 small test patches on Trident submarines and 3 small boats (Table 2.2.4). The recoat and repair package was also applied to the FIT boat. Complete trip reports are included in Appendix 2E.

Table 2.2.4. Field applications of the GE fouling release coatings. Yellow highlights indicate the downselected coating system.

Application	Topcoat	Tiecoat	Date	Area (m^2)	Results
Trident Submarine Patches (3) USS Nevada	RTV11® + 10% DMSC15 RTV11® + 10% SF1154 RTV11® + 10% DBE224	J501 w/ mistcoat	Aug 97	9.29	100% delamination
Trident Submarine Patch USS Nevada	RTV11® + 10% DMSC15	J501 w/ mistcoat	Aug 99	9.29	65% delamination
FIT boat # 1	RTV11® + 10% DMSC15	J501 w/ mistcoat and mistcoat elim	June 98	9.29	Success 3 yrs
FIT boat # 2	RTV11® + 10% SF1147	Commercial tiecoat	Jan 00	8.36	Success 1½ yrs (still in service)
FIT boat # 3	RTV11® + 10% SF1147	GE SEA210A/ SCM501C	July 00	13.93	Success 1 yr (still in service)
FIT Boat # 1 (recoat)	RTV11® + 10% SF1147	GE SEA210A/ SCM501C	July 01	13.93	Success

Bilge Keel Panels

Panels were deployed along the bilge keel of three active Navy vessels (Table 2.2.5). The results of this evaluation showed good fouling rating and paint deterioration rating for all coatings.

Table 2.2.5. Deployment and results of bilge keel panels. Yellow highlights indicated final coating composition.

Application	Topcoat	Tiecoat	Deployed	Results

Bilge Keel	RTV11® + 10% DMSC15	J501 w/ mistcoat	USS John Paul Jones- May 99 USS Thomas Gate – July 01	FR – 40 PDR – 0 FR – 10 PDR – 0
		Commercial	USS Thomas Gate - July 01	
	RTV11® + 10% SF1154	J501 w/ mistcoat	USS Paul Foster - Feb 01	FR – 10 PDR – 0
		Commercial	USS Thomas Gate - July 01	
	RTV11® + 10% SF1147	J501 w/ mistcoat	USS Paul Foster - Feb 01	FR – 10 PDR – 20 delamination
		Commercial	USS Paul Foster - Feb 01	FR – 10 PDR – 0
		GE SEA210A/ SCM501C	USS Thomas Gate -July 01	

Flow Channel Evaluation

Panels in the flow channel at NRL performed well after one fouling cycle. Both of the coatings released greater than 90% of the fouling (Table 2.2.6). One coating showed delamination this has been addressed by the use of an alternative tiecoat.

Table 2.2.6. Panels tested at the NRL Key West flow channel.

Application	**Topcoat**	**Tiecoat**	**Deployed**	**Results**
Flow Channel	RTV11® + 10% DMSC15	J501 w/ mistcoat	Nov 98 inspected May-99	99% fouling release @ 20 kts
				99% fouling release @ 30 kts
	RTV11® + 10% SF1147	J501 w/ mistcoat	Nov 98 inspected May-99	90% fouling release @ 20 kts 30% delamination
				90% fouling release @ 30 kts 40% delamination

Through Hull Drag and Fouling-Release Meter

Results are presented for 3 GE and 1 commercial prototype silicone fouling-release formulations (Table 2.2.7). Where replicate panels were available, the coatings were tested at different time intervals of static immersion.

Table 2.2.7. Test panel identification

Tiecoat	**Formulation**	**Days Exposure**
Mistcoat/Silgan J501	RTV11®	686
Mistcoat/Silgan J501	RTV11® + 10% DMSC15	603
Commercial tiecoat	RTV11®+ 10% SF1147	45, 65, 135, 225, 322, and 603

	Complete commercial system	45, 65, 135, and 225

The fouling communities typically consisted of barnacles, tubeworms, bryozoans, sponges, silt and slime. There was considerable variation in the fouling cover among coatings (Navy fouling rating ranged from 40 to 100). The biological communities were influenced by exposure time and seasonal differences in the natural populations.

The drag forces generated by the fouled, hydrodynamically cleaned, and cleaned conditions for two of the panels exposed for 45 days are shown in Figures 2.2.4 and 2.2.5. Selected images showing the fouling on the panels before hydrodynamic testing and after running at 4, 8 and 11 m/s, are shown in Figure 2.2.6. All soft fouling became detached from the panels after 6 m/s and barnacles, tubeworms, and encrusting bryozoans were shown to release throughout testing. However, after 11 m/s, some tubeworms and an area of encrusting bryozoans remained on the commercial sample. The starting FR for RTV11® + SF1147 and the commercial coating were 50 and 75 respectively. After running at 11 m/s these were reduced to 35 for RTV11® + SF1147 and 45 for the commercial system. The drag forces directly reflected the fouling communities present on the surfaces, and it was clearly seen that increases in drag due to fouling were greater for the commercial coating.

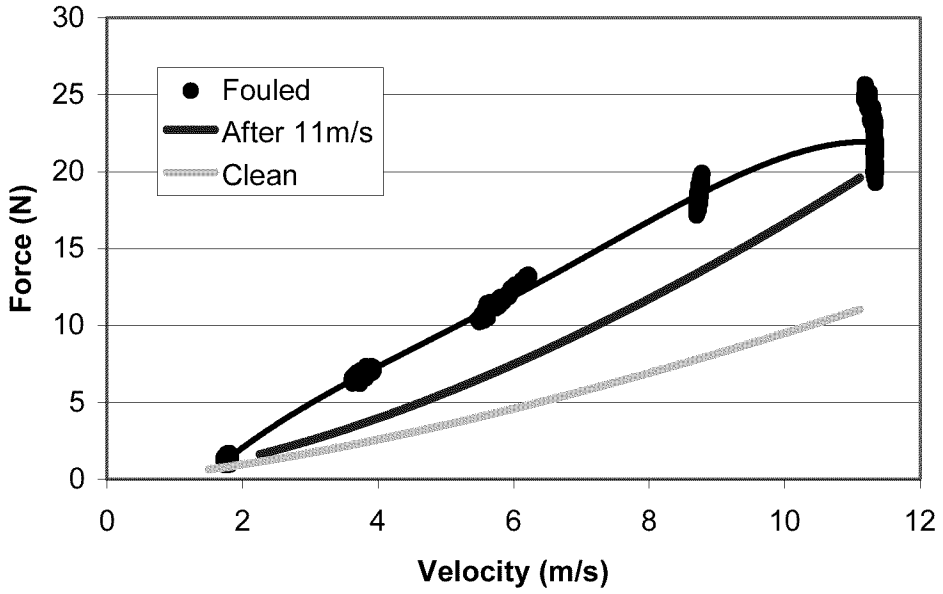


Figure 2.2.4. Skin friction drag curves of a fouling-release surface RTV11 + SF1147 (45 days).

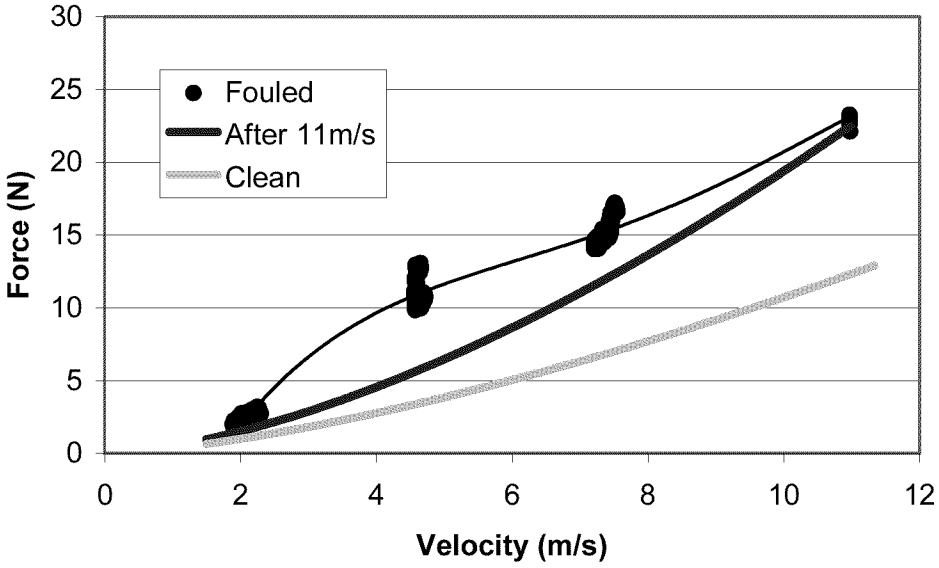
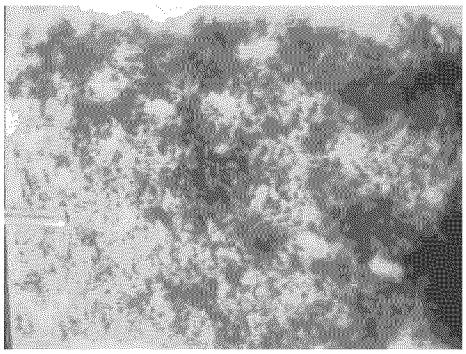
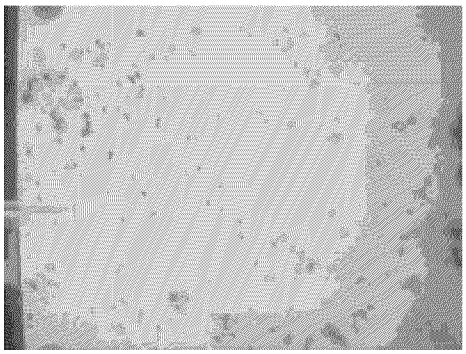


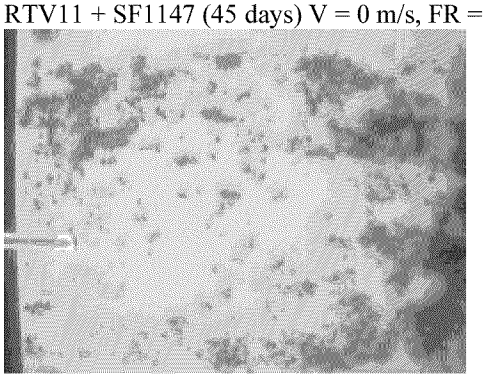
Figure 2.2.5. Skin friction drag curves of a fouling-release surface commercial coating (45 days).



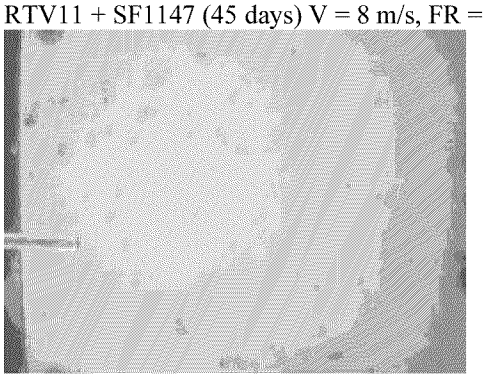
RTV11 + SF1147 (45 days) V = 0 m/s, FR = 50



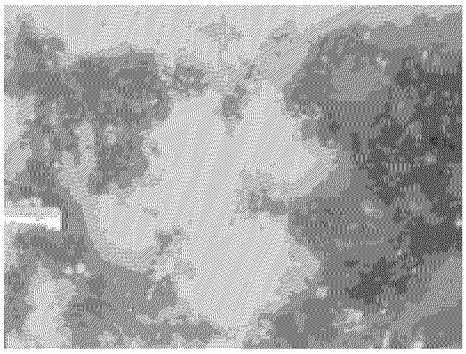
RTV11 + SF1147 (45 days) V = 8 m/s, FR = 40



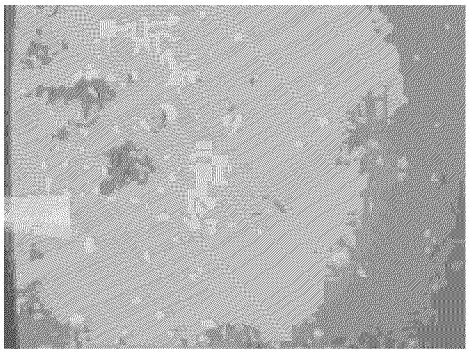
RTV11 + SF1147 (45 days) V = 4 m/s, FR = 45



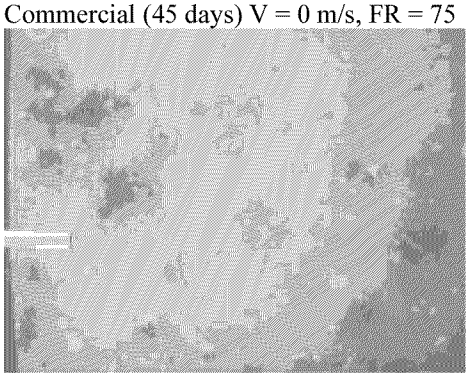
RTV11 + SF1147 (45 days) V = 11 m/s, FR = 35



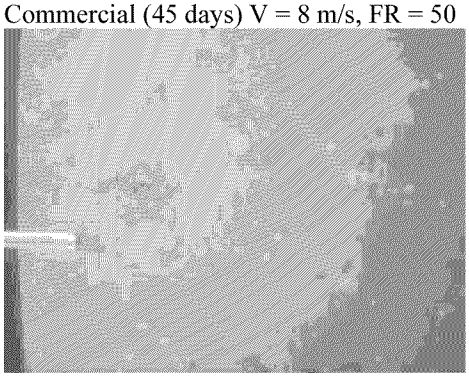
Commercial (45 days) V = 0 m/s, FR = 75



Commercial (45 days) V = 8 m/s, FR = 50



Commercial (45 days) V = 4 m/s, FR = 50



Commercial (45 days) V = 11 m/s, FR = 45

Figure 2.2.6. Video frame grab of testing RTV11 + SF1147 (45 days) and commercial coating (45 days).

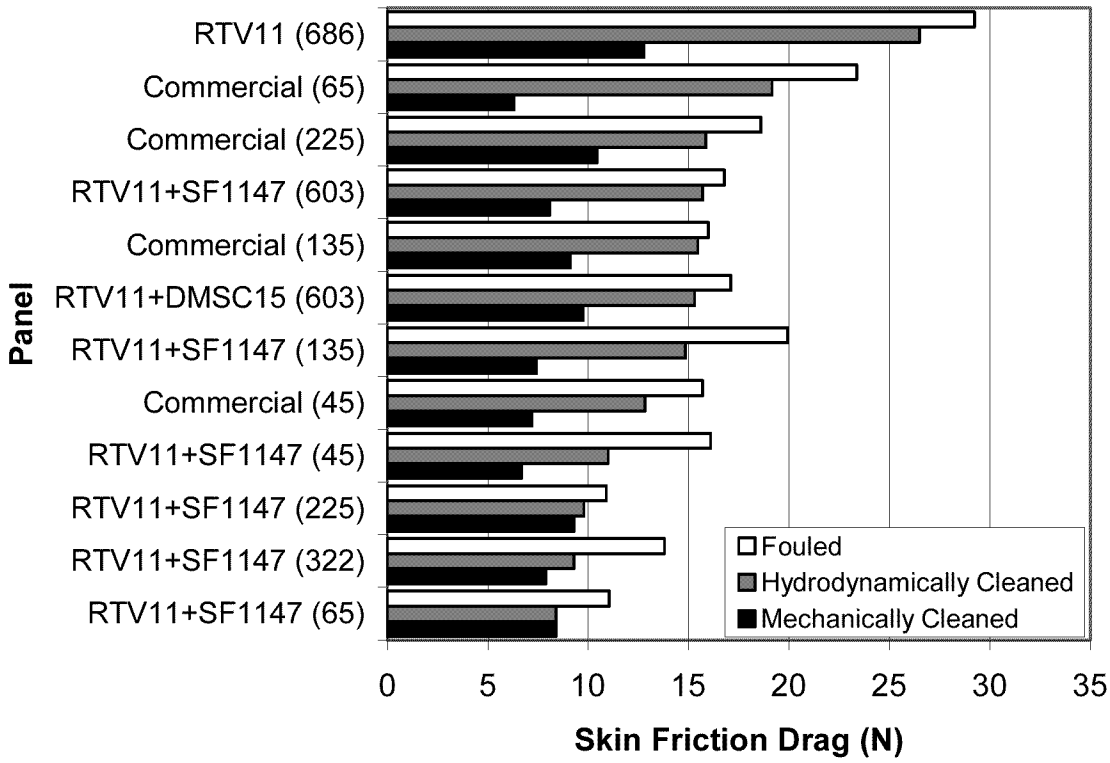


Figure 2.2.7. The skin friction drag penalty taken at 7 m/s (days of exposure for each formulation is found in parentheses)

The drag penalty of each panel in its non-fouled, fouled, and hydrodynamically cleaned condition was analyzed for the 7 m/s velocity (Figure 2.2.7). There were significant differences in the drag penalty among the surfaces in the non-fouled state. This was due to surface roughness and minor damage to the coating that had occurred during the static immersion exposure period. The mean skin friction drag for the non-fouled panels at this velocity was 8.5 ±1.8 N.

The panel drag in the fouled condition was extremely variable and reflected the fouling communities that became established on the surfaces. The highest drag was recorded on RTV11® (686 days). It also had a very high Navy fouling rating (FR 60). The drag measured after the fouled panels had been run at 11 m/s represented the ability for that coating to hydrodynamically self clean. The best performing coatings would ideally have a drag value close to that of the clean condition. This was found to be the case for the RTV11® + SF1147coating after 65 days, 225 days and 322 days exposure.

The relationship between fouling and drag was investigated by comparing the percent increase in drag due to fouling with the U.S. Navy fouling rating (Figure 2.2.8). This was done for the drag data at 11m/s. The percent increase in drag was calculated as the difference between the hydrodynamically cleaned condition and the clean condition at 11m/s. A second order polynomial curve fit showed that there was a significant

correlation between drag and FR (R^2= 0.65).

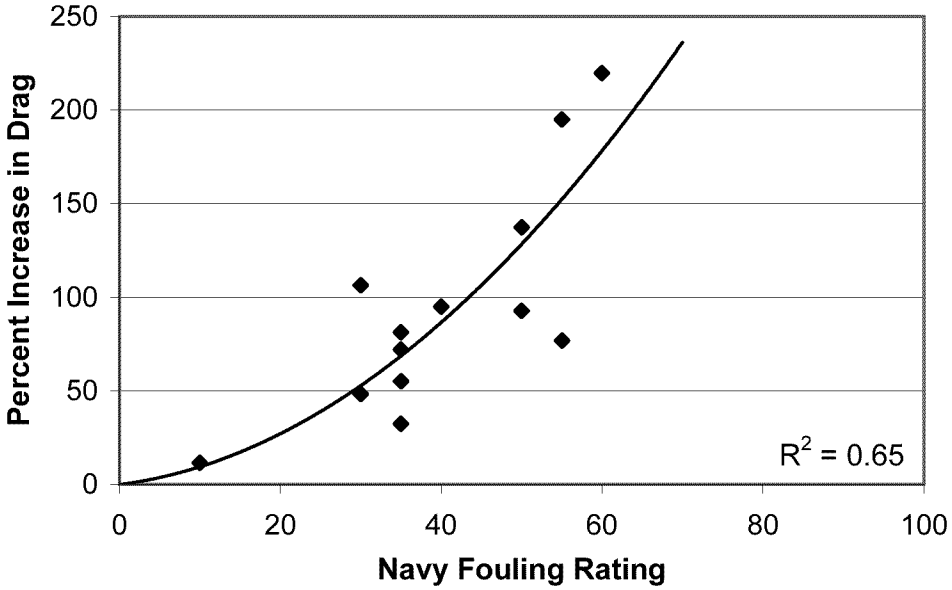


Figure 2.2.8. Percent change in skin friction drag at 11m/s with respect to the clean panel condition.

A subset of the panels (RTV11® + 10% SF1147 and the commercial fouling-release silicone) were exposed at the static immersion site at the same time and tested at set intervals to examine the effect of time on fouling performance. The fouling on each panel was left undisturbed and the change in fouling with time is shown in Figure 2.2.9. The fouling on the commercial panels increased more than the GE panels and this is reflected in the percent increase in drag that was measured at 11 m/s after hydrodynamic cleaning (Figure 2.2.10). It was apparent that there was a fairly close relationship between the fouling, fouling release and skin friction performance of the coatings.

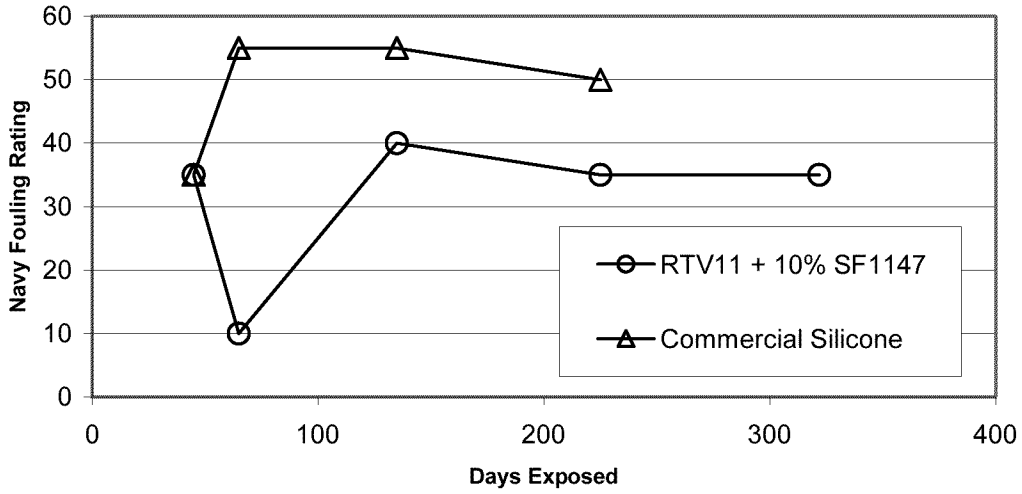


Figure 2.2.9. Navy Fouling Rating with respect to time of static immersion.

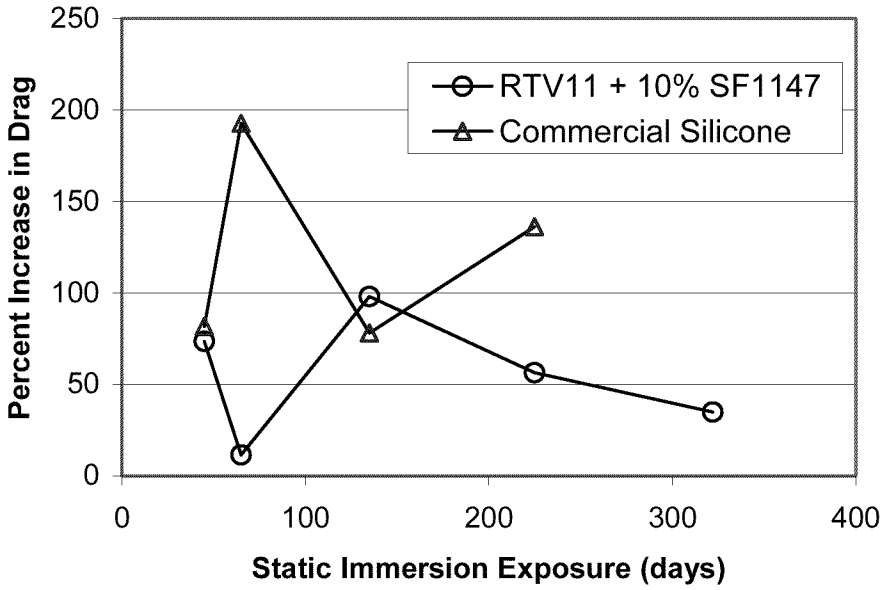


Figure 2.2.10. Percent increase in drag at 11m/s with respect to time of static immersion.

It is difficult to run direct comparisons of coating performance due to the influence of the initial fouling communities on each panel. However, in the side-by-side comparison of RTV11® + 10% SF1147 with the commercial coating for the same respective exposure, the RTV11® + 10% SF1147 exhibited better self-cleaning performance.

T-Craft Power Trials

Four power trials were run during the test period, which ran from June 1998 to December 2000. These were as follows:

23 June 1998, clean hull baseline power data.
17 July 1998, fouled hull and hydrodynamically self cleaned hull power data.
30 October 1998, fouled hull and hydrodynamically self cleaned hull power data.
16 February 2000, fouled hull and hydrodynamically self cleaned hull power data.

Complete reports from the powering trials can be found in Appendix 2F. The boat powering data are presented as propeller revolutions per minute (rpm) versus boat speed (knots) (Figures 2.2.11 to 2.2.13). The data obtained for the 23 June clean hull run was used as the baseline from which the performance of the hull in the fouled and hydrodynamically self cleaned conditions were compared. The rpm vs. boat speed curves were fitted with third order polynomials. Using the curve fit equations, the performance data were plotted as percentage change in rpm from the clean hull condition (Figure 2.2.14). Because the boat is a planing hull, there was not an exact match of rpm and boat speed, however, the data clearly show differences in performance due to biofouling. The July 1998 power trial results showed that the fouling caused in an increase in drag (Figure 2.2.11). After running the boat at 28 knots for 10 minutes, however, most of the fouling had been removed and the power required for propulsion returned close to that of the clean boat. The power trial run on October 30 showed an increase in drag caused by fouling (Figure 2.2.12). After running the boat at 28 knots for 10 minutes some of the fouling had been removed by hydrodynamic forces. The power required for propulsion did not, however, return to that of the clean boat and a small penalty due to biofouling remained. For the final power trial run February 2000 the fouling resulted in a higher drag penalty than was seen in either of the July or October trials (Figure 2.2.13). The fouling also appeared more tenacious which resulted in only a small decrease in drag after the boat was run at 28 knots for 10 minutes.

This system demonstrated excellent performance characteristics during the first year of operation. The majority of the fouling communities were removed by the hydrodynamic forces generated when operating the boat at high speed. Any subsequent cleaning was easily performed with a light wipe of a towel. The fouling-release properties of this coating diminished with time (Figure 2.2.15). It is speculated that the DMSC 15 oil was lost from the coating at a faster rate on the boat hull than the static immersion panels. The coating also demonstrated variation in fouling-release performance among the different hard fouling types, which made it less suitable for release of tubeworms and oysters.

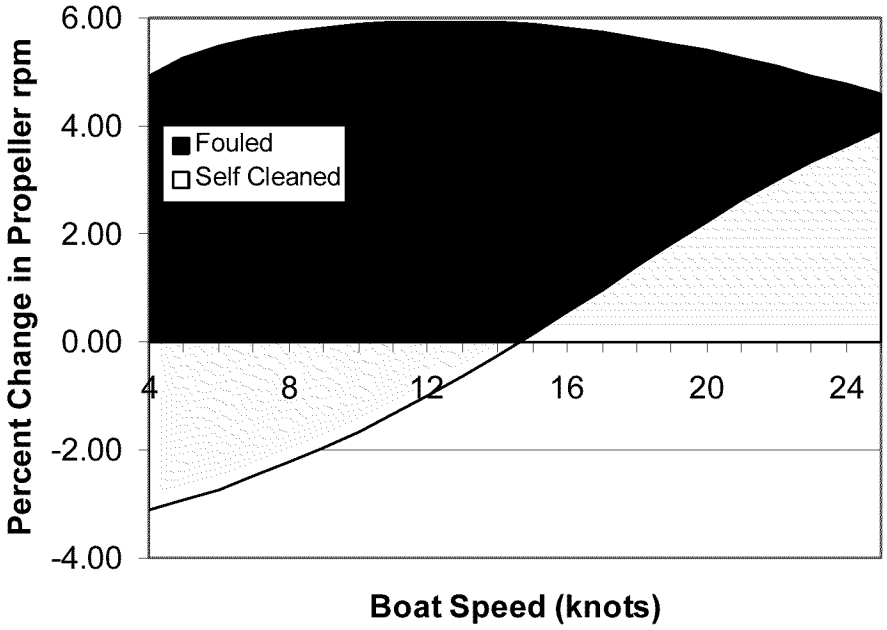


Figure 2.2.11. Percent change in propeller rpm to achieve boat speeds for the fouled and self cleaned hull condition, 17 July 1998

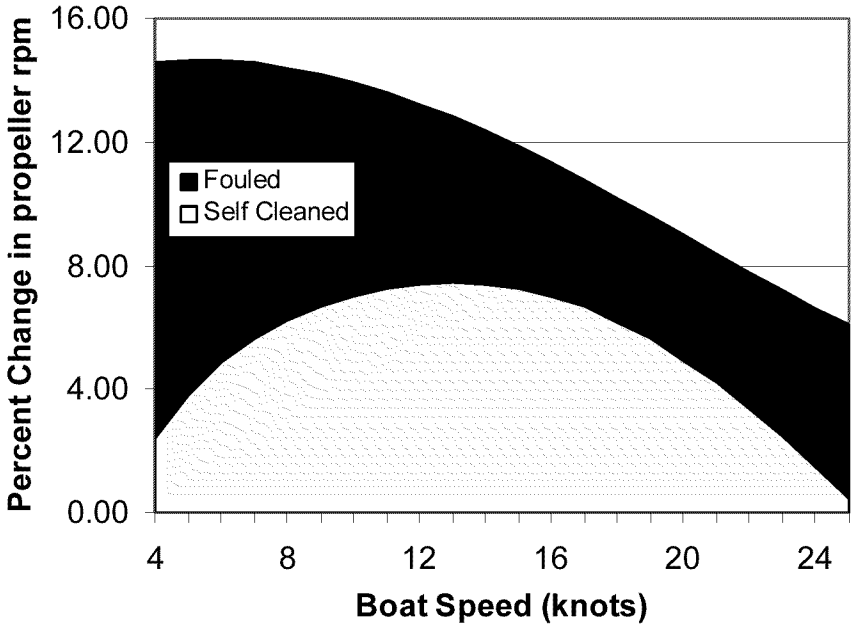


Figure 2.2.12. Percent change in propeller rpm to achieve boat speeds for the fouled and self cleaned hull condition, 30 October 1998

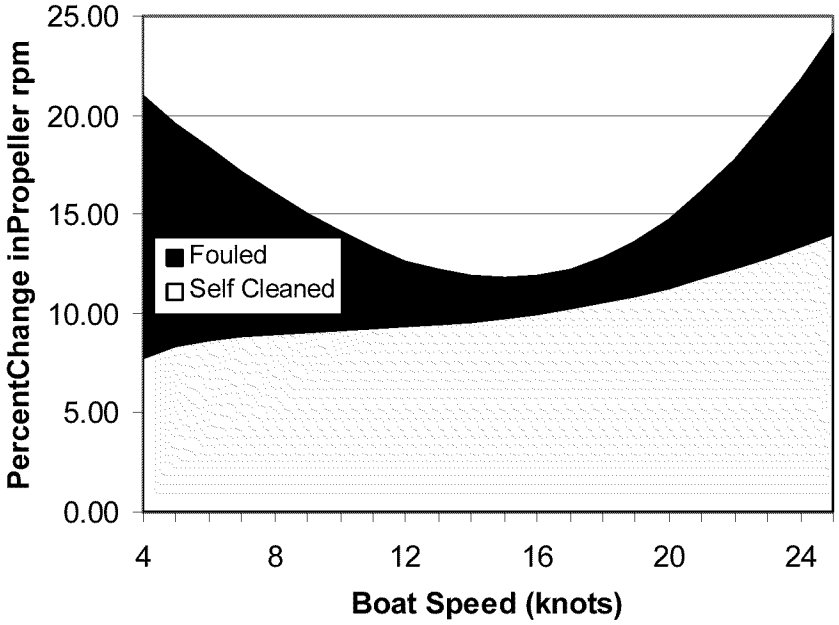


Figure 2.2.13. Percent change in propeller rpm to achieve boat speeds for the fouled and self cleaned hull condition, 16 February 2000

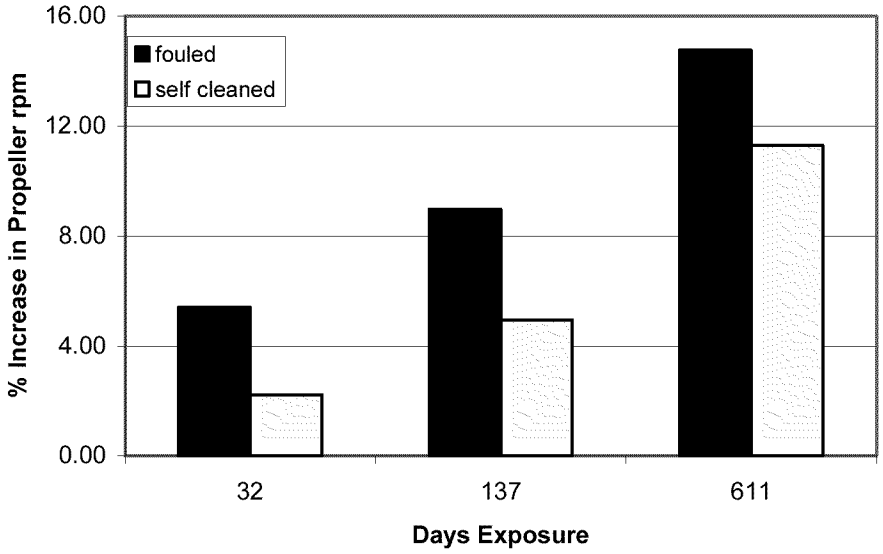


Figure 2.2.14. Percentage increase in propeller rpm at 20 knots due to biofouling of the hull of the T-Craft during the test period.

The overall physical condition of the coating was excellent, with no signs of blistering or delamination. There was been some mechanical damage to the bow area of the coating due to launching and retrieval of the boat onto the boat trailer. This occurred when the boat moved off the bow rollers and hit the metal supports on the trailer. The damage was in the form of long cuts, which showed no signs of spreading.

References

1. ASTM D3623. *American Standard for Testing and Materials, Marine coatings,* **06.02**, 573 (1978).
2. Dean, R. G. and Dalrymple, R. A., *Water Wave Mechanics for Engineers and Scientists*; Prentice-Hall: Englewood Cliffs, NJ, 1984.
3. Kovach, B. *Hydrodynamic Performance of Silicone Fouling-Release Surfaces*; Florida Institute of Technology: Melbourne, 2001.
4. , Swain G. W., Nelson, W. G., and Preedeekanit, S, *Biofouling* **10,** 187 (1998).

SECTION 2. 3 COATING APPLICATION DEVELOPMENT

The final downselected fouling release coating system (Amerlock 400FD; SEA210A/SCM501C; RTV1®1 + SF1147) was evaluated under military specification MIL-24647B (Table 2. 3.1). Technical data sheets are provided for application of the GE fouling release coating system. These were developed based on the data collected from the field applications described in Task 2.2.

EXPERIMENTAL

All testing was performed in accordance with the appropriate military specification. Technical data sheet information was compiled from best practices in the field.

RESULTS

Military Specifications

Table . 2.3.1. Military specifications for the GE coating system.

Requirements	Test Method	Epoxy (Anticorrosive)	SEA210A/SCM501C (Tiecoat)	RTV11® + 10 % SF1147 (Topcoat)
Pigment	FED-STD-141 4021.1	39.70%	13.90%	25.60%
Volatiles, %	ASTM-D 2369	40.90%	4.50%	1.80%
Non volatile vehicle, %	FED-STD-141 4053.1	19.40%	81.60%	72.60%
Consistency, gm equ KU	ASTM-D 562	132 Krebs units	182x10^3 centipoise	11.2x10^3 centipoise
Weight per unit volume	ASTM-D 1475	1.41 gm/mL	1.36 gm/mL	1.14 gm/mL
Copper content of pigment	ASTM-D 283	Not done	Not done	Not done
Drying time	FED-STD-141 4061.2	off tech sheets temp dependant	1 to 1 1/2 hrs	1 1/2 hrs
Flash point	ASTM-D 3278	55°C base/ 29°C cure	142°C base/ 29°C cure	298°C base/ 235°C cure
Sag resistance	ASTM-D 4400	sag index 11.6	on card- sag index 26 on epoxy-sag index 26	on card- total sag no index on tiecoat- sag index 13.6
Condition in container	FED-STD-141 3011.2	OK	OK	OK
Shelf life	Mil-P-24647 4.5.4.1	1 yr	6 months	6 months
Partially full container	Mil-P-24647 4.5.4.2	139.2 Krebs units 138 Krebs units	182x10^3 centipoise, 189x10^3 centipoise	11.3x10^3 centipoise, 11.7x10^3 centipoise
Accelerated storage stability	Mil-P-24647 4.5.4.3	10.1x10^3 centipoise slight separation	202x10^3 centipoise	13.4x10^3 centipoise some oil separation
Resistance to tropical biofouling organism attachment	Mil-P-24647 4.5.1	NA	NA	SF1147 with J501 1996 SF1147 with Sigma 1999 SF1147 with SEA 2000 in at MMRTS and Hawaii
Erosion	ASTM-D 4939/ Mil-P-24647 4.5.1.3	NA	NA	dynamic panels to MMRTS 2000
Shallow Submergence	ASTM-D 3623/ Mil-P-24647 4.5.1.4	NA	NA	SF1147 with J501 1996 SF1147 with Sigma 1999 SF1147 with SEA 2000 in at MMRTS and Hawaii
Ship tests	Mil-P-24647 4.5.1.5	NA	NA	55 sq. m patch on USS Wyoming
Spraying properties	Mil-P-24647 4.5.5	Good	Good	Good
Brushing properties	Mil-P-24647 4.5.6	OK	OK	OK
Rolling properties	Mil-P-24647 4.5.7	OK	OK	OK
Freeze thaw stability	Mil-P-24647 4.5.9	137.4 Krebs units	165x10^3 centipoise	11.3x10^3 centipoise

Preliminary technical data sheets:

GE fouling release coating system

Product Description and Intended Uses

The GE fouling release coating system is a silicone elastomeric coating designed to prevent the firm adhesion of marine organisms to structures and allow the removal of these growths with a sponge or stream of water.

The GE fouling foul-release coating system relies on the natural tendency of silicone to prevent firm attachment to a variety of structures in marine environments. The GE fouling release coating system is intended to be suitable for use on ships (military tankers, cruisers, boats, pleasure craft, service vessels), water intakes at power plants and other utilities, bridges, locks, dams and associated structures.

Unlike antifouling coatings, the GE fouling release system is intended to not poison marine life.

Key Performance Properties
- Designed to be non-toxic to marine organisms
- Can be spray-applied for large jobs, or brush/roller-applied for small jobs
- Marine growth can be removed from structures with a sponge or a stream of water

Typical System Data

Coating	Product	# of Layers	Wet Film Thickness	Dry Film Thickness
Anticorrosive	Amerlock 400FD	1 or 2	5-6 mils	3-4 mils
Tiecoat	GE tiecoat	1	14-16 mils	6-7 mils
Topcoat	GE topcoat	1	12-14 mils	9-10 mils

Storage/Warrantee Period

Both compound and curing agents will remain useful up to six months from the date of shipment when stored in the original unopened containers in a dry place at temperatures below 27°C (80°C)

Regulatory Data

Material Safety Data Sheets are available upon request from GE Silicones. Similar information for solvents and other chemicals used with GE products should be obtained from your suppliers. When solvents are used, proper safety precautions must be observed.

Instructions for Use

All surfaces to be coated should be clean, dry and free from contamination for each layer.

Surface Preparation

Steel surfaces
GE topcoat should always be applied over the recommended anti-corrosive coating and GE tiecoat. The tiecoat must be dry and the topcoat applied within the overcoating interval specified.

Preliminary technical data sheets:

GE fouling release coating system

Application

Mixing All base materials should be well mixed prior to use.

The following is a guide; suitable equipment from other manufacturers may be substituted. Changes in pressure, hose and tip size may be needed for proper spray characteristics.

Airless spray: Recommended pumps, tips and lines

Coating Applied	Tip Size (in)	Pump Ratio	Line Specs (Length; Inside Diameter (ID))
Epoxy			Refer to manufacture's instructions
Tiecoat	0.017-0.021	30:1 or larger	50 ft.; 3/8 in. ID + 6 ft; 3/8 in. ID (whip)
Topcoat	0.017-0.023	45:1 or larger	50 ft; 1/2 in. ID + 6 ft; 3/8 in. ID (whip)

Brush or Roller - Recommended only for touching up or repairing of small surface areas.

Environmental Conditions

Product	Air and Surface Temperature	Humidity (max)
Amerlock 400 FD	20-122 ^{o}F	
GE Tiecoat	60-90 ^{o}F	85 %
GE Topcoat	50-95 ^{o}F	90 %

Surface temperatures must be a least 5^{o}F (3^{o}C) above the dew point to prevent condensation.

Refer to Ameron's guidelines for more information about the epoxy base coat (Amerlock 400FD).

Pot life - See specific material technical data sheets.

Procedure

Application
1. Flush epoxy pump with Amercoat #12.
2. Apply 6-8 mils of an Amerlock 400FD (gray) epoxy to the properly prepared surface. This will provide a base coat and corrosion protection. Follow the manufacturer's instructions for surface preparation and application of the Amerlock 400FD (gray). If a second coat is required, repeat steps 1 and 2.
3. Flush tiecoat and topcoat equipment with naphtha prior to use.
3. After a minimum overcoat interval of 12 hours the GE tiecoat is applied (14-16 mils wft).
4. After a minimum overcoat interval of 12 hours, the GE topcoat can be applied.
5. Ventilate confined areas with clean air between coats and while curing the final coat. Prevent moisture condensation on the surface between coats.
6. Flush tiecoat and topcoat equipment thoroughly with toluene** upon completion of the job to prevent material from curing within the spray equipment.

Preliminary technical data sheets:

GE fouling release coating system

** If toluene cannot be used, contact GE Silicones for alternative solvent

TASK 3. ENVIRONMENTAL IMPACT AND TOXICOLOGICAL TESTING

TASK 3.1 ENVIRONMENTAL IMPACT

The fouling release coatings developed under this contract contained silicone oils to reduce the attachment strength of macrofouling species. Since non-bonded oils were employed, it was theorized that oil might exude from these coatings during [their] use. Oil depletion may adversely affect the biofouling release performance and result in increased levels of silicone and silicone degradation products in the marine environment. In this section, we summarize the results from extraction experiments of radiolabeled polydimethylsiloxane, DMSC15, and SF1154 oils from RTV11® under marine and freshwater conditions. Total weight loss in aqueous environments from RTV11 and RTV11 amended with SF1154, SF1147, or DMSC15 as a function of time was also measured. The radiolabeled studies indicated that the oils exude very slowly from RTV11® in both environments. The total weight loss experiments showed that RTV11® amended with either SF1154 or SF1147 lost the same percentage of weight as the control (RTV11®) with no oil. The coatings containing DMSC15 lost the largest percentage of weight (5-7%) over the duration of the experiment. Most of the weight loss of this coating occurred within the first eight months of immersion. These studies verified that, with the exception of DMSC15, degradation of these coatings in the marine and freshwater environments is negligible.

INTRODUCTION

The most effective silicone fouling release coatings contain 10-20% free oil. We have evaluated the performance of oil-amended coatings and have substantiated that oil incorporation may have a beneficial effect on decreasing the attachment strength of macrofouling species[1]. Although the mechanism of enhanced foul-release of these coatings is not well understood, it has been shown that attachment forces are lower on liquid-like layers compared to solid layers[2]. However, it may be possible for non-bonded oils to exude into the water column, thereby increasing the level of silicone in the environment. It has been shown that silicones will selectively migrate onto soils and that slow degradation occurs on moist soils. The products of soil induced abiotic degradation are typically silanol terminated monomers and oligomers[3]. Depletion of the oil from the coating is anticipated to also adversely affect the biofouling release performance. This section comprises our results on the extraction of polydimethylsiloxane, SF1154, DMSC15 and SF1147 from RTV11® using radiolabeled oils, and total weight loss measurements in aqueous environments as a function of time.

EXPERIMENTAL

Synthesis of Oils

Materials

Dodecamethylpentasiloxane, tetramethyldisiloxane, octaphenylcyclotetrasiloxane, and DMSC15 were obtained from Gelest, Inc. (Tullytown, Pennsylvania) Amberlyst® 15, methyl sulfoxide, toluene, allyloxyethanol, and dichloromethane were obtained from Aldrich Chemical Company.

Octamethylcyclotetrasiloxane, silyl phosphate, Karstedt's catalyst, SF4155, potassium trimethylsilanolate, RTV11®,SF1147, and SF1154 were obtained from GE Silicones (Schenectady, NY). Ameron 400 was obtained from the Ameron Marine Paints Corporation. Silgan J501 was obtained from Wacker Chemie.

Synthesis of ^{14}C Octamethylcyclotetrasiloxane

Wizard Laboratories (West Sacramento, California) performed all radiolabeled syntheses. The radiolabeled precursor to both the polydimethylsiloxane and SF1154 oils consisted of a ^{14}C-labeled octamethylcyclotetrasiloxane (D_4), which was prepared by the reaction of tetrachlorotetramethylcyclotetrasiloxane with ^{14}C-labeled methyl Grignard reagent.

Synthesis of ^{14}C Polydimethylsiloxane

^{14}C-D_4 was equilibrated with dodecamethylpentasiloxane (MD_3M) using Amberlyst® 15, a strong-acid ion exchange resin (Figure 3.1.1). To a 250 mL one-neck round-bottom flask equipped with a magnetic stir bar and a condenser with a nitrogen inlet, 100 grams (0.338 mol) of a mixture of ^{14}C-labeled and unlabeled D_4 (5 mCi total), 3.25 grams (8.4×10^{-3} mol) MD_3M, and 1.33 grams Amberlyst® 15 were added. The flask was heated to 100 °C for 24 hours while stirring under a blanket of nitrogen. After 24 hours, the reaction mixture was cooled to room temperature, diluted with 100 mL dichloromethane, and filtered through a Whatman® glass microfibre filter to remove the ion-exchange resin. The dichloromethane was removed from the product by rotary evaporation, and the resultant solvent-free oil was vacuum distilled to remove the low molecular weight volatile oligomers. The fluid was ultimately maintained at a temperature of 200°C / 0.1-1.0 mm Hg for 3 hours to remove the remaining volatiles. A clear fluid was obtained (85% yield). The average dimethylsiloxy block length (x, Figure 3.1.1) was determined to be 149 by ^{29}Si NMR spectroscopy.

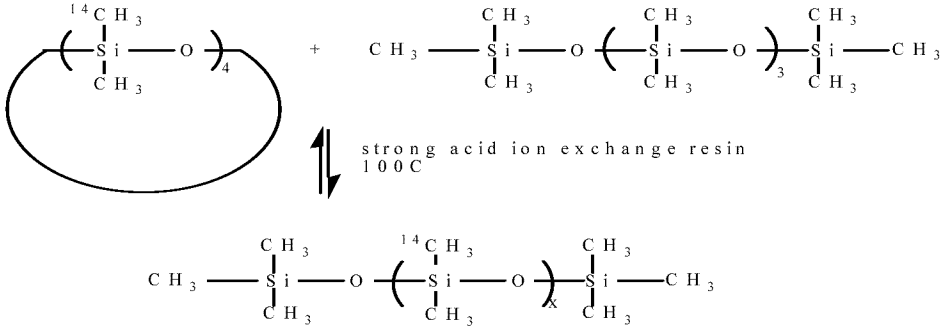


Figure 3.1.1. Synthesis of ^{14}C-labeled polydimethylsiloxane.

Synthesis of ^{14}C SF1154

^{14}C-D_4 was equilibrated with octaphenylcyclotetrasiloxane (D_4^{Ph}) and MD_3M in the presence of potassium trimethylsilanolate (Figure 3.1.2). To a 50 mL one-neck round-bottom flask equipped with a magnetic stir bar and a condenser with a nitrogen inlet, 2.0 grams (6.8×10^{-3} mol) of a mixture of ^{14}C-labeled and unlabeled D_4 (5 mCi total), 3.80 grams (9.9x10-3 mol) MD_3M, 4.20 grams (5.3×10^{-3} mol) D_4^{Ph}, and 100 µL of a solution of potassium trimethylsilanolate in methyl sulfoxide (3.4×10^{-5} mol potassium trimethylsilanolate) were added. The flask was heated to 170 °C for 6 hours while stirring under a blanket of nitrogen. After 6 hours, the reaction mixture was

cooled to room temperature. 30.2 mg ($3.4x10^{-5}$ mol) phosphoric acid, in the form of silyl phosphate, was added, and the contents were stirred for a minimum of 30 minutes at room temperature. The resulting oil was then vacuum distilled at a temperature of 250 °C / 0.03 mm Hg for 3 hours to remove the volatiles. The flask was cooled to room temperature and a clear fluid was obtained (70% yield). Gel permeation chromatography (GPC) provided M_w = 1,256 Da, M_n = 811 Da, M_w/M_n = 1.55. The composition was confirmed by ^{13}C NMR, ^{29}Si NMR and ^{1}H NMR spectroscopies.

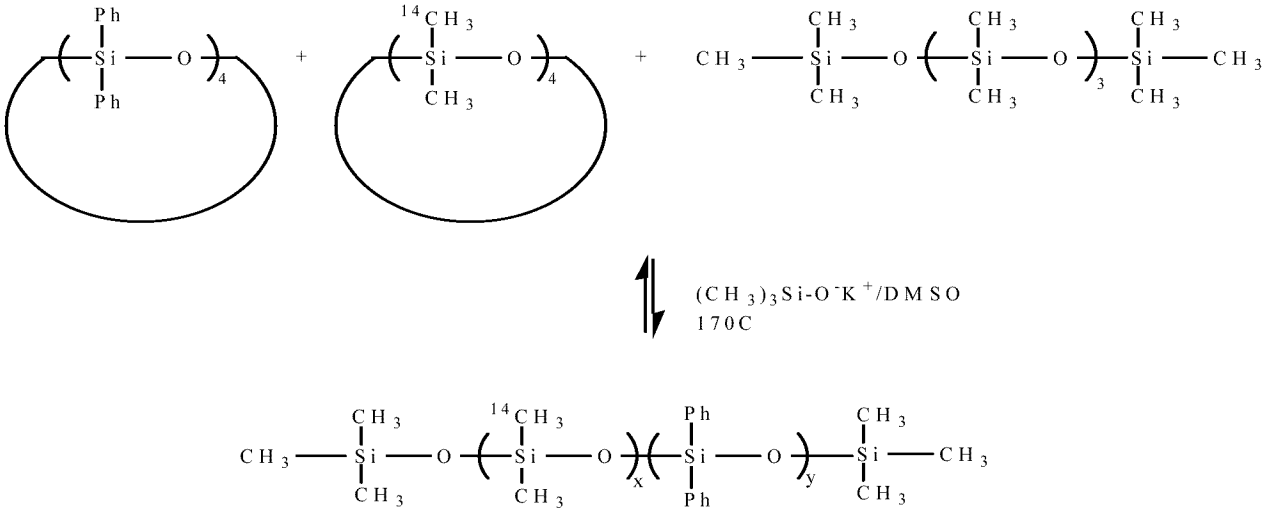


Figure 3.1.2. Synthesis of ^{14}C-labeled SF1154.

Synthesis of DMSC15 Containing No Low Molecular Weight Oligomers

DMSC15 was prepared using a two-step process: (1) To a round bottom flask fitted with a reflux condenser and a magnetic spin bar, 0.64 grams ($5.2x10^{-3}$ mol) tetramethyldisiloxane, 3.54 grams ($1.2x10^{-2}$ mol) of D_4, and 0.07 grams Amberlyst® 15 were added. The flask was heated to 100 °C for 24 hours while stirring. Upon cooling, the resultant silicon hydride terminated oligomers were cooled to room temperature and filtered through a Whatman® glass microfibre filter to remove the ion-exchange resin. The fluid was devolitalized up to 150 °C and 0.3 mm Hg. After stripping, gas chromatography-mass spectroscopy analysis (GC-MS) confirmed that all oligomers lower than dodecamethylhexasiloane had been removed. (2) To a round bottom flask equipped with an addition funnel, a reflux condenser, and a magnetic spin bar 4.25 grams ($8.8x10^{-3}$ mol H) of the silicon hydride terminated oligomers from step 1, and 1.7 grams toluene were added. To the addition funnel, 1.35 grams ($1.32x10^{-2}$ mol, 1.5 equivalents) of allyloxyethanol and 10.2 µL (10 ppm based on Pt) of a solution of Karstedt's catalyst in toluene were also added. The mixture was heated to 85-90 °C with stirring, and then the allyloxyethanol/Pt mixture was added drop wise over a 15-30 minutes period. Following these additions, the reaction was maintained at 85 °C for 4 hours prior to cooling to room temperature. The resulting carbinol terminated siloxane oil was heated on a rotary evaporator to remove most of the toluene and excess allyloxyethanol, followed by devolatilization under a vacuum at 150°C/0.05 mm Hg for two hours. ^{1}H NMR spectroscopy confirmed M_n = 1430 Da.

Preparation of Silicone Coatings Containing Silicone Oils

For the radiolabeled studies, aluminum strips (2.5 cm by 10.1 cm) coated with Ameron 400 epoxy were weighed, primed with SS4155 and then painted with a mixture of RTV11® (using dibutyltindilaurate at 0.5 wt % loading as the cure catalyst) and ^{14}C-labeled silicone oil (10 wt %). The coating was allowed to cure for one week; the aluminum strips were then reweighed to determine the total amount of silicone topcoat (RTV11® + oil) applied to each strip. Assuming a uniform distribution of ^{14}C-oil throughout the RTV11®, the amount of ^{14}C-oil in each panel was calculated. The panels were then soaked in water for several days to leach out the tin catalyst. This rinse water was analyzed for total ^{14}C by liquid scintillation analysis to measure any radiolabeled oil that may have exuded into the water.

In the total weight loss experiments, the RTV11® and RTV11® amended with 10% SF1154 were applied to coupons as described above. The other coatings were composed of the complete duplex system[4] including anticorrosive epoxy, mistcoat, Wacker Silgan J501, and topcoat. The following topcoats were applied: RTV11® + 6% DMSC15, RTV11® + 10% stripped DMSC15, and RTV11® + 10% SF1147. Samples were allowed to cure for one week. The coupons were weighed and soaked in deionized water for several days prior to the start of the immersion evaluation. After the presoak period, samples were dried under ambient conditions for three days before reweighing. This weight was used as the initial weight in calculations to determine the amount of weight loss during immersion exposure.

Experimental Design

For the radiolabeled study, the painted aluminum strips were suspended in both salt and fresh water fish tanks (11 L) containing marine and fresh water sediments, respectively (Figure 3.1.3). Marine sediment (pH 7.9) was obtained from Tampa Bay, Florida and fresh water sediment (pH 7.5) was obtained from the Scioto River, Columbus, Ohio. Each experimental tank contained 6 liters of distilled water and 305.25 grams of the appropriate sediment (based on sediment dry weight). To the marine tank, 31 mL of sea salts per liter of water were added. Twelve coated aluminum panels were immersed in each tank. The tanks were maintained in the dark, and the water was stirred from overhead to simulate movement of a boat through water.

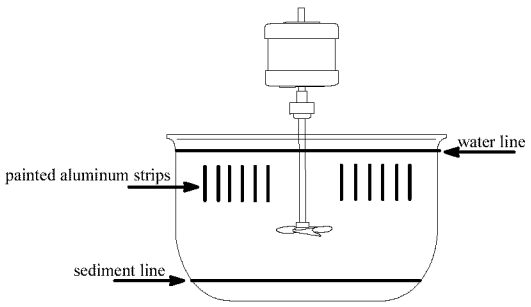


Figure 3.1.3. Fish tank system design for the radiolabeled experiments.

In the total weight loss study, sample coupons coated with the experimental systems were suspended in 37.8 L fish tanks filled with deionized water. These tanks contained an aeration

system and a charcoal filter, through which the water circulated (Figure 3.1.4). One-third of the water was changed daily to ensure that the saturation of the oil in the water was not rate limiting.

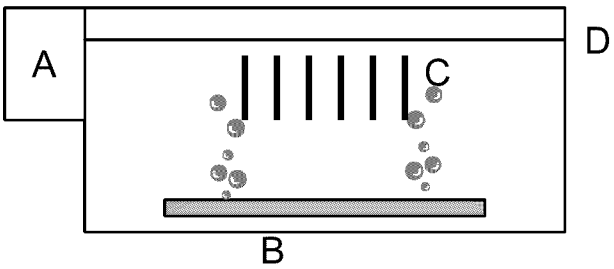


Figure 3.1.4. Fish tank system design for the weight loss experiments (A = charcoal filter, B = aeration strip, C = test coupons, D = water line).

Analysis

Each month, 1 coated coupon was removed from each experimental tank (1 fresh water and 1 salt water tank for both of the ^{14}C-oils) and the amount of ^{14}C-labeled oil remaining in the RTV11® was determined by thermal oxidation. In this procedure, 50-200 mg samples of the silicone topcoat were combusted in a Packard Model 307 sample oxidizer. Any ^{14}C-labeled oil was oxidized to $^{14}CO_2$, trapped in a liquid scintillation cocktail, and analyzed using an LKB-Wallace Model 1214 Rackbeta liquid scintillation counter. Based on the average of 3 to 5 samples per aluminum strip, the amount of ^{14}C-oil per gram of silicone topcoat was determined. The total amount of oil in each aluminum strip was then calculated based on the total weight of the silicone topcoat for a given aluminum strip. Each month, the amount of ^{14}C in the water and sediment was determined by liquid scintillation analysis and thermal oxidation/liquid scintillation analysis, respectively.

In the total weight loss experiment, 2 – 4 coupons were removed from the immersion tanks monthly and allowed to air dry for 5 days, followed by weighing on 3 consecutive days, and then were placed back into the designated tank. The percent difference in weight loss was calculated using the weight at time of testing and the initial weight of the coupon.

RESULTS

^{14}C Radiolabeled Oils

After 12 months in both fresh water and salt water, <0.4% and ≤0.03% of the total ^{14}C-polydimethylsiloxane was detected in the water and sediment, respectively. The mass balance of ^{14}C for the salt and fresh water systems combined was 102.23±3.99% (Table 3.1.1). Mass balance data (Table 3.1.1 and 3.1.2) reveal that, on average, >99% of the theoretical amount of ^{14}C-labeled oil remained in the silicone topcoat. Thus, the levels of ^{14}C in the water (and sediment?) were only slightly higher than background.

Table 3.1.1. Mass balance of ^{14}C-polydimethylsiloxane in fresh water and marine environments.

Freshwater Time (months)	% of total ^{14}C In Tin Rinse	In Water	In Sediment	In RTV11®	Total
1	0.05	0.05	0.01	100.03	100.14
2	0.05	0.07	0.01	101.54	101.67
3	0.05	0.13	0.01	100.74	100.93
4	0.05	0.13	0.01	101.82	102.01
5	0.05	0.16	0.02	96.08	96.31
6	0.05	0.19	0.02	99.64	99.9
7	0.05	0.19	0.01	97.2	97.45
8	0.05	0.2	0.03	98.6	98.88
9	0.05	0.24	0.01	100.31	100.61
10	0.05	0.3	0.01	101.6	101.96
11	0.05	0.24	0.02	99.31	99.62
12	0.05	0.25	0.03	106	106.33
Marine					
1	0.05	0.04	0.02	95.31	95.42
2	0.05	0.07	0.01	105.53	105.66
3	0.05	0.12	0.02	103.3	103.49
4	0.05	0.13	0.03	109.64	109.85
5	0.05	0.15	0.01	104.91	105.12
6	0.05	0.17	0.01	102.89	103.12
7	0.05	0.16	0.02	101.29	101.52
8	0.05	0.18	0.01	98.89	99.13
9	0.05	0.19	0.02	99.7	99.96
10	0.05	0.23	0.02	106.92	107.22
11	0.05	0.24	0.03	105.86	106.18
12	0.05	0.36	0.03	110.53	110.97
				Average	**102.23**
				Std. Dev.	**3.99**

After 12 months in both fresh and salt water, <1.1% and $\leq$0.07% of the total ^{14}C-SF1154 was detected in the water and sediment, respectively. The mass balance of ^{14}C for the salt water and fresh water systems combined was 100.65$\pm$6.50% (Table 3.1.2).

Table 3.1.2. Mass balance of ^{14}C-poly(dimethyldiphenyl)siloxane (SF1154) in fresh water and marine environments.

Freshwater Time (months)	% of total ^{14}C In Tin Rinse	In Water	In Sediment	In RTV11®	Total
1	0.4	0.11	0.02	103.49	104.02
2	0.4	0.15	0.02	94.84	95.41
3	0.4	0.19	0.03	102.52	103.14
4	0.4	0.34	0.05	94.11	94.90
5	0.4	0.08	0.05	89.7	90.23
6	0.4	0.06	0.05	100.26	100.77
7	0.4	0.64	0.06	98.37	99.47
8	0.4	0.33	0.06	99.69	100.48
9	0.4	0.62	0.06	95.41	96.49
10	0.4	0.25	0.08	95.02	95.75
11	0.4	1.01	0.08	88.61	90.10
12	0.4	1.03	0.06	96.6	98.09
Marine					
1	0.4	0.09	0.04	103.98	104.51
2	0.4	0.08	0.03	92.36	92.87
3	0.4	0.11	0.03	102.94	103.48
4	0.4	0.11	0.02	105.02	105.55
5	0.4	0.07	0.05	101.97	102.49
6	0.4	0.2	0.05	104.55	105.20
7	0.4	0.09	0.06	93.21	93.76
8	0.4	0.05	0.03	107.65	108.13
9	0.4	0.04	0.06	98.3	98.80
10	0.4	0.1	0.06	114.3	114.86
11	0.4	0.15	0.08	102.5	103.13
12	0.4	0.97	0.07	112.6	114.04
				Average	**100.65**
				Std. Dev.	**6.50**

Weight Loss Experiments

Coatings containing DMSC15 lost the largest amount of weight over the time period of the experiment (Table 3.1.3). It is unlikely that preferential loss of more water-soluble lower molecular weight oligomers occurs since the same normalized percentage of oil was lost from the 6% DMSC15 sample as the 10% stripped DMSC15 sample. RTV11® without oil lost 2.6% of it's initial weight. The coatings containing SF1154 and SF1147 had similar percentage weight losses compared to the RTV11® control. The weight loss of RTV11® + 10 % SF1147 and RTV11® + 10% stripped DMSC15 over the 24 months is shown in Figure 3.1.5.

Table 3.1.3. Final percent weight loss for all coatings evaluated. The numbers in parentheses are the coating's downselect number.

Coating	Total Days of Immersion	% Weight Loss
RTV11® (no J501) (1)	973	2.59 + 0.93
RTV11® + 10% SF1154 (no J501) (2)	973	3.08+ 0.98
RTV11® + 6% DMSC15	700	5.1 + 1.4
RTV11® + 10% stripped DMSC15	700	7.3 + 0.5
RTV11® + 10% SF1147 (8)	750	3.24 + 1.0

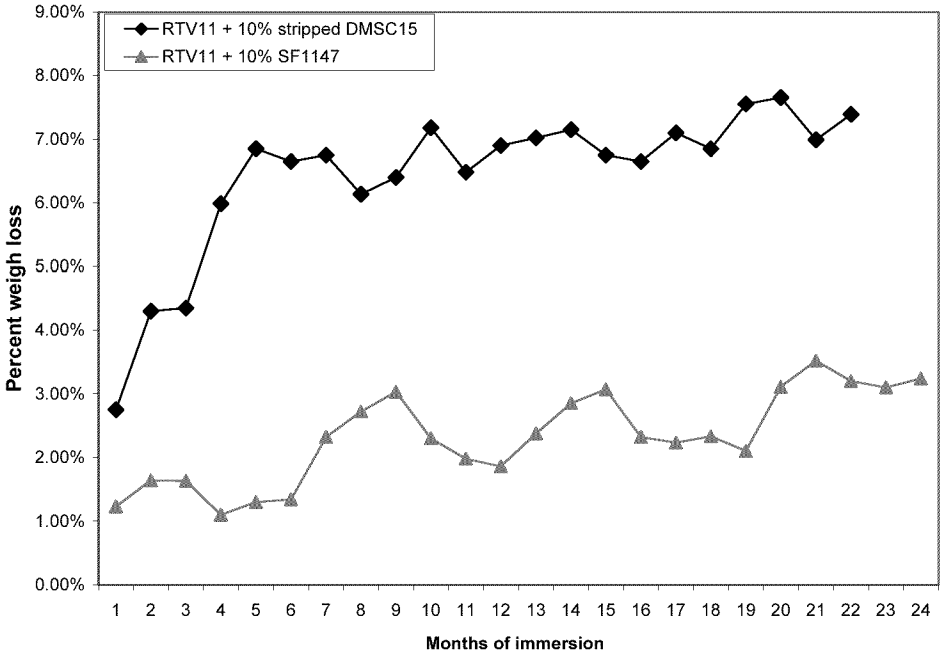


Figure 3.1.5. Percent weight loss of coatings over 24 months.

The radiolabeled data indicate RTV11® amended with either polydimethylsiloxane or SF1154 exhibit extremely low levels of oil loss during the 1-year exposure period. The weight loss experiments show that coatings containing SF1154 and SF1147 oils have similar weight loss profiles as the [unamended] RTV11® control. RTV11® amended with DMSC15 shows a greater weight loss than the RTV11® control. Removal of lower molecular weight oligomers from the DMSC15 oil did not reduce the weight loss of coatings containing the stripped oil. Retention of these oils in RTV11® amended with either SF1147 or DMSC15 suggests that silicone paint systems of this type should not result in significant accumulation of silicone oils in marine and fresh water environments.

TASK 3.2 TOXICOLOGY STUDIES

A necessary attribute of a successful candidate foul-release coating is that it exhibits low toxicity towards aquatic organisms. Toxicology studies performed on our silicone fouling release topcoats indicated that the downselected coatings show significantly less toxicity than copper ablative paints in standard EPA protocol tests. Toxicity was evaluated against three organisms: mysid shrimp (Mysidopsis bahia), the inland silverside fish (Menidia beryllina), and the marine chain diatom (Skeletonema costatum). The most sensitivity to the coating exudates was shown by the chain diatom, followed by mysid shrimp and, lastly, silverside fish. The catalyst, dibutyltindilaurate was measurable in all coating exudates, but a general correlation between toxicity and dibutyltindilaurate concentration was not observed. Of the downselected coatings, RTV11® + 10 % SF1147 (8) and RTV11® + 10% DMSC15 (5) were the least toxic to all the test organisms.

INTRODUCTION

A successful silicone foul release coating must exhibit significantly less toxicity to aquatic species than copper ablative paints. The approved method for evaluation of toxicity is comprised of a series of static-renewal (96 hour) Environmental Protection Agency (EPA) bioassays which estimate toxicity toward the mysid shrimp (*Mysidopsis bahia*), the inland silverside (*Menidia beryllina*), and the marine chain diatom (*Skeletonema costatum*). Mysid shrimp are employed to represent a benthic, or bottom-dwelling, response, while inland silversides (fish) represent a pelagic, or swimming, animal response. The phytoplankton marine chain diatom is chosen to evaluate any potential effects on the primary producers in marine waters. The endpoints of the tests are survival in the mysids and fish (LC_{50s}: concentration of a toxicant that results in mortality of 50% of the tested population), and biomass, or chlorophyll fluorescence, in the diatoms (IC_{50s}: concentration of a toxicant that inhibits 50% of a physiological process). The coating extracts, to which the organisms are exposed, are analyzed for the concentration of the catalyst dibutyltindilaurate or for total copper in the exudate. A copy of the final report submitted by SPAWAR can be found in Appendix 3.B.

EXPERIMENTAL

Preparation of Seawater Extracts from all Coatings

Sheets of topcoat were cut into coupons (~ 3.8 cm x 3.8 cm x 0.2 cm in size) and soaked in filtered (0.45 μm) seawater for 24 hours at 25°C prior to use. Exposure solutions were prepared daily by soaking a pre-exposed coupon in 250 mL of seawater for 24 hours. A single coupon was repeatedly soaked for successive 24 hours periods, for a total of 96 hours. Coupons were removed from solution prior to organism exposure. A solution containing a single coupon soaked in 250 mL was designated as a 100% extract. An increased dosage was accomplished by soaking 3 coupons in 250 mL of filtered seawater (300% extract). Dilution of a 300% extract yielded solutions of lower concentration. Exudates (100% concentration) were analyzed for tin by purge and trap hydride derivitization followed by atomic absorption[5]. Identification of dibutyltindilaurate was accomplished by gas chromatography[6,7]. The detection limit of tin was less than 1 part per trillion (nanograms per liter). The exudate solution obtained from soaking a

commercially available copper coating coupon was analyzed for copper with a HACH DR/2000 Spectrophotometer.

Bioassays

One-day-old mysids and seven-day-old fish were received from Aquatic Indicators, St. Augustine, Florida. The shrimp and fish were fed daily with freshly hatched *Artemia* (brine shrimp). The marine diatom *Skeletonema costatum* was obtained from [supplier?],Monterey, California. The cultures were maintained on an enriched seawater medium (ESM)[8] using filtered (0.22 μm) seawater collected at the SPAWAR test facility in Point Loma, California.

Experimental Test Design and Protocols for Mysidopsis bahia and Menidia beryllina

Toxicity testing of all coatings consisted of 4-day static-renewal acute tests. Reference tests with the toxicant copper sulfate were conducted alongside the coating tests to validate good health and normal sensitivity of the test organisms. EPA test protocols were employed for the mysid and fish bioassays[9]. Replicates were run for each test concentration. Approximately 50 mL of the appropriate test dilution was poured into beakers, organisms were pipetted from holding tanks into the beakers, and topped off with test solution to a final volume of 200 mL for mysid shrimp and 250 mL for the silverside fish. Test concentrations for the extracts ranged from 18.75% to 300%. Test beakers were covered with glass lids and held in a recirculating waterbath at 25°C. During the assay, all animals were fed daily with newly hatched *Artemia.* Solutions were renewed every 24 hours, at which time beakers were cleaned and seawater chemistry measurements (temperature, pH, dissolved oxygen) were recorded. LC_{50} was estimated by linear interpolation between the two concentrations whose responses bracketed the response of interest[10].

Minimum requirements for test acceptability for dissolved oxygen were 40% saturation for acute tests. The seawater temperature fluctuations were required to be less than ± 2°C. In addition, seawater controls were used for each test. The EPA requires at least 90% survival of the larvae in the controls in order for the test to be valid.

Experimental Test Design and Protocols for Chain Diatom Biomass (Fluorescence) in Skeletonema costatum

Prior to testing, subcultures of *Skeletonema* were maintained in an enriched seawater medium (ESM) in 500 mL borosilicate Erlenmeyer flasks under a light regime of 12:12 hours (light:dark) at a light intensity of approximately 4000 lumen from cool white fluorescent bulbs. Culture temperature was maintained at 20°C. Test protocols were from the American Society for Testing and Materials Standard Guide for Conducting Static 96-hr Toxicity Test with Microalgae E1218[8]. At the beginning of each assay, test flasks containing 150 mL of test solution were inoculated with approximately 2 x 10^4 cells/mL *Skeletonema.* The test solution was made by combining exudate and filtered (0.22 μm) seawater to achieve the desired dilution. For most tests, dilutions ranged from 18.75% to 300%. Seawater controls were used in each test. Seawater was collected from the SPAWAR test facility. None of the exudates exhibited a background fluorescence that could confound test results. A Turner Model 112 fluorometer was used to measure *in-vivo* fluorescence from the growing cultures. The fluorometer was equipped with a combination T-5 lamp, a red sensitive photomultiplier tube (R-136), a blue excitation

filter (5-60), and a red filter (2-64) to detect fluorescence at wavelengths > 640 nanometers (nm) since chlorophyll *a* has maximum emission at 663 nm. The fluorometer was zeroed between readings with filtered (0.22 μm) seawater. All flasks were read within 1 hour after introduction of the diatoms,and at 24-hour intervals for a period of 96 hours. The measured fluorescence can be directly correlated to cell number and to the presence of viable diatom cells relative to the exudate concentration. Mean relative fluorescence, standard deviation, and the coefficient of variation were calculated for the controls and each exudate concentration. Relative fluorescence, expressed as percent of control was plotted over time for the entire test. An IC_{50} was calculated from 96-hour data. The test acceptability criteria for this test required that the controls contained at least 10^5 cells/mL at 96 hours.

All bioassays were deemed valid according to EPA acceptability criteria (i.e. control survival greater than or equal to 90% in the mysid and silverside fish tests, and control densities greater than 105 cells/mL in the diatom test). Water quality parameters were also within acceptable ranges and copper sulfate reference tests resulted in acceptable LC_{50s}.

RESULTS

The RTV11® base exhibited moderate toxicity towards mysids and higher toxicity towards diatoms but were nontoxic with respect to the silverside fish (Table 3. 2.1.). Coatings amended with oil typically had lower toxicity than unamended coatings particularly, in the case of diatoms. The commercial silicone product was the only coating that did not produce an LC_{50} in the mysids. However, diatoms were very sensitive to this coating, where an IC_{50} of 10% was observed.

Table 3.2.1. Summary of coating toxicity measured using EPA test methods. DBTDL refers to dibutyltindilaurate.

Coating	Mysid LC_{50}	Silverside Fish LC_{50}	Diatom IC_{50}	DBTDL (μg/L) 100% Exudate (1st 24 soak)	DBTDL (μg/L) 100% Exudate (4th 24 soak)
RTV11® (1)	135%	>300%	9%	966	1823
RTV11® + 10% DMSC15	246%	>300%	105%	57	95
RTV11® + 10% SF1147	221%	>300%	205%	36	111
Commercially available silicone coating	>300%	>300%	10%	267	73
Copper coating	10%	5%	8%	820 ug/L Cu++	820 ug/L Cu++

The following order was determined for sensitivity of the organisms to the exudates from the silicone coatings: chain diatom > mysid shrimp> silverside fish. IC_{50s} were observed in all diatom tests. Dibutyltindilaurate was measurable in all coating exudates, but a general correlation between toxicity and dibutyltindilaurate concentration was not apparent. The GE downselected coatings were much less toxic to the test organisms than the currently available copper paint.

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TASK 4. SCALE VALIDATION

The final large-scale application was performed on a 55.5 m^2 patch of surface on the USS Wyoming (SSBN-742) at the Trident Refit Facility (TRF) in Kings Bay, Georgia. The patch was applied on October 12-17, 2001. The application consisted of the GE SEA201A/SCM501C tiecoat, and RTV11® amended with 10% SF1147 as the foul-release topcoat. The preliminary inspection (24 hours after the application of the topcoat) indicated good adhesion of the coating system. Peel adhesion samples prepared during the application were tested before and after a 30-day aqueous immersion period. Excellent interfacial system adhesion was observed in both cases (pre-exposure = 964 +/-127 N/m and post exposure = 736 +/- 25 N/m). The USS Wyoming was inspected by NSWC in the third quarter of 2001 and no delamination was evident.

INTRODUCTION

In order to validate the performance of the coating on a larger scale vessel exposed to many different marine environments, a test patch was applied to the hull of a vessel in the active fleet. The demonstration consisted of an application on a U.S. Navy Trident submarine, based at Trident Refit Facility (TRF) in Kings Bay, Georgia. This application also served to verify the improvements in application protocol of the downselected coating system to a large structure. A test patch application on a military vessel is also one of the scale-up tests required by the US Military (MIL-P-24647 4.5.1.5) prior to qualification and implementation of any anticorrosive or antifouling paint system. The complete application and inspection report for this demonstration is presented in Appendix 4.A.

EXPERIMENTAL

The fouling release coating system was applied to a test area on the port side of the USS Wyoming (SSBN-742). The majority of the test patch was located just below maximum beam between frames 42 and 53, and was approximately 9.1 m. long by 6.1 m high. A smaller area extended up above maximum beam between frames 51 and 53, and measured about 1.5 m by 1.5 m. The entire application covered a 55.5 m^2 area.

The surface preparation was performed by TRF, Shop 71A, and consisted of wet grit blasting of the surface to a near white metal finish according to standards published by the Steel Structures Painting Council (SSPC SP 10, "Standards of Surface Finish"). The blast media, Black Beauty coal slag, was mixed with water at the blast nozzle to reduce dust. Rust-Lick B (ITW Fluid Products Group) rust inhibitor was used during the blasting to prevent flash rusting.

Following surface preparation, two layers of Mil-P-24441 type III epoxy were applied by TRF, Shop 71A. The fouling release coating system was applied over the military epoxy by personnel from General Electric (Schenectady, New York). The complete system

consisted of Amerlock 400 FD epoxy, GE SEA210A/SCM501C tiecoat, and GE RTV11® plus SF1147 amended topcoat (Table 4.1).

Airless spray equipment was used in the application of all coating layers (Table 4.2).

Table 4.1. Fouling release coating system applied to the USS Wyoming.

Coating Layer	**Coating System**	**Wet Film Thickness**
		Meters (10^4)
Epoxy (coats)	MIL-P-24441, Type III	
Epoxy	Ameron Marine Coatings Amerlock 400 (Gray epoxy)	1.5-2.0
Tiecoat	GE Silicones SEA 210A /SCM 501C	4.1-4.4
Topcoat	GE Silicones RTV11 plus10% SF1147 oil	3.0-3.6

Table 4.2. Spray equipment parameters employed for application of the coating system

Coating Layer	**Tip Size Meters (10^4)**	**Pump Ratio**	**Line Specs (Length; Inside Diameter (ID))**
Amerlock 400 (gray)	4.3	30:1	15.4 m.; $9.5x10^{-3}$ m. ID + 1.8 m; $9.5x10^{-3}$ m ID (whip)
SEA210A/SCM501C	5.3	40:1	15.4 m.; $9.5x10^{-3}$ m. ID + 1.8 m; $9.5x10^{-3}$ m ID (whip)
RTV11 + 10% SF1147	4.3	74:1	15.4 m; $1.2x10^{-2}$ m. ID + 1.8 m; $9.5x10^{-3}$ m ID (whip)

All coating layers were easily sprayed. The Amerlock 400 epoxy was thinned by approximately 5% with Sherwin-Williams K10 lacquer thinner. The SEA210A/SCM501C tiecoat was thinned with Sherwin-Williams Retarder Thinner K27 (20% by weight) and VM&P naphtha (20% by weight). The topcoat, RTV11 with 10% SF1147, was thinned by approximately 20% with VM&P naphtha. All coatings were filtered prior to application.

Wet film thickness measurements (WFT), obtained by the applicator, were used to achieve the proper thickness of each layer of the coating system (Table 4.1). Dry film thickness measurements (DFT) were obtained after application of the epoxy layers (300 readings, 17.7+/- 2.7 mils), and the thickness of the complete coating system (300

readings, 35.4 +/- 5.6 mils) was confirmed using an Elcometer 345 Digital Coating Thickness Gauge DFT gauge calibrated to 35 mils.

Environmental conditions at the time of the application were measured and recorded. A sling psychrometer was used to measure wet and dry bulb temperatures prior to coating application. Dew point was calculated from the wet and dry bulb temperatures. Surface temperature was measured using a surface temperature thermometer. The dew points, corresponding surface temperatures, and relative humidities are shown in Table 4.2. The surface temperature always exceeded the dew point by at least 5^{o} F to ensure that no moisture was present on the surface during paint application. Airless spray equipment was used in the application of all coating layers (Table 4.3).

Table 4.3. Environmental conditions during application of the coating system

Coating Layer	**Dew Point (^{o}C)**	**Surface Temperature (^{o}C)**	**Relative Humidity (%)**
Amerlock 400 (gray)	13.9	17.2	64
SEA210A/SCM501C	12.8	17.2	59
RTV11 + 10% SF1147	11.7	16.7	69

RESULTS

Application of the coating system was successful. The preliminary inspection (scratching the coating) to observe delamination 24 hrs after the application of the topcoat indicated good adhesion of the coating system. Peel adhesion samples were prepared during the application, as described in Task 2. These were shipped to GECRD and tested before and after a 30-day aqueous immersion period. Excellent interfacial system adhesion was observed in both cases (pre-exposure = 964 ± 127 N/m; post-exposure = 736 ± 25N/m). The patch was inspected by NSWC in the third quarter of 2001 and no delamination had occurred.

Life cycle costs

Life cycle costs were based on current sales volumes with a life cycle of 5-7 years. Blastco provided application costs and maintenance values were obtained from NE Power (Table 4.3.1).

Table 4.3.1. Life cycle costs

Approximate Life Cycle Costs of Silicone vs. Copper Ablative Paints[a]

Item	frequency (life cycle)		cost/ft^2 (life cycle)	
	Cu- Ablative	Silicone	Cu - Ablative	Silicone
Materials	once (installation)	once (installation)	$1.20	$4.46
Labor	once (installation)	once (installation)	$4.00	$5.00
Maintenance	twice	twice	$2.00	$2.00
Disposal	once (removal)	once (removal)	$2.00-$5.00	$1.00
Totals			$9.20-$12.20	$12.46

APPENDIX 0. ACCOMPLISHMENTS UNDER THIS PROGRAM

0.A. List of patents issued under this program

1.	U.S. 6,107,381	Condensation Curable Silicone Foul Release Coatings and Articles Coated Therewith, Judith Stein, Timothy Burnell and James Cella, August 22, 2000.
2.	U.S. 6,126,991	Method for Enhancing the Properties of Biofouling Release Coatings, Judith Stein, October 31, 2000.
3.	U.S. 6,180,249	Curable Silicone Foul Release Coatings and Articles, Judith Stein, January 30, 2001.

US006107381A

United States Patent [19]

Stein et al.

[11] **Patent Number: 6,107,381**

[45] **Date of Patent: Aug. 22, 2000**

[54] **CONDENSATION CURABLE SILICONE FOUL RELEASE COATINGS AND ARTICLES COATED THEREWITH**

[75] Inventors: **Judith Stein**; **Timothy Brydon Burnell**, both of Schenectady; **James Anthony Cella**, Clifton Park, all of N.Y.

[73] Assignee: **General Electric Company**, Schenectady, N.Y.

[21] Appl. No.: **09/094,975**

[22] Filed: **Jun. 15, 1998**

[51] **Int. Cl.**[7] **C08G 77/06**

[52] **U.S. Cl.** **524/265**; 524/267; 524/268; 524/731; 524/858; 524/859; 524/863; 528/14; 528/17; 528/18; 528/901

[58] **Field of Search** 106/287.12, 287.13, 106/287.14, 287.16; 528/14, 17, 18, 33, 34, 901; 524/261, 265, 267, 268, 588, 731, 859, 860, 863

[56] **References Cited**

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Primary Examiner—D. S. Nakarani

Attorney, Agent, or Firm—Bernadette M. Bennett; Donald S. Ingraham

[57] **ABSTRACT**

Anti-fouling coatings comprise a room temperature vulcanizable polyorganosiloxane composition and a polyorganosiloxane free from silanol groups and comprising at least one hydroxy- or alkoxy-terminated polyoxyalkylenealkyl radical. The latter is capable of blooming to the surface of the cured room temperature vulcanizable composition, thus inhibiting the deposition of marine life on the coated article.

16 Claims, No Drawings

CONDENSATION CURABLE SILICONE FOUL RELEASE COATINGS AND ARTICLES COATED THEREWITH

This invention was made with government support under Contract No. N61533-93-C-0062 awarded by the Department of the Navy and Contract No. N00014-96-C-0145 awarded by DARPA. The government has certain rights in this invention.

BACKGROUND OF THE INVENTION

This invention relates to foul release coatings and articles coated therewith.

As poetically stated in U.S. Pat. No. 4,861,670, "Marine fouling due to pernicious and pestiferous sessile organisms is a problem which reaches from ancient times to the present." In more simple terms, a perennial major aggravation to shippers and users of marine equipment in contact with water is the tendency of such equipment to become encrusted with varieties of wildlife, as illustrated by barnacles and zebra mussels.

Said patent goes on to describe in considerable detail the types of treatments that have been employed, starting as early as 1854, to minimize marine fouling. Treatment materials have included compounds of such metals as copper, tin, arsenic, mercury, zinc, lead, antimony, silver and iron, as well as toxic organic materials such as strychnine and atropine. With increasing interest in the state of the environment, the use of such materials has been strongly discouraged.

More recently, polyorganosiloxanes (hereinafter sometimes designated "silicones" for brevity) have been found useful as anti-fouling coatings. They include condensation cured room temperature vulcanizable (hereinafter sometimes "RTV") compositions comprising silica as a filler in combination with silanol- or trialkoxy-terminated silicones, catalysts and crosslinking agents. They may be made sprayable by dilution with solvents, typically volatile organic compounds such as hydrocarbons.

There is still a need, however, to improve various properties of RTV-based foul release coatings, particularly their release efficiency and their effective lifetime.

SUMMARY OF THE INVENTION

The present invention is based on the discovery that addition of specifically defined water-insoluble silicones to a conventional RTV formulation improves foul release properties. It includes foul release coatings having said improved properties and articles coated therewith.

In one of its aspects, the invention is directed to condensation curable coating compositions comprising the following and any reaction products thereof:

(A) a one- or two-part room temperature vulcanizable polyorganosiloxane composition, and

(B) a marine foul release-enhancing proportion of at least one polyorganosiloxane free from silanol groups and comprising about 10–60% by weight of at least one hydroxy- or alkoxy-terminated polyoxyalkylenealkyl radical,

component B being capable of blooming to the surface of the cured product of component A.

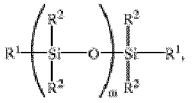
Another aspect of the invention is articles comprising a marine structure coated with an anti-fouling coating which is the condensation cured reaction product of the composition defined hereinabove.

DETAILED DESCRIPTION; PREFERRED EMBODIMENTS

The word "component" is frequently employed herein for brevity to designate the materials present in the compositions of the invention. Its use is independent of the possible interreaction of said materials to form other chemical constituents.

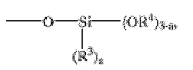
Component A of the compositions of the invention may be a conventional one-part or two-part RTV composition; it is most often a two-part composition. It typically comprises at least one reactive silicone, at least one condensation catalyst and at least one crosslinking agent.

The reactive silicone is most often a polydialkylsiloxane, typically of the formula



(I)

wherein each R^1 is hydroxyl or



(II)

each R^2 is independently a hydrocarbon or fluorinated hydrocarbon radical, each R^3 and R^4 is a hydrocarbon radical, a is 0 or 1 and m has a value such that the viscosity of said reactive silicone under ambient temperature and pressure conditions is up to about 50,000 centipoise. Illustrative hydrocarbon radicals are C_{1-20} alkyl, C_{6-20} aryl and alkaryl, vinyl, isopropenyl, allyl, butenyl and hexenyl, with C_{1-4} alkyl and especially methyl being preferred. An illustrative fluorinated hydrocarbon radical is 3,3,3-trifluoropropyl. Most often, each R^2, R^3 and R^4 is alkyl and preferably methyl.

It is within the scope of the invention to employ two or more reactive silicones, differing in average molecular weight. This may afford a bimodal composition having performance advantages over a simple monomodal composition.

The condensation catalyst may be any of those known to be useful for promoting condensation curing of an RTV material. Suitable catalysts include tin, zirconium and titanium compounds as illustrated by dibutyltin dilaurate, dibutyltin diacetate, dibutyltin methoxide, dibutyltin bis (acetylacetonate), 1,3-dioxypropanetitanium bis (acetylacetonate), titanium naphthenate tetrabutyl titanate and zirconium octanoate. Various salts of organic acids with such metals as lead, iron, cobalt, manganese, zinc, antimony and bismuth may also be employed, as may non-metallic catalysts such as hexylammonium acetate and benzyltrimethylammonium acetate. For most purposes, the tin and titanium compounds are preferred.

As crosslinking agents, trifunctional (T) and tetrafunctional (Q) silanes are useful, the term "functional" in this context denoting the presence of a silicon-oxygen bond. They include such compounds as methyltrimethoxysilane, methyltriethoxysilane, 2-cyanoethyltrimethoxysilane, methyltriacetoxysilane, tetraethyl silicate and tetra-n-propyl silicate. The Q-functional compounds, i.e., tetraalkyl silicates, are often preferred.

Component A may contain other constituents, including reinforcing and extending (non-reinforcing) fillers. Typical reinforcing fillers are commercially available in the form of relatively large aggregated particles, typically having an average size significantly greater than 300 nm. The preferred fillers are the silica fillers, including fumed silica and precipitated silica. These two forms of silica have surface areas in the ranges of 90–325 and 80–150 m^2/g, respectively.

The reinforcing filler is most often pretreated with a treating agent to render it hydrophobic. Typical treating agents include cyclic silicones such as cyclooctamethyltetrasiloxane and acyclic and cyclic organosilazanes such as hexamethyidisilazanc, 1,3-divinyl-1,1,3,3-tetramethyldisilazane, hexamethylcyclotrisilazane, octamethylcyclotetrasilazane and mixtures of these. Hexamethyidisilazane is often preferred.

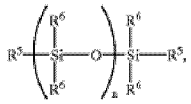
Non-reinforcing fillers include titanium dioxide, lithopone, zinc oxide, zirconium silicate, iron oxides, diatomaceous earth, calcium carbonate, glass fibers or spheres, magnesium oxide, chromic oxide, zirconium oxide, aluminum oxide, crushed quartz, calcined clay, talc, kaolin, asbestos, carbon, graphite, cork, cotton and synthetic fibers.

The proportions of the constituents of component A may be varied widely. The amount of filler is generally about 5–200 parts and preferably about 10–150 parts by weight per 100 parts of reactive silicone. Catalysts and crosslinkers are generally present in the amounts of about 0.001–2.5% and about 0.25–5.0% by weight respectively, based on the combination of reactive silicone and filler.

Component B is a water-insoluble polyorganosiloxane free from silanol groups and containing at least one hydroxy- or alkoxy-terminated polyoxyalkylenealkyl radical. Said radical or radicals comprise about 10–60% by weight of component B; that is, the molecular weight attributable to said radicals is about 10–60% by weight of the total molecular weight attributable to component B.

In general, component B comprises compounds of the formula

(III)



wherein each R^5 is a hydrocarbon radical and each R^6 is a hydrocarbon or fluorinated hydrocarbon radical, with the proviso that at least one of the R^{5-6} radicals has the formula

$$—R^7—(OR^8)_n—OR^9, \quad (IV)$$

wherein R^7 and each R^8 is independently C_{2-6} alkylene and R^9 is hydrogen or C_{1-4} primary or secondary alkyl; n has a value such that the weight average molecular weight of the compound of formula III is in the range of about 500–40,000; and z and the number of radicals of formula IV are such that said radicals of formula IV comprise about 10–60% by weight of component B. The illustrative and preferred hydrocarbon radicals for R^{5-6} are the same as those for R^{1-2}. R^7 and R^8 may be, for example, ethylene, propylene or trimethylene; R^7 is preferably trimethylene and R^8 is preferably ethylene. R^9 is most often hydrogen or methyl.

Illustrative compounds of formula III are available from Gelest, Inc., under the trade designations "DMS-C" and "DBE". One illustration of such a compound is "DMS-C15" which has a molecular weight of 1,000 and a viscosity in the range of 30–50 centipoise and in which each R^6 is methyl, each R^5 has formula IV, R^7 is trimethylene, R^8 is ethylene, R^9 is hydrogen and the radicals of formula IV constitute about 20% by weight of the molecule. Another is "DBE-224", which has a molecular weight of 10,000 and a viscosity of about 400 centipoise and in which each R^5 and each R^6 is methyl, with the proviso that enough R^6 radicals have formula IV in which R^7 is trimethylene, R^8 is ethylene and R^9 is methyl to provide about 25% by weight of the molecule. More generally, the compounds employed as component B which contain internal radicals of formula IV should contain them in an amount to provide about 20–30% by weight of the molecule.

Component B is present in the compositions of the invention in an effective proportion to enhance foul release properties. For the most part, about 5–20 parts by weight per 100 parts of component A is adequate. The essential property of component B is that of blooming to the surface of the cured product of component A during or after the curing process, by reason of its higher polarity than component A.

The compositions of this invention may also incorporate further constituents such as non-reactive silicone oils, dyes, solubilizing agents and solvents to render them sprayable if sprayability is desirable. These may be introduced as part of component A or as adjuvants to the entire composition, as appropriate.

Suitable solvents include aromatic hydrocarbons such as toluene or xylene and aliphatic hydrocarbons such as petroleum naphtha. Solubilizing agents include vinyl-substituted silicones, generally present, if at all, in amounts up to about 25% by weight based on the combination of components A and B.

The marine structures in the articles of the invention are often ships' hulls. However, other underwater articles such as liquid collecting and discharge pipes, dry dock equipment and the like are included. Suitable materials therefor include metals such as iron and aluminum and resinous materials such as fiber-reinforced thermoplastic or thermoset resins.

Application of the compositions of the invention is typically preceded by the application of conventional pretreatment layers. These may include, for example, anti-corrosive epoxy primers, mist coats and tie-layers comprising polyorganosiloxanes and toughening components. The compositions of the invention may be applied by conventional techniques such as brushing or drawing down, or by spraying if they are suitably diluted.

The invention is illustrated by the following examples. All parts and percentages are by weight.

EXAMPLE 1

A condensation curable RTV composition was prepared by blending the following constituents in the amounts indicated:

Part I:

- Silanol-stopped polydimethylsiloxane, viscosity 30,000 centipoise—100 parts;
- non-reactive polydimethylsiloxane oil, viscosity 20 centipoise—38.5 parts;
- n-propyl silicate—12.13 parts;
- fumed silica, hexamethyldisilazane-treated—37 parts.

Part II: dibutyltin dilaurate.

The two parts, also containing conventional additives such as non-reinforcing fillers, dyes and compatibilizers, were combined in proportions such that the dibutyltin dilaurate was present in the amount of 2.43 parts per 100 parts of silanol-stopped polydimethylsiloxane. To the resulting RTV

composition was added 10% by weight, based on RTV composition, of a polydimethylsiloxane having hydroxy-terminated 3-(polyoxyethylene)propyl end groups and a weight average molecular weight of about 1,000. The composition thus prepared was applied by curtain coating to aluminum test panels which had been previously coated with a commercially available epoxy anti-corrosion coating, mist coat and tie-layer. The test panels were exposed to water for 12 months, after which time the 91–99% of their surface area was unfouled and no encrusting bryozoans were present. A control panel, coated with the RTV composition alone, had 66–69% of its surface area unfouled and had 25–50% encrusting bryozoans.

EXAMPLES 2–3

An RTV composition was prepared by blending (Part I) 70 parts of a silanol-terminated polydimethylsiloxane having a viscosity of 3,100 centipoise, 29 parts of calcium carbonate and 2 parts of tetraethyl silicate, and (Part II) 0.5 part of dibutyltin dilaurate. There were then added 10%, based on RTV composition, of the following

Example 2—the hydroxy-terminated 3-(polyoxyethylene) propyl polydimethylsiloxane of Example 1.

Example 3—a methyl-terminated polydimethylsiloxane containing internal methoxy-terminated 3-(polyoxyethylene)propyl groups and having a weight average molecular weight of 10,000.

Aluminum test panels similar to those of Example 1 were primed with a commercially available primer and then curtain coated with the compositions of Examples 2–3. They were then submerged in a salt water lagoon in Florida in cages until barnacle settlement occurred. At the end of the test period, barnacle adhesion, as determined by ASTM test procedure D5618, for the panels coated with the products of Examples 2 and 3 were 0.69 psi and 5.18 psi, respectively. A control panel coated with the RTV composition only had a barnacle adhesion of 10.35 psi.

What is claimed is:

1. A condensation curable coating composition comprising the following and any reaction products thereof:

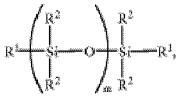
(A) a one- or two-part room temperature vulcanizable polyorganosiloxane composition, and

(B) a marine foul release-enhancing proportion of at least one polyorganosiloxane free from silanol groups and comprising about 10–60% by weight of at least one hydroxy- or alkoxy-terminated polyoxyalkylenealkyl radical,

component B being capable of blooming to the surface of the cured product of component A.

2. A composition according to claim **1** wherein component A comprises at least one reactive silicone, at least one condensation catalyst and at least one crosslinking agent.

3. A composition according to claim **2** wherein the reactive silicone is a polydialkylsiloxane having the formula



(I)

wherein each R^1 is hydroxyl or

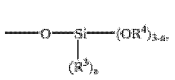
(II)

each R^2 is independently a hydrocarbon or fluorinated hydrocarbon radical, each R^3 and R^4 is a hydrocarbon radical, a is 0 or 1 and m has a value such that the viscosity of said reactive silicone under ambient temperature and pressure conditions is up to about 50,000 centipoise.

4. A composition according to claim **3** wherein each R^2 is methyl.

5. A composition according to claim **3** wherein each R^3 is hydroxyl.

6. A composition according to claim **3** wherein each R^3 is



(II)

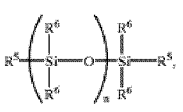
wherein each R^3 and R^4 is a hydrocarbon radical and a is 0 or 1.

7. A composition according to claim **2** wherein the condensation catalyst is a tin, zirconium or titanium compound.

8. A composition according to claim **2** wherein the crosslinking agent is a trifunctional or tetrafunctional silane.

9. A composition according to claim **8** wherein the crosslinking agent is a tetraalkyl silicate.

10. A composition according to claim **1** wherein component B comprises compounds of the formula



(III)

wherein each R^5 is a hydrocarbon radical and each R^6 is a hydrocarbon or fluorinated hydrocarbon radical, with the proviso that at least one of the R^{5-6} radicals has the formula

$$—R^7—(OR^8)_z—OR^9, \quad \text{(IV)}$$

wherein R^7 and each R^8 is independently C_{2-6} alkylene and R^9 is hydrogen or C_{1-4} primary or secondary alkyl; n has a value such that the weight average molecular weight of the compound of formula III is in the range of about 500–40,000; and z and the number of radicals of formula IV are such that said radicals of formula IV comprise about 10–60% by weight of component B.

11. A composition according to claim **10** wherein each R^5 and R^6 that does not have formula IV is methyl.

12. A composition according to claim **11** wherein component B has a viscosity in the range of 30–50 centipoise and each R^6 therein is methyl, each R^5 has formula IV, R^7 is trimethylene, R^8 is ethylene and R^9 is hydrogen.

13. A composition according to claim **11** wherein R^7 is trimethylene, each R^8 is ethylene and R^9 is hydrogen or methyl.

14. A composition according to claim **12** wherein each R^5 has formula IV and R^9 is hydrogen.

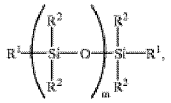
15. A composition according to claim **11** wherein component B has a viscosity of about 400 centipoise and each R^5

and each R^6 is methyl, with the proviso that enough R^6 radicals have formula IV in which R^7 is trimethylene, R^8 is ethylene and R^9 is methyl to provide about 20–30% by weight of the molecule.

16. A condensation curable coating composition comprising components (A) and (B) and any reaction products thereof:

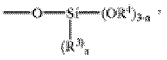
wherein the first component (A) comprises a one- or two-part room-temperature vulcanizable polyorganosiloxane composition which comprises at least one crosslinking agent wherein the agent comprises tetraalkyl silicate; at least one condensation catalyst wherein the catalyst comprises a tin, zirconium or titanium compound; and at least one reactive silicone wherein the reactive silicone is a polydialkylsiloxane having the formula

(I)



wherein each R^2 is methyl, and each R^1 is hydroxyl or

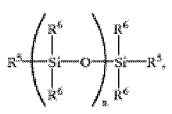
(II)



wherein each R^5 and R^6 is a hydrocarbon radical and a is 0 or 1, and

wherein the second component (B) comprises a marine foul release-enhancing proportion which comprises compounds of the formula

(III)



wherein each R^5 has the formula

(IV)

wherein each R^6 therein is methyl, R^7 is trimethylene, R^8 is ethylene and R^9 is hydrogen; n has a value such that the weight average molecular weight of the compound of formula is in the range of about 500–40,000; and z and the number of radicals of formula IV are such that said radicals of formula IV comprise about 10–60% by weight of component B,

component B being capable of blooming to the surface of the cured product of component A.

* * * * *

US006126991A

United States Patent [19]

Stein

[11] **Patent Number: 6,126,991**

[45] **Date of Patent: Oct. 3, 2000**

[54] **METHOD FOR ENHANCING THE PROPERTIES OF BIOFOULING RELEASE COATINGS**

[75] Inventor: **Judith Stein**, Schenectady, N.Y.

[73] Assignee: **General Electric Company**, Schenectady, N.Y.

[21] Appl. No.: **09/294,069**

[22] Filed: **Apr. 19, 1999**

[51] **Int. Cl.**[7] **B32B 35/06**; B05D 1/38

[52] **U.S. Cl.** **427/140**; 427/142; 427/407.1; 427/258; 427/334; 427/416

[58] **Field of Search** 427/140, 142, 427/2.24, 2.28, 2.3, 2.31, 258, 333, 334, 340, 407.1, 202, 205; 106/287.12, 287.16; 252/384; 556/450, 463

[56] **References Cited**

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Primary Examiner—Shrive Beck
Assistant Examiner—Jennifer Kolb
Attorney, Agent, or Firm—Noreen C. Johnson; Douglas E. Stoner

[57] **ABSTRACT**

The present invention relates to a method of introducing enhanced biofouling release properties to intact biofouling release coatings by exposing the surface of the biofouling release coating to a restorative compound for a time sufficient to effect enhancement of biofouling release properties. Also disclosed are kits useful in carrying out these processes.

11 Claims, No Drawings

METHOD FOR ENHANCING THE PROPERTIES OF BIOFOULING RELEASE COATINGS

BACKGROUND OF THE INVENTION

This invention was made with Government support under Government Contract No. N00014-96-C-0145 awarded by DARPA. The Government may have certain rights to the invention.

This invention is related to the field of biofouling release coatings for use in industrial, commercial or military marine and freshwater applications. In particular, this invention relates to a method for regenerating a biofouling release coating which has decreased release efficacy due to depletion or lack of an incorporated oil.

Damage to underwater power cables, ships, and the like due to colonization of their surfaces by organisms (including, but not limited to, barnacles) has serious economic consequences in marine and freshwater industries. Antifouling and fouling release coatings have been developed to prevent or reduce biofouling, and to loosen the strength of the attachment of marine organisms to make cleaning surfaces easier. There are many commercial foul release coatings including, for example, GE EXSIL® 2200. However there have been no reports of renewal methods for these coatings.

There has been a continuing need in the coatings industry for new methods for increasing the useful life of fouling release and antifouling coatings. At present, the useful lifetime of a copper ablative antifouling coating is approximately three years, after which time the coating must be removed from the hull and reapplied. It is estimated that the effective life span of silicone fouling release coatings is about 5–7 years.

The release characteristics of silicone fouling release coatings are known to be significantly enhanced by the addition of oils such as mineral oil and silicone oils. Barnacle adhesion measurements on fouling release coatings substantiate that removal of fouling requires less work when the silicone topcoat has been prepared with incorporated oils. For example, silicone oils such as dimethyl silicone oils, phenyl-modified silicone oils, and polyether-modified silicone oils have been incorporated into biofouling release coatings.

Unfortunately, these additives tend to diffuse out of the coating during use and are thus rapidly depleted. The depleted coatings lose their enhanced foul-release properties, and consequently their effectiveness is reduced. Depletion of the additive therefore limits the useful life of the coating, necessitating periodic removal and reapplication of a new silicone biofouling release coating. A recoat technology for these coatings which does not require complete removal and reapplication of the coating would significantly reduce life- cycle costs and enhance the attractiveness of these coatings to the power utility, military, industrial, and commercial markets.

To forestall the rapid oil-depletion of oil-containing biofouling release coatings, larger amounts of oil have been incorporated into these coatings. This solution to the problem does curtail the rapid depletion of the oil, but unfortunately it tends to severely impair the mechanical properties of the coatings, particularly tear strength and abrasion resistance. Increasing the original additive content of biofouling release coatings, therefore, does not provide a workable method of increasing the life of the coatings.

Silicone biofouling release coatings made without additives also have been used to make cleaning surfaces of organisms easier, but they are not as effective as coatings with incorporated oils. A method for enhancing the properties of these coatings, as well as restoring the enhanced release properties of older coatings originally containing additives is highly desirable.

SUMMARY OF THE INVENTION

The present invention relates to a method of introducing enhanced biofouling release properties to an intact biofouling release coating, which method comprises exposing the surface of the biofouling release coating to a restorative compound for a time sufficient to effect enhancement of biofouling release properties.

In a further aspect, the present invention relates to a kit for the enhancement of the biofouling release properties of an intact biofouling release coating, said kit comprising a container containing a restorative compound suitable for said enhancement.

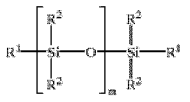
In yet another aspect, the present invention relates to a kit for the enhancement of the biofouling release properties of an intact biofouling release coating, said kit comprising a container containing a biofouling release coating, and a container containing a restorative compound suitable for said enhancement.

DETAILED DESCRIPTION OF THE INVENTION

The term "oil-depleted" referring to release coatings will be used in this application to denote any biofouling release coating, whether manufactured with or without incorporated oils, which has been depleted of the oil additive or lacks the oil additive, and therefore has a reduced effectiveness compared to coatings containing the oil additive. It is not to be construed as limited solely to coatings which were manufactured containing oil and have subsequently been depleted of the oil.

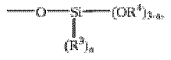
The biofouling release coatings which may be enhanced by the present invention include generally any coating into which a restorative compound may be incorporated for enhancement of biofouling release properties. The present invention is particularly applicable to release coatings which include a conventional one-part or two-part RTV composition, preferably a two-part composition. It may comprise at least one reactive silicone, at least one condensation catalyst and at least one crosslinking agent.

The reactive silicone is preferably at least one of a polydialkylsiloxane, a polydiarylsiloxane, or a polyalkylarylsiloxane typically of the formula



(I)

wherein each R^1 is a hydroxyl radical or



(II)

each R^2 is independently a hydrocarbon or fluorinated hydrocarbon radical, each R^3 and R^4 is independently a

hydrocarbon radical, a is 0 or 1, and m has a value such that the viscosity of said compound under ambient temperature and pressure conditions is up to about 50,000 centipoise. Illustrative hydrocarbon radicals are C_{1-20} alkyl, C_{6-20} aryl and alkaryl, vinyl, isopropenyl, allyl, butenyl and hexenyl, with phenyl, C_{1-4} alkyl and especially methyl being preferred. An illustrative fluorinated hydrocarbon radical is 3,3,3-trifluoropropyl. Preferably, each R^2, R^3 and R^4 is alkyl and preferably methyl. The biofouling release coatings may comprise two or more reactive silicones, differing in average molecular weight, which may afford a bimodal composition having performance advantages over a simple monomodal composition.

The condensation catalyst may be any of those known to be useful for promoting condensation curing of an RTV material. Suitable catalysts include tin, zirconium, titanium, and aluminum compounds as illustrated by dibutyltin dilaurate, dibutyltin diacetate, dibutyltin methoxide, dibutyltin bis(acetylacetonate), 1,3-dioxypropanetitanium bis (acetylacetonate), titanium naphthenate, tetrabutyl titanate, zirconium octanoate, and aluminum acetylacetonate. Various salts of organic acids with such metals as lead, iron, cobalt, manganese, zinc, antimony and bismuth may also be employed. For most purposes, the tin and titanium compounds are preferred.

As crosslinking agents, trifunctional (T) and tetrafunctional (Q) silanes are useful, the term "functional" in this context denoting the presence of a silicon-oxygen bond. They include such compounds as methytrimethoxysilane, methyltriethoxysilane, 2-cyanoethyltrimethoxysilane, methyltriacetoxysilane, tetraethyl silicate and tetra-n-propyl silicate. The Q-functional compounds, i.e., tetraalkyl silicates, are often preferred.

The coating may contain other constituents, including reinforcing and extending (non-reinforcing) fillers. Suitable reinforcing fillers are commercially available in the form of relatively large aggregated particles typically having an average size significantly greater than about 300 nanometers (nm). The preferred fillers are the silica fillers, including fumed silica and precipitated silica. Those two forms of silica have surface areas in the ranges of 90–325 and 8–150 m^2/g, respectively.

The reinforcing filler is most often pretreated with a treating agent to render it hydrophobic. Typical treating agents include cyclic silicones such as cyclooctamethyltetrasiloxane and acyclic and cyclic organosilazanes such as hexamethyldisilazane, 1,3-divinyl-1,1,3,3-tetramethyldisilazane, hexamethylcyclotrisilazane, octamethylcyclotetrasilazane, and mixtures thereof. Hexamethyldisilazane is often preferred.

Non-reinforcing fillers include titanium dioxide, lithopone, zinc oxide, zirconium silicate, iron oxides, diatomaceous earth, calcium carbonate, glass fibers or spheres, magnesium oxide, chromic oxide, zirconium oxide, aluminum oxide, crushed quartz, calcined clay, talc, kaolin, asbestos, carbon, graphite, cork, cotton and synthetic fibers.

The proportions of the constituents of the silicone component may be varied widely. The amount of filler is generally about 5–200 parts and preferably about 10–150 parts by weight per 100 parts of reactive silicone. Catalysts and crosslinkers are generally present in the amounts of about 0.001–2.5% and about 0.25–5.0% by weight respectively, based on the combination of reactive silicone and filler.

Restorative compounds which may be used in connection with the present invention include oils such as polyorganosiloxanes (e.g., polyalkylsiloxanes, organic-compatible siloxanes, polymethylphenylsiloxanes, polydiphenylsiloxanes, hydrophilic siloxanes, carbinolfunctional siloxanes, and related compounds); crude oil products (e.g., paraffin wax, petroleum waxes, petrolatum, liquid paraffin, and greases); and fats, oils and waxes.

Oil-depleted biofouling release coatings may be restored by applying the restorative compound to the release coating surface. Such application may be by soaking, dipping, spraying, wiping, brushing, coating or otherwise exposing the coating surface to the desired restorative compound. During the application process, it is desirable to maintain the restorative compound in contact with the coating for a period of time sufficient to ensure adequate uptake of the restorative compound by the coating. The optimum period will vary according to a number of factors, including the identity and condition of the coating, the identity of the restorative compound, etc. The best contact time period for a given set of conditions may be readily determined by one of ordinary skill. A preferred period is at least about 10 hours, more preferably from about 10 to about 90 hours, and most preferably from about 24 to about 72 hours. Sufficient volumes of restorative compound to completely cover or immerse the surface of the coating are desirable, but not necessary. After treatment, the surface may be wiped dry, if desired. Any excess restorative compound may be recovered from the wipe for reuse by means known in the art.

The restorative compound useful in the present invention may be sold in the form of a kit, i.e., in a suitable container (e.g., a drum, can, carton, etc.), optionally with instructions for use being present in the kit, for example attached to or in association with the container. The kit may also comprise a container having a biofouling release coating, preferably compatible with the restorative compound.

The invention will be illustrated by the following non-limiting Examples.

EXAMPLES

1. PREPARATION OF BIOFOULING RELEASE COATING

An aluminum platen (4 in.×12 in.) was primed by wiping the surface with the commercially available primer SS4155 (GE Silicones). A coating was then prepared from 100 grams (g) of a silicone RTV composition (approx. 71% polydimethylsiloxane [viscosity, 310 centipoise], 29% calcium carbonate, and 2% ethyl silicate), catalyzed with 0.5 g dibutyltin dilaurate, and applied to the platen to a dry film thickness of 15 mils using a draw down blade. The coating was allowed to cure at room temperature for 7 days.

2. PREPARATION OF EXTRACTED (AGED) BIOFOULING RELEASE COATING

A biofouling release coating prepared as in Example 1 was extracted seven times in 200 milliliters (ml) toluene over a period of 3 days and dried.

3. PREPARATION OF REGENERATED BIOFOULING RELEASE COATING

An extracted biofouling release coating prepared as in Example 2 was soaked in a bath of approximately 300 ml polydimethyldiphenylsiloxane oil (number average molecular weight [Mn] about 2000) for 3 days, and then wiped dry.

4. PREPARATION OF ADDITIVE-ENHANCED BIOFOULING RELEASE COATING

An aluminum platen primed as in Example 1 was coated with a biofouling release coating prepared from 100 g of a

silicone RTV composition (described in example 1), 10 g polydimethyldiphenylsiloxane oil (Mn about 2000), and 0.5 g dibutyltin dilaurate, to a dry film thickness of 15 mils using a draw down blade. The coating was allowed to cure at room temperature for 7 days.

5. PREPARATION OF EXTRACTED (AGED) ADDITIVE-ENHANCED BIOFOULING RELEASE COATING

A biofouling release coating prepared as in Example 4 was extracted in toluene as described in Example 2.

6. REGENERATION OF ADDITIVE-ENHANCED BIOFOULING RELEASE COATING

An extracted biofouling release coating was prepared as in Example 5, then soaked in a bath of approximately 300 ml polydimethyidiphenylsiloxane oil (Mn about 2000) for 3 days, and wiped dry.

7. DETERMINATION OF BIOFOULING RELEASE PROPERTIES

Samples prepared according to each of the examples 1–6 were placed in the Indian River in Florida in cages until barnacle settlement occurred. The barnacle attachment strength was measured on two identically prepared panels for each surface coating, according to the barnacle adhesion test method as described below. Results are shown in Table 1. The data indicate that the enhanced biofouling release properties of an oil-depleted sample is restored by exposure to a new additive source.

Biofouling release properties were quantitated by a standard barnacle adhesion test. This test measures the force required to remove barnacles from a surface and provides data that can be used to compare the ability of surfaces to reduce biofouling (barnacle) adhesion under field conditions as described in Example 7. This test was approved as an ASTM standard in 1994 (ASTM D5618, 1994).

Live barnacles selected for testing were between 5 and 20 millimeters (mm) diameter at the base adhering to the surface to be tested. Their species and condition were noted. Barnacles were preferably at least 20 mm from the edge of the test substrate panel, attached to undamaged areas of the test surface, and not in direct contact with other barnacles. The barnacle base was measured with calipers in four directions (0, 45, 90, 135 degrees) to obtain an average base diameter, taking care not to dislodge the barnacle. The barnacle base plate area, A, was then estimated using the average base diameter, d_a, according to the formula

$$A=(\pi d_a^2)/4.$$

A shear force was then applied to the barnacle base, parallel to the testing surface using a hand-held Shimpo mechanical dial force gauge (range=0–89 N (0–20 lb); accuracy=±0.3%; resolution=0.45N (0.1 lb)) at a rate of approximately 4.15N s^{-1} (1.0 lb s^{-1}) until the barnacle became detached or the maximum shear force was reached. The force (F) required for detachment was noted. If more than 10% of the barnacle base plate was left attached to the substrate, the test was deemed void since incomplete removal of the barnacle base plate from the surface during testing may lead to erroneous adhesion values. The strength of adhesion, τ, was then calculated according to the formula

$$\tau=F/A.$$

Whenever possible, a minimum of ten measurements were made per coating.

TABLE 1

Barnacle Adhesion Values

Example	Barnacle Adhesion (psi)
Ex. 1: release coating manufactured without incorporation of additives	panel 1 13.95 +/- 4.27 panel 2 14.07 +/- 4.01
Ex. 2: release coating manufactured without incorporation of additives (extracted)	panel 1 12.63 +/- 3.36 panel 2 16.38 +/- 5.10
Ex. 3: release coating manufactured without incorporation of additives (restored)	panel 1 5.43 +/- 2.24 panel 2 7.75 +/- 6.19
Ex. 4: release coating manufactured with incorporation of additives	panel 1 8.29 +/- 2.16 panel 2 0.29 +/- 0.24
Ex. 5: release coating manufactured with incorporation of additives (extracted)	panel 1 14.96 +/- 3.79 panel 2 15.39 +/- 3.68
Ex. 6: release coating manufactured with incorporation of additives (restored)	panel 1 10.81 +/- 4.21 panel 2 9.91 +/- 3.88

The tests provide data for surfaces that have been coated with a biofouling release coating manufactured with or without an additive to increase the release properties of the coating (examples 1 and 4), and those same coated surfaces after an oil depletion treatment (examples 2 and 5), and after subsequent restoration with the inventive method (examples 3 and 6).

The data confirm that experimental oil-depletion of biofouling release coatings manufactured with oil reduces the effectiveness of the release coating (compare examples 4 and 5), as does the oil-depletion known to occur with aging. Coatings lacking the additive were unaffected by the simulated aging, as expected (compare examples 1 and 2).

Use of the inventive method for restoring enhanced biofouling release properties to such a coating decreases the amount of force needed to remove the barnacles, evidencing a restoration of the enhanced release properties (compare examples 5 and 6). The inventive method also improves the biofouling release properties of coatings not originally manufactured with oils (compare examples 1 and 2 with example 3). The results in Table 1 demonstrate clearly that intact silicone biofouling release coatings are capable of capturing or recapturing additives applied to their surfaces, and acquiring or reacquiring the enhanced biofouling release properties those additives impart.

What is claimed is:

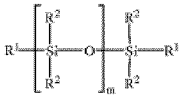
1. A method of introducing enhanced biofouling release properties to an intact, oil-depleted biofouling release coating, which method comprises exposing the surface of the biofouling release coating to a restorative compound for a time sufficient to effect enhancement of biofouling release properties, wherein the restorative compound is selected from the group consisting of silicone oil, a hydrocarbon oil, a grease, a wax, and combinations thereof.

2. The method of claim 1, wherein the biofouling release coating comprises a silicone-based polymer.

3. The method of claim 2, wherein the polymer comprises a polydialkylsiloxane.

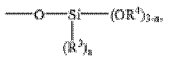
4. The method of claim **3**, wherein the polydialkylsiloxane has the formula:

(I)



wherein each R^1 is a hydroxyl radical or

(II)



each R^2 is independently a hydrocarbon or fluorinated hydrocarbon radical, each R^3 and R^4 is a hydrocarbon radical, a is 0 or 1, and m has a value such that the viscosity of said compound under ambient temperature and pressure conditions is up to about 50,000 centipoise.

5. A method according to claim **1**, wherein the restorative compound is a silicone oil.

6. A method according to claim **5**, wherein the silicone oil is a polymethylphenylsiloxane oil.

7. A method according to claim **1**, wherein the time of exposure is at least about 10 hours.

8. A method according to claim **7**, wherein the time of exposure is from about 10 to about 90 hours.

9. A method according to claim **8**, wherein the time of exposure is from about 24 to about 72 hours.

10. A method according to claim **1**, wherein the biofouling release coating was manufactured without enhancing additives.

11. A method according to claim **1**, wherein the biofouling release coating was manufactured with enhancing additives.

* * * * *

US006180249B1

(12) **United States Patent**
Stein

(10) **Patent No.: US 6,180,249 B1**
(45) **Date of Patent: *Jan. 30, 2001**

(54) **CURABLE SILICONE FOUL RELEASE COATINGS AND ARTICLES**

(75) Inventor: **Judith Stein**, Schenectady, NY (US)

(73) Assignee: **General Electric Company**, Schenectady, NY (US)

(*) Notice: Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/149,063**

(22) Filed: **Sep. 8, 1998**

(51) **Int. Cl.**[7] **B32B 9/04**; C08G 77/06

(52) **U.S. Cl.** **428/447**; 106/287.14; 106/287.16; 427/387; 524/265; 524/267; 524/268; 524/493; 524/731; 524/837; 524/858; 524/859; 524/863; 528/14; 528/17; 528/18; 528/901

(58) **Field of Search** 427/387; 428/447; 524/493, 731, 837, 265, 267, 268, 858, 859, 863; 528/14, 17, 18, 901, 33, 34; 106/287.14, 287.16

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Primary Examiner—D. S. Nakarani
(74) *Attorney, Agent, or Firm*—Noreen C. Johnson; Douglas E. Stoner

(57) **ABSTRACT**

A condensation curable coating composition comprises the following and any reaction product thereof: (A) a room temperature vulcanizable polyorganosiloxane composition; and (B) a marine foul release-enhancing proportion of at least one organic compatible silicone fluid free from silanol groups and being capable of blooming to the surface of a cured product of component A.

35 Claims, No Drawings

CURABLE SILICONE FOUL RELEASE COATINGS AND ARTICLES

This invention was made with government support under Contract No. N0001 4-96-C-0 145 awarded by DARPA. The government may have certain rights in the invention.

BACKGROUND OF THE INVENTION

This invention relates to foul release coatings and articles coated therewith. More particularly, this invention relates to foul release coatings containing organic compatible oils that have enhanced foul release performance.

A perennial major aggravation to shippers and users of marine equipment in contact with water is the tendency of such equipment to become encrusted with varieties of wildlife, as illustrated by barnacles and zebra mussels. This tendency is often referred to as marine fouling.

U.S. Pat. No. 4,861,670 describes in considerable detail, the types of treatments that have been employed, starting as early as 1854, to minimize marine fouling. Treatment materials have included compounds of such metals as copper, tin, arsenic, mercury, zinc, lead, antimony, silver and iron, as well as toxic organic materials such as strychnine and atropine. Due to environmental concerns, the use of such materials has been discouraged.

More recently, polyorganosiloxanes (hereinafter sometimes designated "silicones" for brevity) have been found useful as anti-fouling coatings. They include condensation cured room temperature vulcanizable (hereinafter sometimes "RTV") compositions comprising silica or calcium carbonate as a filler in combination with silanol- or dialkoxy-terminated silicones, catalysts and crosslinking agents. They may be made sprayable by dilution with solvents, typically volatile organic compounds such as hydrocarbons.

There is still a need, however, to improve various properties of RTV-based foul release coatings, particularly their release efficiency and their effective lifetime.

SUMMARY OF THE INVENTION

The present invention satisfies this need by the discovery that the addition of specifically defined organic compatible oils to a conventional RTV formulation improves foul release properties. It includes foul release coatings having said improved properties and articles coated with said improved foul release coatings.

In one of its aspects, the invention is directed to condensation curable coating compositions comprising the following and any reaction products thereof:

(A) a one- or two-part room temperature vulcanizable polyorganosiloxane composition, and

(B) a marine foul release-enhancing proportion of at least one organic compatible silicone fluid free from silanol groups and being capable of blooming to the surface of the cured product of component A.

Another aspect of the invention is articles comprising a marine structure coated with an anti-fouling coating, which is the condensation cured reaction product of the composition defined hereinabove.

DETAILED DESCRIPTION

The word "component" is frequently employed herein for brevity to designate the materials present in the compositions of the invention. Its use is independent of the possible interreaction of said materials to form other chemical constituents.

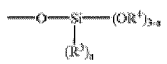
Component A of the compositions of the invention may be a conventional one-part or two-part RTV composition; it is most often a two-part composition. It typically comprises at least one reactive silicone, at least one condensation catalyst and at least one crosslinking agent.

The reactive silicone is most often a polydialkylsiloxane, typically of the formula

(I)

wherein each R^1 is a hydroxyl radical or

(II)



each R^2 is independently a hydrocarbon or fluorinated hydrocarbon radical, each R^3 and R^4 is a hydrocarbon radical, a is 0 or 1 and m has a value such that the viscosity of said reactive silicone under ambient temperature and pressure conditions is up to about 50,000 centipoise. Illustrative hydrocarbon radicals are C1–20 alkyl, C6–20 aryl and alkaryl, vinyl, isopropenyl, allyl, butenyl and hexenyl, with C1–4 alkyl and especially methyl being preferred. An illustrative fluorinated hydrocarbon radical is 3,3,3-trifluoropropyl. Most often, each R^2, R^3 and R^4 is alkyl and preferably methyl.

It is within the scope of the invention to employ two or more reactive silicones, differing in average molecular weight. This may afford a bimodal composition having performance advantages over a simple monomodal composition.

The condensation catalyst may be any of those known to be useful for promoting condensation curing of an RTV material. Suitable catalysts include tin, zirconium and titanium compounds as illustrated by dibutyltin dilaurate, dibutyltin diacetate, dibutyltin methoxide, dibutyltin bis (acetylacetonate), 1,3 -dioxypropanetitanium bis (acetylacetonate), titanium naphthenate, tetrabutyl titanate and zirconium octanoate. Various salts of organic acids with such metals as lead, iron, cobalt, manganese, zinc, antimony and bismuth may also be employed, as may non-metallic catalysts such as hexylammonium acetate and benzyltrimethylammonium acetate. For most purposes, the tin and titanium compounds are preferred.

As crosslinking agents, trifunctional (T) and tetrafunctional (Q) silanes are useful, the term "functional" in this context denoting the presence of a silicon-oxygen bond. They include such compounds as methyltrimethoxysilane, methyltriethoxysilane, 2-cyanoethyltrimethoxysilane, methyltriacetoxysilane, tetraethyl silicate and tetra-n-propyl silicate. The Q-functional compounds, i.e., tetraalkyl silicates, are often preferred.

Component A may contain other constituents, including reinforcing and extending (non-reinforcing) fillers. Suitable reinforcing fillers have a primary particle size of about 10 nm and are available in the form of aggregated particles of about 100 to about 250 nm. The preferred fillers are the silica fillers, including fumed silica and precipitated silica. These two forms of silica have surface areas in the ranges of 90–325 and 8–150 m^2/g, respectively.

The reinforcing filler is most often pretreated with a treating agent to render it hydrophobic. Typical treating agents include cyclic silicones such as cyclooctamethyltetrasiloxane and acyclic and cyclic organosilazanes such as hexamethyidisilazane, 1,3-divinyl-1,1,3, 3-tetramethyld isilazane, hexamethylcyclotrisilazane, octamethylcyclotetrasilazane and mixtures of these. Hexamethyldisilazane is often preferred.

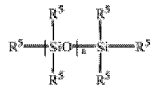
Non-reinforcing fillers include titanium dioxide, lithopone, zinc oxide, zirconium silicate, iron oxides, diatomaceous earth, calcium carbonate, glass fibers or spheres, magnesium oxide, chromic oxide, zirconium oxide, aluminum oxide, crushed quartz, calcined clay, talc, kaolin, asbestos, carbon, graphite, cork, cotton and synthetic fibers.

The proportions of the constituents of component A may be varied widely. The amount of filler is generally about 5–200 parts and preferably about 10–150 parts by weight per 100 parts of reactive silicone. Catalysts and crosslinkers are generally present in the amounts of about 0.001–2.5% and about 0.25–5.0% by weight respectively, based on the combination of reactive silicone and filler.

Component B is an organic compatible silicone fluid. An organic compatible silicone fluid is an organosiloxane fluid that has imparted organic character from incorporated alkyl groups or aromatic substituted alkyl (aryl-alkyl and aryloxy-alkyl) groups. Preferably, the organic compatible silicone fluid comprises about 2 to 100 mole % higher alkyl (C6–C20) or substituted aryl-alkyl radicals. More preferably, the organic compatible silicone fluid comprises about 10 to 70 mole % higher alkyl (C6–C20) or substituted aryl-alkyl radicals. The organic compatible silicone fluids suitable in the present invention are free from silanol groups and are characterized by pour points in the range from about −60° C. to about 80° C., preferably from about −50° C. to about 30° C. and most preferably from about −50° C. to about 0° C. These fluids exhibit an extended range of organic compatibility and lubricity.

Examples of organic compatible silicone fluids include alkylmethylsiloxane homopolymers such as polyoctylmethylsiloxane, polytetradecylmethylsiloxane and polyoctyidecylmethylsiloxane; alkylmethylsiloxane/arylmethylsiloxane copolymers such as ethylmethylsiloxane/2-phenylpropylmethylsiloxane copolymer, hexylmethylsiloxane/phenylpropylmethylsiloxane copolymer, decylmethylsiloxane/butylated aryloxypropylmethylsiloxane copolymer and dodecylmethylsiloxane/2-phenylpropylmethylsiloxane copolymer; alkylmethylsiloxane/dimethylsiloxane copolymers such as octadecylmethylsiloxane/dimethylsiloxane copolymer and triacontylmethylsiloxane/dimethylsiloxane copolymer; and dialkylsiloxane homopolymers such as dicyclopentylsiloxane polymer.

One class of illustrative organic compatible silicone fluids is disclosed in U.S. Pat. No. 4,005,023, which is incorporated herein by reference. Some of these fluids are included in the following formula that represents suitable linear and nonlinear polymers and copolymers;



(III)

where n varies from 1 to 8000 and R^5 is selected from the class consisting of monovalent hydrocarbon radicals, halogenated monovalent hydrocarbon radicals, monovalent alkoxyalkyl and monovalent aryloxyalkyl radicals and the viscosity of the fluid varies from 20 to 4000 centistokes at 25° C. In the present invention, the R^5 radicals on the polymer can be the same or different. Preferably each radical is selected from lower alkyl radicals of 1 to 20 carbon atoms, substituted alkyl radicals of 6 to 20 carbon atoms and aryloxyalkyl radicals of 7 to 50 carbon atoms.

Illustrative organic compatible silicone fluids are available from Gelest, Inc., under the trade designations ALT. One illustration of such a compound is ALT251, which is a decylmethylsiloxane/butylated aryloxypropylmethylsiloxane copolymer with a pour point of −51° C. and a viscosity of 40–60 centipoise.

Component B is present in the compositions of the invention in an effective proportion to enhance foul release properties. For the most part, about 5–20 parts by weight per 100 parts of component A is adequate.

A member of a mixture that forms a thin coating will sometimes migrate to the surface of the coating because of its incompatibility with another member of the mixture. This phenomena is called "blooming." The essential property of component B is that of blooming to the surface of the cured product of component A during or after the curing process, by reason of its incompatibility with component A.

The compositions of this invention may also incorporate further constituents such as non-reactive silicone oils, dyes, solubilizing agents and solvents to render them sprayable if sprayability is desirable. These may be introduced as part of component A or as adjuvants to the entire composition, as appropriate.

The marine structure in the articles of the invention is often a ship's hull. However, any structure that is utilized in a marine environment and is subject to fouling can be the marine structure of the invention. Such marine structures include, for example, liquid collecting and discharge pipes, dry dock equipment and the like. Suitable materials for such structures include metals such as iron and aluminum and resinous materials such as fiber-reinforced thermoplastic or thermoset resins.

Application of the compositions of the invention is typically preceded by the application of conventional pretreatment layers. These may include, for example, anti-corrosive epoxy primers, mist coats and tie-layers comprising polyorganosiloxanes and toughening components. The compositions of the invention may be applied by conventional techniques such as brushing or drawing down, or by spraying if they are suitably diluted.

Solvent can be mixed into the composition of the invention to prepare the composition for application to a marine structure. Suitable solvents for spray applications include aromatic hydrocarbons such as toluene or xylene and aliphatic hydrocarbons such as petroleum naphtha.

The invention is illustrated by the following examples. All parts and percentages in the examples are by weight.

EXAMPLE 1

A condensation curable RTV composition was prepared by blending the following constituents in the amounts indicated:

Part I:

The following were combined as part I: silanol-stopped polydimethylsiloxane, viscosity 30,000 centipoise—100 parts; non-reactive polydimethylsiloxane oil, viscosity 20 centipoise—38.5 parts; n-propyl silicate—12.13 parts; fumed silica, hexamethyldisilazane-treated—37 parts.

Part II:

Dibutyltin dilaurate was added as part II.

The two parts were combined in proportions such that the dibutyltin dilaurate was present in the amount of 2.43 parts per 100 parts of the silanol-stopped polydimethylsiloxane.

To the resulting RTV composition was added 10% by weight, based on the RTV composition, of an organic compatible silicone fluid, which was a polydimethylsiloxane having 47 mole % decyl groups and 2 mole % butylated aryloxypropyl groups and a viscosity of 40–60 centipoise.

The composition thus prepared was applied by spray coatings to steel panels which had been previously coated with a commercially available epoxy anti-corrosion coating, mist coat and tie-layer. The test panels were exposed to water for 7 months, after which time the barnacle adhesion strength was measured in accordance with ASTMD 5618. The barnacle adhesion value was 5.1 psi where the control value was 10.9 psi.

EXAMPLE 2

An RTV composition was prepared by blending (Part I) 70 parts of a silanol-terminated polydimethylsiloxane having a viscosity of 3,100 centipoise, calcium carbonate and 2 parts tetraethyl silicate and (Part II) 0.5 part of dibutyltin dilaurate. An organic compatible silicone fluid was added in the amount of 10% based on RTV composition. The organic compatible silicone fluid was a polydimethylsiloxane having 47 mole % decyl groups and 2 mole % butylated aryloxypropyl groups and a viscosity of 40–60 centipoise.

Steel test panels similar to those of Example 1, were coated with an anticorrosion coating, primed with a commercially available primer and then spray coated with the composition of Example 2. The test panels were then submerged in a salt water lagoon in Florida in cages for seven months. At the end of the test period, barnacle adhesion, as determined by ASTM test procedure D5618, for the panels coated with the product of Examples 2 were 5.9 psi. A control panel coated with the RTV composition only had a barnacle adhesion of 10.35 psi.

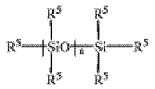
What is claimed is:

1. A condensation curable coating composition comprising the following and any reaction product thereof:

(A) a room temperature vulcanizable polyorganosiloxane composition; and

(B) a marine foul release-enhancing proportion of at least one organic compatible silicone fluid free from silanol groups and comprising polymers and copolymers of the formula:

(III)



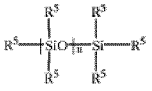
where n varies from 1 to 8000 and R^5 is the same or different and is alkyl, halogenated alkyl, alkoxyalkyl, aryloxyalkyl or aromatic substituted alkyl and being capable of blooming to the surface of a cured product of component A.

2. A composition according to claim **1**, wherein component A comprises at least one reactive silicone, at least one condensation catalyst and at least one crosslinking agent.

3. A composition according to claim **1**, wherein the organic compatible silicone fluid is selected from the group consisting of an alkylmethylsiloxane homopolymer, an alkylmethylsiloxane/dimethylsiloxane copolymer and a dialkylsiloxane homopolymer.

4. A composition according to claim **1**, wherein the organic compatible silicone fluid has a viscosity

(III)



where from 40 to 4000 centistokes at 25° C.

5. A composition according to claim **4**, wherein R^5 is selected from lower alkyl radicals of 1 to 20 carbon atoms, halogenated alkyl radicals of 6 to 20 carbon atoms, alkoxyalkyl radicals of 6 to 20 carbon atoms and aryloxyalkyl radicals of 7 to 50 carbon atoms.

6. A composition according to claim **1**, wherein the organic compatible silicone fluid comprises about 2 to 100 mole % C_{6-20}alkyl radicals.

7. A composition according to claim **1**, wherein the organic compatible silicone fluid comprises about 10 to 70 mole % C_{6-20}alkyl radicals.

8. A composition according to claim **1**, wherein the organic compatible silicone fluid is characterized by a pour point in the range from about −60° C. to about 80° C.

9. A composition according to claim **1**, wherein the organic compatible silicone fluid is characterized by a pour point in the range from about −50° C. to about 30° C.

10. A composition according to claim **1**, wherein the organic compatible silicone fluid is characterized by a pour point in the range from about −50° C. to about 0° C.

11. A composition according to claim **10** wherein the reactive silicone is a polydialkylsiloxane having the formula:

(I)

wherein each R^1 is a hydroxyl radical or

(II)

wherein each R^2 is independently a hydrocarbon or fluorinated hydrocarbon radical, each R^3 and R^4 is a hydrocarbon radical, a is 0 or 1 and m has a value such that the viscosity of said reactive silicone under ambient temperature and pressure conditions is up to about 6,000 centipoise.

12. A composition according to claim **11** wherein each R^2 is methyl.

13. A composition according to claim **12** wherein each R^1 is hydroxyl.

14. A composition according to claim **12** wherein each R^1 is structure II.

15. A composition according to claim **11** wherein the condensation catalyst is a tin, zirconium or titanium compound.

16. A composition according to claim **11** wherein the crosslinking agent is a trifunctional or tetrafunctional silane.

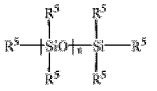
17. A composition according to claim 16 wherein the crosslinking agent is a tetraalkyl silicate.

18. An article comprising a marine structure coated with an anti-fouling coating which is the condensation cured reaction product of a condensation curable coating composition comprising the following and any reaction product thereof:

(A) a room temperature vulcanizable polyorganosiloxane composition; and

(B) a marine foul release-enhancing proportion of at least one organic compatible silicone fluid free from silanol groups and comprising polymers and copolymers of the formula:

(III)



where n varies from 1 to 8000 and R^5 is the same or different and is alkyl, halogenated alkyl, alkoxyalkyl, aryloxyalkyl or aromatic substituted alkyl and being capable of blooming to the surface of a cured product of component A.

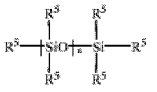
19. An article according to claim 18, wherein the organic compatible silicone fluid comprises about 2 to 100 mole % C_{6-20}alkyl radicals.

20. An article according to claim 18, wherein the organic compatible silicone fluid comprises about 10 to 70 mole % C_{6-20}alkyl radicals.

21. An article according to claim 18, wherein the organic compatible silicone fluid is selected from the group consisting of an alkylmethylsiloxane homopolymer, an alkylmethylsiloxane/dimethylsiloxane copolymer and a dialkylsiloxane homopolymer.

22. An article according to claim 18, wherein the organic compatible silicone fluid has a viscosity

(III)



from 40 to 4000 centistokes at 25° C.

23. An article according to claim 22, wherein R^5 is selected from lower alkyl radicals of 1 to 20 carbon atoms, halogenated alkyl radicals of 6 to 20 carbon atoms, alkoxyalkyl radicals of 6 to 20 carbon atoms and aryloxyalkyl radicals of 7 to 50 carbon atoms.

24. An article according to claim 18, wherein the organic compatible silicone fluid is characterized by a pour point in the range from about −60° C. to about 80° C.

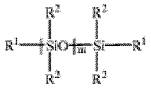
25. An article according to claim 18, wherein the organic compatible silicone fluid is characterized by a pour point in the range from about −50° C. to about 30° C.

26. An article according to claim 18, wherein the organic compatible silicone fluid is characterized by a pour point in the range from about −50° C. to about 0° C.

27. An article according to claim 18, wherein component A comprises at least one reactive silicone, at least one condensation catalyst and at least one crosslinking agent.

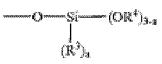
28. An article according to claim 27, wherein the reactive silicone is a polydialkylsiloxane having the formula:

(I)



wherein each R^1 is a hydroxyl radical or

(II)



wherein each R^2 is independently a hydrocarbon or fluorinated hydrocarbon radical, each R^3 and R^4 is a hydrocarbon radical, a is 0 or 1 and m has a value such that the viscosity of said reactive silicone under ambient temperature and pressure conditions is up to about 6,000 centipoise.

29. An article according to claim 28, wherein each R^2 is methyl.

30. An article according to claim 29, wherein each R^1 is hydroxyl.

31. An article according to claim 29, wherein each R^1 is structure II.

32. An article according to claim 28, wherein the condensation catalyst is a tin, zirconium or titanium compound.

33. An article according to claim 28, wherein the crosslinking agent is a trifunctional or tetrafunctional silane.

34. A method of producing a condensation curable coating composition, comprising combining (A) and (B) of claim 1.

35. A method of protecting a structure from marine fouling, comprising coating said structure with a condensation curable coating composition comprising the composition of claim 1.

* * * * *

Appendix 0.B List of publications written under this program

1. Burnell, T., Carpenter, J., Carroll, K., Cella, J, Resue J., Rubinsztajn, G., Serth-Guzzo, J., Stein, J., Truby, K., Webb, K., Swain, G., Schultz, M., and Zimmerman, R., "Advances in Nontoxic Silicone Biofouling Release Coatings", in Proceeding of the Emerging Nonmetallic Materials for the Marine Environment, Honolulu Hawaii, March 18-20, 4-69 (1997).

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3. Burnell, T., Cella, J., Stein, J., Truby, K., Webb, K., Swain, G., and Zimmerman, R., "Chemistry of Nontoxic Silicone Biofoul-releasing Coatings", Proc. Annu. Meet. Adhes. Soc., 20th, 303 (1997).

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7. Kovach, B., and Swain, G., "A Boat Mounted Foil to Measure the Drag Properties of Antifouling Coatings Applied to Static Immersion Panels, " Conference Proceedings, International Symposium on Seawater Drag Reduction, Newport, RI, July 22-24 (1998).

8. Truby, K., Darkangelo Wood, C., Stein, J., Cella, J., Carpenter, J., Kavanagh, C., Swain, G., Wiebe, D., Lapota, D., Meyer, A., Holm, E., Wendt, D., Smith, C., and Montemarano, J., "Evaluation of the Performance Enhancement of Silicone Biofouling-release Coatings by Oil Incorporation," Biofouling, **15**, 141 (2000).

9. Wood, C., Truby, K., Stein, J., Wiebe, D., Holm, E., Wendt, D., Smith, C., Kavanagh, C., Montemarano, J., Swain, G., and Meyer, A., "Temporal and Spatial Variations in Macrofouling of Silicone Fouling-Release Coatings" Biofouling, **16**, 331 (2000).

10. Dalton, H., Stein, J., and March. P., "A Biological Assay for Detection of Heterogeneities in Surface Hydrophobicity of Polymer Coatings Exposed to the Marine Environment" Biofouling, **15**, 83 (2000).

11. Stein, J., Truby, K., Darkangelo Wood, C., Wiebe, D., Montemarano, J., Holm, E., Wendt, D., Smith, C., Meyer, A., Swain, G., Kavanagh, C., Kovach, B., and Lapota, D., "Silicone Biofouling Release Coatings: Correlation of Compositional Variables with Macrofouling Attachment Strength", in Proceeding of the XXVIth International Conference in Organic Coatings, Athens, Greece, July (2000).

12. Stein, J., Truby, K., Darkangelo Wood, C., Wiebe, D., Montemarano, J., Holm, E., Wendt, D., Smith, C., Meyer, A., Swain, G., Kavanagh, C., Kovach, B., and Lapota, D., "Silicone Biofouling Release Coatings: Correlation of Compositional Variables with Macrofouling Attachment Strength**",** Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **42**(1), 236-237 (2001).

13. Kavanagh, C., Schultz, M., Swain, G., Stein, J., Truby, K., and. Darkangelo Wood, C., "Variation in Adhesion Strength of Three Hard-Fouling Types to Fouling-Release Coatings" Biofouling in press.

Appendix 0.C. List of presentations given under this program

1. Burnell, T., Carroll, K., Carpenter, J., Comly, L., Stein, J., Cella, J., Truby, K, and Webb, K., "Self Cleaning Silicone Foul Release Coatings", DARPA Coatings Conference, San Diego, California, 11/18/1996.

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4. Truby, K., Webb, K., Stein, J., and Burnell, T., "Assessment of the Efficacy of Non-toxic Silicone Fouling Release Coatings," Washington Paint Technical Group Symposium, Washington D.C., 4/15-16/1997.

5. Burnell, T., Carpenter, J., Carroll, K. Cella, J., Resue, J., Rubinsztajn, G., Serth-Guzzo, J., Stein, J., Truby, K., Webb, K., Schultz, M., and Swain, G., "Advances in Nontoxic Silicone Biofouling Release Coatings" 30th Organosilicon Symposium, London, Ontario, Canada, 5/30-31/1997.

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9. Carpenter, J., Burnell, T., Carroll, K., Serth-Guzzo, J., J. Stein, J., and Truby, K., Advances in Nontoxic Silicone Foul Release Coatings, Silicones in Coatings II, Orlando, FL, 3/24-26/1998.

10. Carpenter, J., Serth-Guzzo, J., Stein, J., Truby, K., Swain, G., Kavanagh, C., and Wiebe, D., Advances in Nontoxic Silicone Biofouling Release Coatings, National ACS Meeting, Dallas, TX, 3/29-4/ 2/1998.

11. Kovach, B., and Swain, G., "A Boat Mounted Foul to Measure the Drag Properties of Antifouling Coatings Applied to Static Immersion Panels", International Symposium on Seawater Drag Reduction, Newport, RI, 7/ 22-24/1998.

12. Carpenter, J., Kavanagh, C., Serth-Guzzo, J., Stein, J., and Truby, K., "Advances in Nontoxic Silicone Biofouling Release Coatings" poster presented at the Gordon Research Conference on the Science of Adhesion, Tilton, NH, 8/ 4/1998.

13. Stein, J., Carpenter, J., Serth-Guzzo, J., Truby, K., Harblin, O., Burnell, T., Montemarano, J., Poole, K., Wiebe, D., Swain, G., Kovach, B., Kavanagh, C., Meyer, A., Lapota, D., Holm, E., and Smith, C., "Design and Development of Non-toxic Self Cleaning Silicone Foul Release Coatings" ONR Review, Bethesda, MD, 8/14/1988.

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15. Stein, J., Truby, K., Serth-Guzzo, J., Carpenter, J., Kavanagh, C., Swain, G., "The Effect of Coating Additives on Barnacle Adhesion to Silicone Surfaces," MASTEC Conference, Sweden, 8-28/98-8/31/1998.

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21. Darkangelo Wood, C., Truby, K., Stein, J., Wiebe, D., Holm, E., Wendt, D., Smith, C., Kavanagh, C., and Meyer, A., "Temporal and Spatial Variations in Macrofouling on Silicone Biofouling Release Coatings," Marine Biofouling-An International Symposium, Plymouth, England, 7/7-9/1999.

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27. Swain, G., Kovach, B., Kavanagh, C., Stein, J., Darkangelo Wood, C., and Truby, K., " Non Toxic AF Strategies: Non-Stick and Fouling Release," Alternative Antifouling Strategies for Recreational Boats: A Working Conference, San Diego, CA, 9/21-22/2000.

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29. Stein, J., Truby, K., Wood, C., Wiebe, D., Montemarano, J., Wendt, D., Smith, C., Lapota, D., Holm, E., Meyer, A., Swain, G., Kavanagh, C., and Kovach, B., "Silicone Biofouling Release Coatings: Correlation of Compositional Variables with Macrofouling Attachment Strength" RPI, NY, 10/20/2000.

30. Stein, J., "Effect of Oil Incorporation on Macrofouling Attachment Strength", McMaster University, Hamilton, Canada, 2/12/2001.

31. Stein, J., Truby, K., Wood, C., Wiebe, D., Montemarano, J., Wendt, D., Smith, C., Lapota, D., Holm, E., Meyer, A., Swain, G., Kavanagh, C., and. Kovach, B., "Silicone Biofouling Release Coatings: Correlation of Compositional Variables with Macrofouling Attachment Strength" GE Silicones, Waterford NY, 3/29/2001.

32. Stein, J., Truby, K., Wood, C., Wiebe, D., Montemarano, J., Wendt, D., Smith, C., Lapota, D., Holm, E., Meyer, A., Swain, G., Kavanagh, C., and. Kovach, B., "Silicone Biofouling Release Coatings: Correlation of Compositional Variables with Macrofouling Attachment Strength", 221st ACS National Meeting, San Diego, 4/1-5/2001.

33. Stein, J., Truby, K., Wood, C., Wiebe, D., Montemarano, J., Wendt, D., Smith, C., Lapota, D., Holm, E., Meyer, A., Swain, G., Kavanagh, C., and. Kovach, B., "Silicone Biofouling Release Coatings: Correlation of Compositional Variables with Macrofouling Attachment Strength" 34th Organosilicon Symposium, White Plains, NY, 5/5/2001.

APPENDIX 1. FOULING COVERAGE DATA

Appendix 1.A Coverage data

EXPERIMENTAL

Coverage data was collected at two locations: Miami Marine Research and Testing Station, Florida (MMRTS), and at two sites in Massachusetts (NE1, NE2).

Miami Marine Research and Testing Station (MMRTS)

MMRTS is located in Biscayne Bay, a sub-tropical estuary. The major fouling organisms settled in organism-specific seasonal cycles. The community consists primarily of barnacles, tunicates, encrusting bryozoans, hydrozoans, and sponges. At the MMRTS test area, salinity ranged from 34 $^{0}/_{00}$ in the spring, to $20^{0}/_{00}$ in the summer, and the temperature varies from 19°C to 30°C ("South Florida Ecosystem History Database" http://flaecohist.er.usgs.gov/database/BBFieldTree.asp).

Massachusetts Test Sites

Both test sites in Massachusetts are located in temperate estuaries, with water temperatures ranging from 4°C in the winter to 24°C in the summer, and salinities from $25^{0}/_{00}$ to $31^{0}/_{00}$. Fouling at these sites is strongly seasonal, with most recruitment occurring during the spring and summer. Common fouling organisms include encrusting bryozoans, tunicates, sponges, and the gastropod *Crepidula fornicata*.

RESULTS

Coverage at MMRTS

Graphical results of seasonal coverage at MMRTS are given in Figures 1.A.1 – 1.A.3.

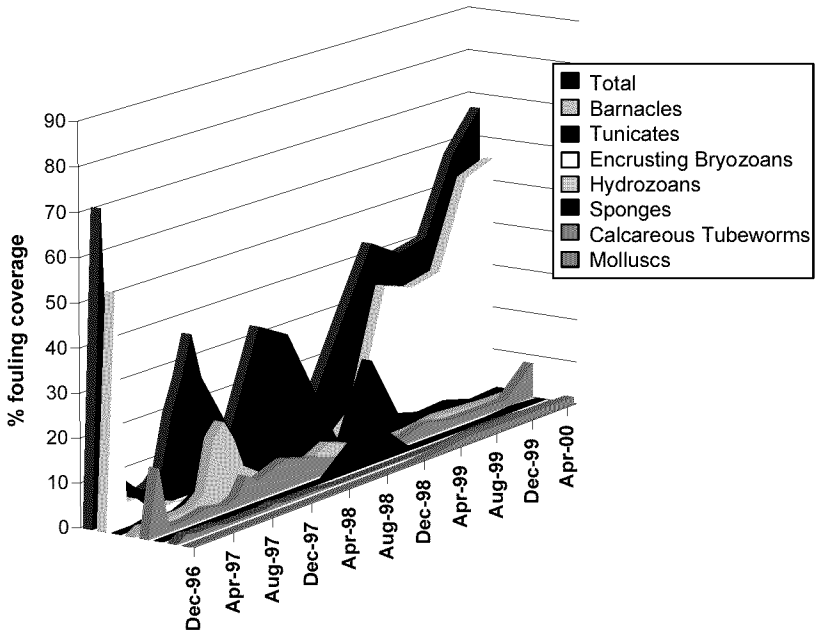


Figure 1.A.1 RTV11® at MMRTS

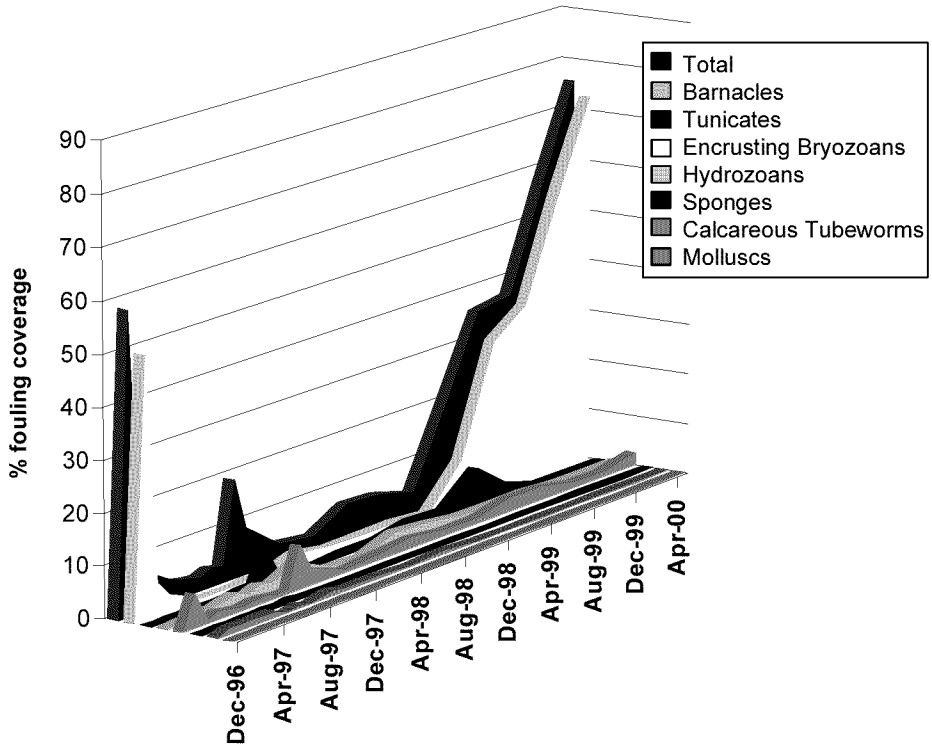


Figure 1.A.2 RTV11® + SF1147 at MMRTS

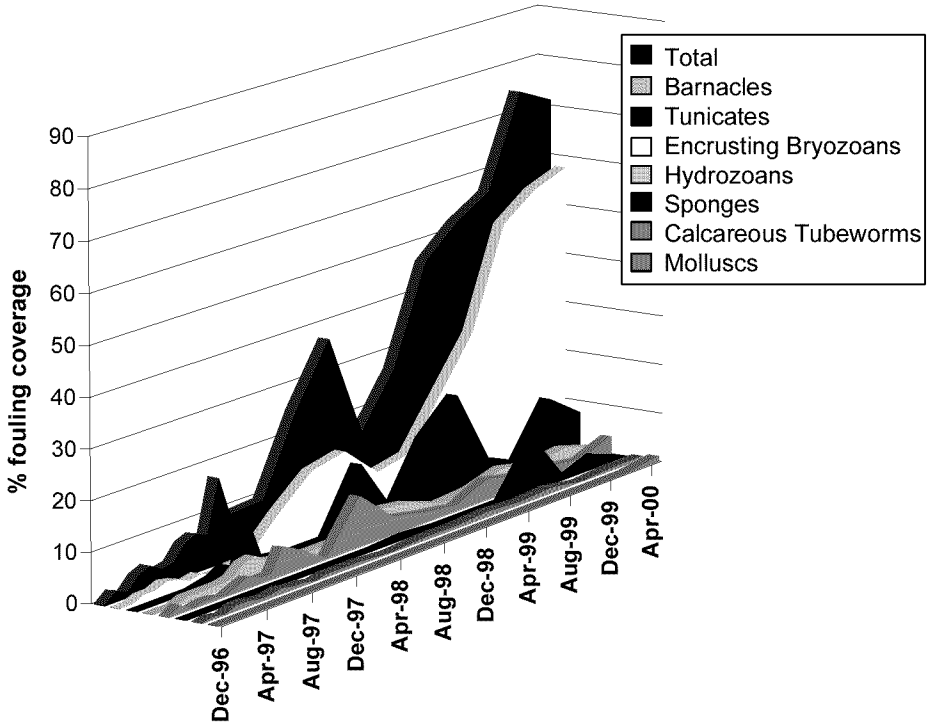


Figure 1.A.3. RTV11® + DMSC15 at MMRTS

Coverage at Massachusetts Test Sites

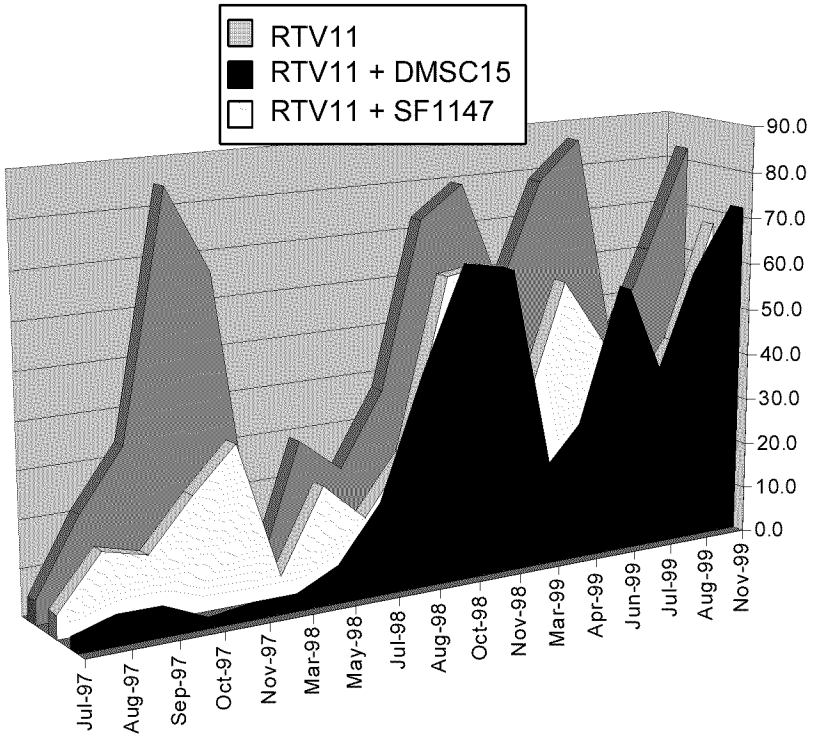


Figure 1.A.4 Massachusetts test site (NE1) fouling profile

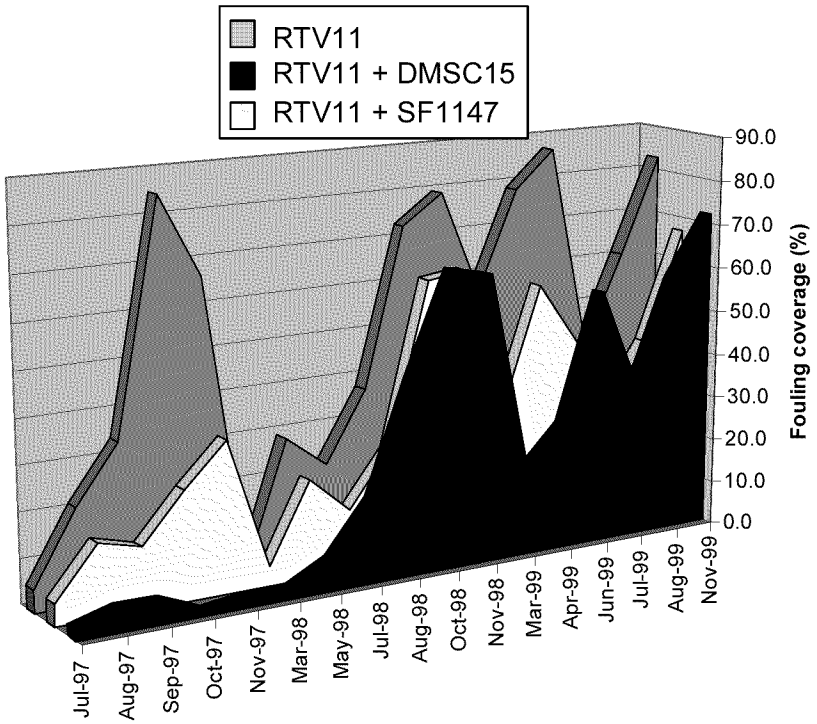


Figure 1.A.5 Massachusetts test site (NE2) fouling profile

Although the two locations were in relatively close geographic proximity, the exposure conditions, pattern of settlement, and composition of the attached fouling community were quite distinct. There also appeared to be seasonal effects and intrasite differences in the rate of attachment and coverage. The extent and proportion of fouling components (soft and hard fouling species) varied among the test coating formulations; however, with prolonged exposure, a general trend toward increased surface coverage by hard foulers, primarily one species of gastropod mollusk, was noted. Differences in the performance of the oil-amended coatings, compared to the RTV11® control, appeared to be related to a delay in surface coverage, which may be due to the surface properties of these materials as well as complex interactions among the localized environment, predation, and/or biological effects. Reduced coverage was observed for most of the oil-incorporated materials, although the magnitude of the improvement relative to the control was also site-dependent. Results from these investigations indicate that some foul-release formulations substantially reduce surface coverage, but the performance of a particular material is site-specific and may not be equally effective, even at locations within the same regional area.

CONCLUSIONS

- Fouling coverage appears to be seasonal at both locations. Total coverage may not be a good discriminator for evaluating foul-release coating performance at these locations. Although coverage at the RTV11® control was equivalent to the RTV11® + SF1154 formulation, the hydrodynamic performance of the oil-amended formulation was significantly better.

Appendix 1.B. Effect of oil state (free or bound) on foul release performance

In this section, we report two methods that were employed to control oil depletion from silicone foul-release coatings: ablative networks, and tethered incompatible oils. The synthesis of ablative and tethered diphenyldimethylsiloxane oils , the incorporation of such oils into the silicone room temperature vulcanized (RTV) network, and the foul-release properties of RTV coatings containing the ablative and tethered oils are discussed. Both ablative networks and tethered oils had a negative effect on foul release performanc,e suggesting that the oil must be able to form a non-bonded boundary layer on the surface in order to be effective.

INTRODUCTION

Improvements in foul- release performance are observed with silicone coatings containing nonbonded oils. RTV11® exhibits superior release properties compared to epoxy controls; however, barnacle adhesion relative to an epoxy control; however, RTV11® containing 10% free diphenyldimethylsiloxane oil (PDMDPS,)(SF1154) has superior performance comparedperforms superior to both the epoxy control and RTV11® controls (Figure 1.B.1.). It is desirable to maximize the residence time of the oil in the topcoat for maximum lifetime foul release performance.

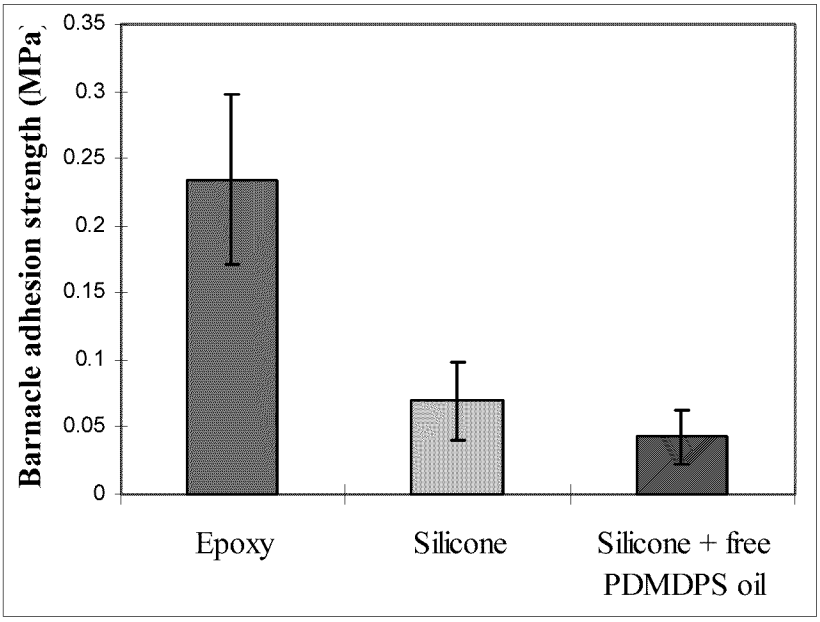
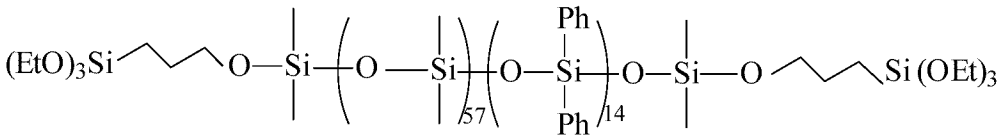


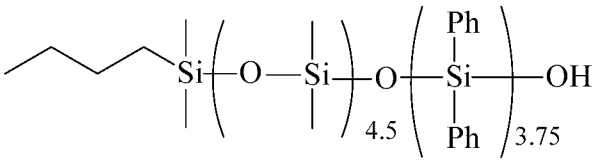
Figure 1.B.1. Effect of oil incorporation on barnacle adhesion strength

The incorporation of ablative and tethered oils into the silicone topcoat of fouling release coatings is a desirable mechanism for slow, controlled release of the silicone oil from the RTV topcoat. Once incorporated into the silicone network, the hydrolytically unstable Si-O-C bond in the ablative oil should slowly degrade in water. Conversely, the tethered

oil is chemically bonded into the silicone network and one end (the non-miscible portion) could phase separate to the surface of the coating. We synthesized both ablative and tethered diphenyldimethylsiloxane copolymers, incorporated the copolymers into the RTV topcoat and measured the foul release performance of the coatings. The structures of the oils are shown below in Figure 1.B.2.



(1)



(2)

Figure 1.B.2 Ablative **(1)** and tethered **(2)** diphenyldimethylsiloxane oils

EXPERIMENTAL

All reagents were purified and/or dried over sieves prior to use. Triethylamine was distilled from CaH_2 and stored over 3Å molecular sieves (55 mg/Lppm H_2O). Toluene was distilled from sodium/benzophenone. Dimethyldichlorosilane was distilled under nitrogen and stored over 3Å molecular sieves. Diethylether was stored over molecular sieves for several days (16 ppm H_2O). PDS-1615 was obtained from Gelest and heated to 60°C under high vacuum with stirring for 1 hour to remove residual water. Allyl alcohol was dried over crushed $CaSO_4$ and 3Å molecular sieves (140 ppm H_2O). Standard schlenk techniques and a nitrogen atmosphere were used.

Synthesis of bis-Cchlorosilane-terminated dDiphenylsiloxanedimethylsiloxane (4)

A 500 mL 3-neck round bottom flask was dried overnight and fitted with an overhead stirrer and a 250 mL pressure equalizing addition funnel. $MeSi_2Cl_2$ (29.0 g, 225 mmol) was added to the flask via cannula. Upon addition of NEt_3 (12.54 mL, 90 mmol) via syringe to the system, a cloudy white gas and a white precipitate formed. An ice bath (5°C) was immediately placed under the round bottom flask and a 50 wt % solution of PDS-1615 (silanol-terminated diphenylsiloxane-dimethylsiloxane copolymer) in toluene was added drop wise from the pressure equalizing addition funnel. The temperature of the ice bath was dropped to -5°C. The silanol-terminated solution was added over 120 minutes and a cloudy white precipitate formed ($HCl{\cdot}NEt_3$). The reaction mixture was filtered two times and residual $MeSi_2Cl_2$ and toluene were removed by distillation. A clear viscous liquid (118.7 g, 35 mmol) was obtained and characterized by ^1H and ^{29}Si NMR spectroscopies. The ^1H NMR was identical to the starting material, silanol terminated diphenyldimethylsiloxane copolymer, except the disappearance of the -OH proton was observed and appearance of methyl protons adjacent to the chlorosilane were observed. ^1H NMR: Si-Cl: 0.3 ppm, 12 H, s; Aryl H (Ph): average δ 7.6 ppm, m, 54H; Aryl H (Ph): average δ 7.2 ppm, m, 81 H; Si-Me_2 (D groups): multitude of singlets at 0-0.5 ppm (342 H).

Synthesis of bis-Aallyloxy-terminated Ddiphenyldimethylsiloxane (5)

A 1 L 3-neck round bottom flask was fitted with an overhead stirrer and a 250 mL pressure equalizing addition funnel containing the chlorosilane-terminated diphenylsiloxane dimethylsiloxane copolymer (118.0 g, 35 mmol). Allyl alcohol (7.14 mL, 105 mmol) and triethylamine (9.76 mL, 35 mmol) were added via syringe to the 1 L flask followed by 500 mL of diethyl ether. The chlorosilane was added drop wise to the ether solution at 5°C over 90 minutes. The solution was allowed to stir an additional 15 min. and was then filtered to remove $HCl{\cdot}NEt_3$. The organic layer washed with acid, water, dried over $MgSO_4$followed by distillation of the ether at 30°C. A clear viscous liquid (116 g) resulted with a molecular weight of 7,000. By ^1H NMR NMR, disappearance of the methyl protons adjacent to the chlorosilane and appearance of the allyl protons were observed. ^1H NMR: terminal CH_2 of allyl: 5.1 ppm, d, 4H; center CH of allyl: 5.9 ppm, ddt, 2H; CH_2-O: 4.2 ppm, m, 4 H. Aryl H (Ph): average δ 7.6 ppm, m, 54H; Aryl H (Ph): average δ 7.2 ppm, m, 81 H; Si-Me_2 (D groups): multitude of singlets at 0-0.5 ppm (354 H).

Synthesis of bis-Ttriethoxy-terminated Ddiphenyldimethylsiloxane (1)

To a 250 mL 3-neck round bottom flask fitted with an overhead stirrer, 5 wt% Karstedt's catalyst in xylenes (0.28 mL, 100 ppm H_2O) and triethoxysilane, which had been distilled under nitrogen (6.12 mL, 33.14 mmol), was added. The solution turned brown upon which ~ 5 ml of the bis-allyloxy copolymer was added directly with stirring. The remaining bis-allyl copolymer was added drop wise at 70-75°C over 60 minutes. ^1H NMR revealed disappearance of the allyl protons and appearance of the propyl and the ethoxy protons. ^1H NMR: propyl CH_2-Si 0.6 ppm, t, 4H; propyl -CH_2-: 1.6 ppm, m, 4H; CH_2-O: ~1.8 ppm, t, 4H; Aryl H (Ph): average δ 7.6 ppm, m, 54H; Aryl H (Ph): average δ 7.2 ppm, m, 81 H; Si-Me_2 (D groups): multitude of singlets at 0-0.5 ppm (354 H).

Synthesis of Ttethered Ddiphenyldimethylsiloxane oil (2)

To a 250 mL round bottom flask, 13.6g of D_3Ph, 30g of D_3, 30 mL of THF and 100 mL of toluene was allowed to stir overnight. The reaction mixture was cooled to 0°C in and 27 mL of n-BuLi (1.6M) was added. The mixture was then heated to 60°C for 6 hrs and the course of the reaction followed by GC until no n-BuLi remained. Ether was added and then the lithium salt was quenched with water/HCl until neutral. The aqueous fraction was extracted 3 times with ether and then washed with water/NaCl. The organic fraction was then dried over Na_2SO_4 and then stripped at 150°C and 2 mmHg to remove low boiling volatiles. ^{1}HNMR: CH_3-CH_2- 2.7 ppm, t, 3 H; -CH_2-CH_2-: 1.2 ppm, m, 4H; CH_2-Si: 0.5 ppm, t, 2 H; OH: 2.5 ppm, broad s, 1H; Aryl H (Ph): average δ 7.6 ppm, m, 15 H; Aryl H (Ph): average δ 7.2 ppm, m, 22.5 H; Si-Me_2 (D groups): multitude of singlets at 0-0.5 ppm, 27 H.

Incorporation of Aablative and Ttethered Ooils into Ssilicone Nnetworks

The ablative diphenyldimethylsiloxane copolymer was incorporated at 10 wt % into the RTV11® The bis-triethoxysiloxane end groups of **(1)** can condense with the silanol terminated polydimethylsiloxane in RTV11®® in the presence of dibutyltindilaurate to give a crosslinked network containing the hydrolytically unstable Si-O-C moiety. The

tethered diphenyldimethylsiloxane oil was also incorporated at 10 wt % into RTV11®®. The silanol endgroups of **(2)** were condensed with tetraethylorthosilicate, in the presence of dibutyltindilaurate to give the triethoxy-terminated copolymer, which subsequently condensed with the silanol-terminated RTV11® to form a crosslinked network. The incompatible butyl-terminated diphenyldimethylsiloxane should phase separate to the surface of the PDMS network

Foul- Rrelease Pperformance of Aablative Nnetworks and Ttethered Ooils

RTV topcoats containing either the ablative or tethered diphenyldimethylsiloxane copolymers were applied to steel panels previously coated with the epoxy and a tie layer developed at NRL*).* After the panels were allowed to cure for one week, they were deployed at both northeast and southeast static test sites for 9 months. Controls of RTV11® and RTV11® containing 10% free diphenyldimethylsiloxane oil were also immersed in these marine environments. The overall fouling coverage was recorded for the northeast site and barnacle adhesion values were measured for the southeast site.

RESULTS AND DISCUSSION

The synthesis of the ablative diphenyldimethylsiloxane oil involved three steps, shown below in Figure 1.B.3. A silanol terminated diphenyldimethylsiloxane copolymer **(3)** containing 16 mole % diphenylsiloxane was reacted with dimethyldichorosilane at -5°C in the presence of triethylamine to give the bis-chlorosilane terminated derivative **(4)**. The chlorosilane derivative was subsequently reacted with allyl alcohol and triethylamine to yield the bis-allyl terminated diphenylmethylsiloxane **(5)**. Hydrosilyation with triethoxysilane and Karstedt's catalyst gave the product, bis-triethoxy terminated diphenyldimethylsiloxane **(1).** Note some chain extension was observed in **(4)**, where the molecular weight doubled from approximately 3,300 to 7,000.

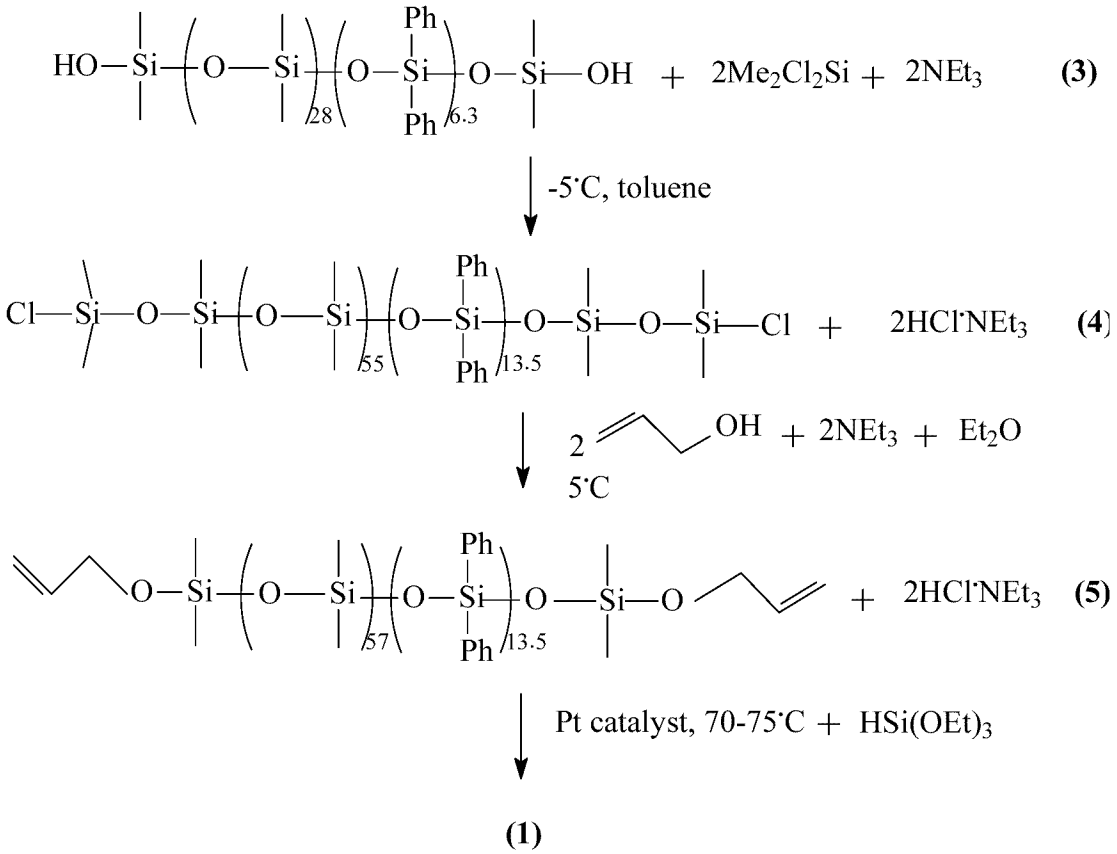


Figure 1.B.3. Synthesis of the ablative polydimethyldiphenylsiloxane oil **(1)**

The tethered diphenyldimethylsiloxane oil was prepared by a kinetically controlled anionic ring opening polymerization of hexamethylcyclotrisiloxane (D_3) and hexaphenylcyclotrisiloxane (D_3^{Ph}) in the presence of n-BuLi (Figure 1.B.4)*).* Polymerization was quenched with water to give a monofunctional diphenyldimethylsiloxane product **(2).**

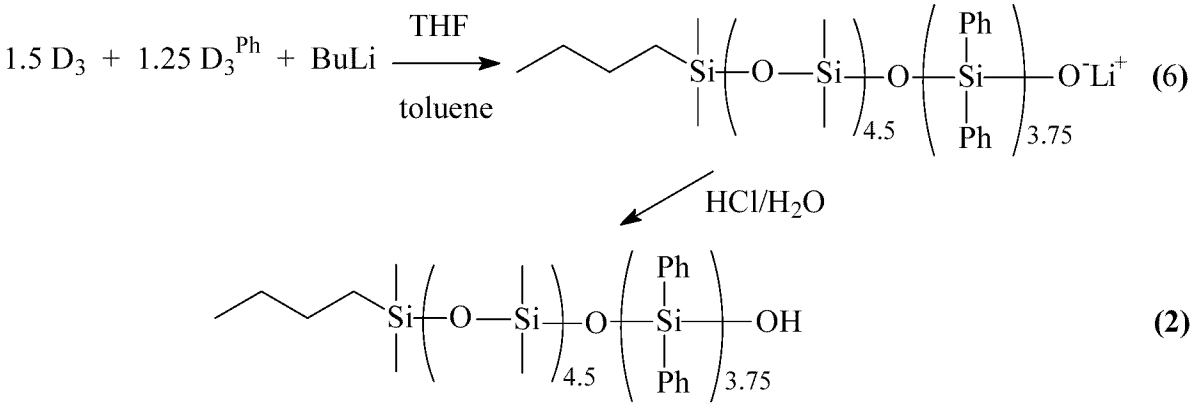


Figure 1.B.4. Synthesis of tethered polydimethyldiphenylsiloxane oil **(2)**

The ablative oil was incorporated into the network using tin condensation chemistry (Figure 1. B.5.)

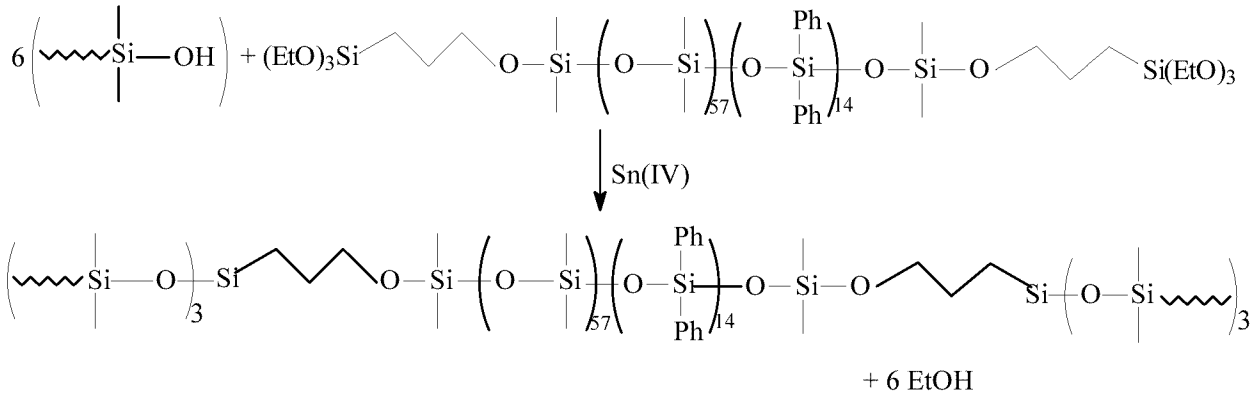


Figure 1.B.5. Incorporation of ablative diphenyldimethylsiloxane oil into RTV11®® network

The monofunctional oil used for tethering was reacted with the crosslinker followed by condensation reaction with the silanol polymers of RTV11®®.

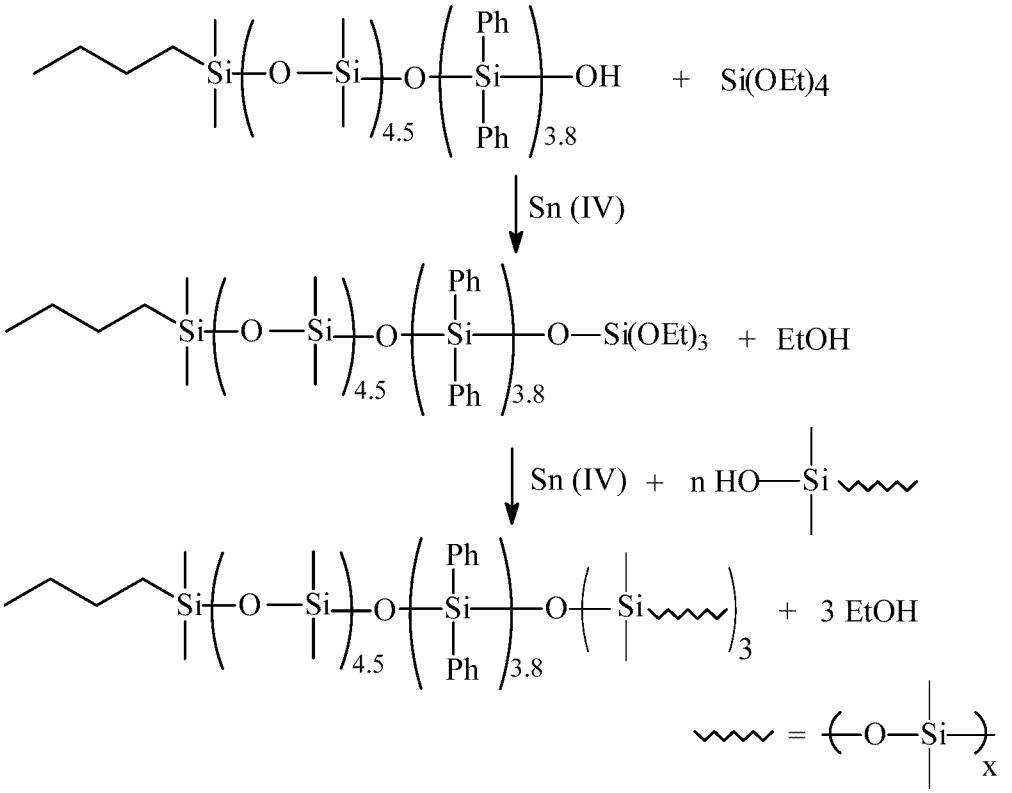
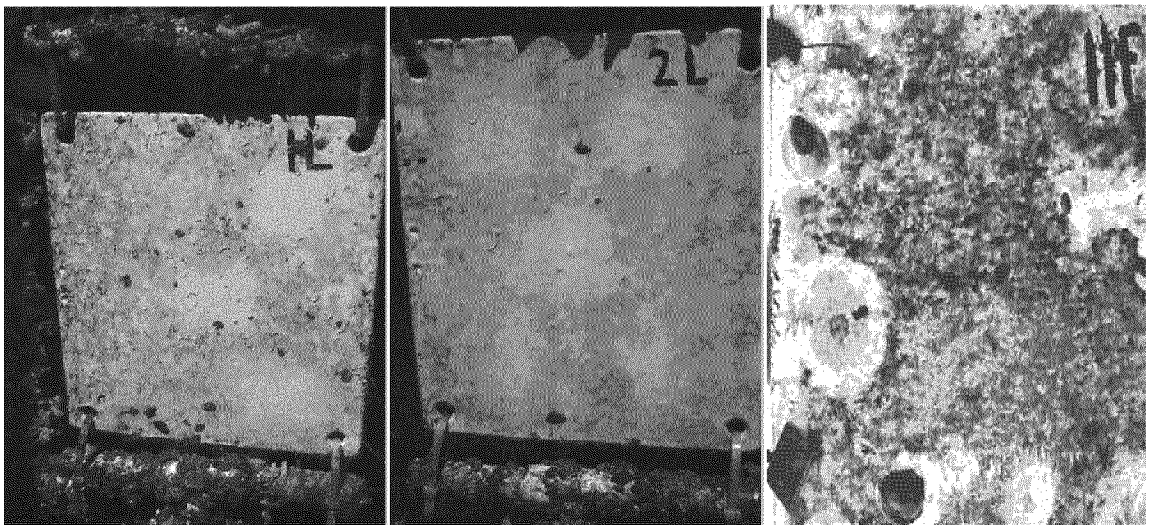


Figure 1.B.6. Incorporation of tethered diphenyldimethylsiloxane oil into the RTV11®® network

The overall fouling coverage was evaluated at onethe Massachusetts's site,e for the northeast site and barnacle adhesion values were measured at FIT (Figure 1. B.7 and Figure 1. B.8).



RTV11 Free Oil Ablative Coating

Figure 1.B.7. Foul- release performance of the of ablative diphenyldimethylsiloxane coating

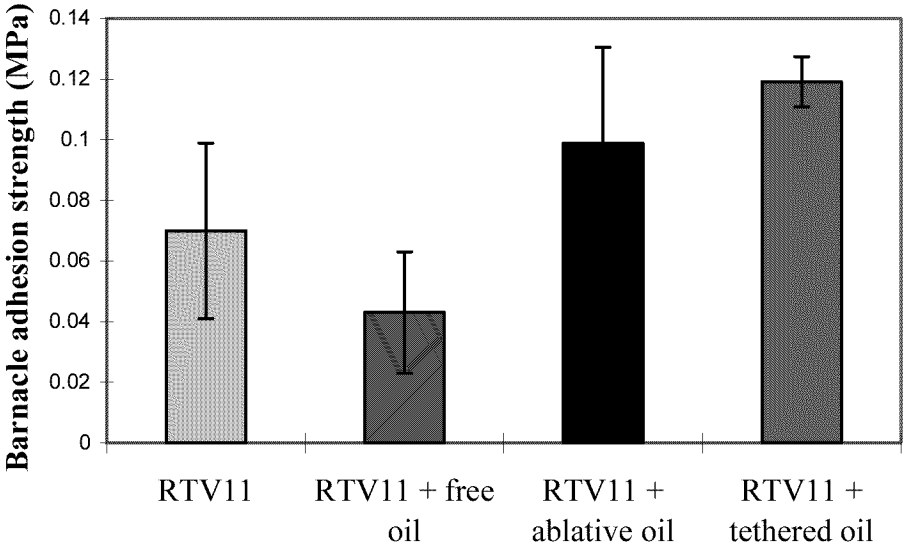


Figure 1.B.8. Foul- release performance of ablative networks and tethered oils

We observed that the ablative oil, which is chemically bound to the PDMS topcoat, provided inferior antifouling performance compared to both the oil-amendedfree

diphenyldimethylsiloxane oil in RTV11® and the RTV1®1 control (Figure 1.B.7; 1.B.8). The barnacle adhesion data confirmed that the coating containing the tethered oil or the ablative network coating performed poorly relative to the controls (RTV11® and RTV11 + free oil) Figure 1.B.8). From these results, we can conclude that free oil is necessary in the silicone coating for optimal foul release performance.

APPENDIX 2. PHYSICAL PROPERTIES OF DEVELOPMENTAL COATINGS

Appendix 2.A Physical properties of fouling release formulations

Table 2.A.1. Physical properties of fouling release topcoat formulations

Downselect number	Composition	Tensile Stress (MPa)	Elongation at Break (%)	Die B Tear Maximum Stress (MPa)
1	RTV11®	2.130 ± 0.372	228 ± 42	0.159 ± 0.007
-	Silica filled base	2.255 ± 0.365	198 ± 20	0.128 ± 0.005
2	RTV11® + 10% SF1154	1.951 ± 0.324	212 ± 21	0.152 ± 0.006
3	Silica filled base + 10% SF1154	1.531 ± 0.634	170 ± 60	0.131 ± 0.002
4	RTV11® + 10% DBE224	2.186 ± 0.972	141	0.145 ± 0.009
5	RTV11® + 10% DMSC15	1.503 ± 0.965	140	0.172 ± 0.024
6	Silica filled base + 10% DMSC15	2.027 ± 0.228	242 ± 18	0.127 ± 0.004
7	Silica filled base + 10% SF1147	2.117 ± 0.262	232 ± 23	0.103 ± 0.005
8	RTV11® + SF1147	1.703 ± 0.331	186 ±10	0.131 ± 0.006
9	RTV11® + 5% DBE224 + 5% SF1154	1.868 ± 0.228	170 ± 10	0.145 ± 0.011
10	RTV11 ®+ 10% Ablative carbinol oil	0.841 ± 0.228	108 ± 16	0.145 ± 0.007
11	RTV11® + 10% Ablative phenyl oil	1.834 ± 0.138	129 ± 6	0.017 ± 0.013

Table 2.A.2. Tensile moduli for oil amended foul release coatings

DS Number	Composition	Storage Modulus (MPa)	Loss Modulus (MPa)	tan δ
1	RTV11®	1.44	0.0182	0.01
2	RTV11® + 10% SF1154	1.19	0.0157	0.013
5	RTV11® + 10%DMSC15	0.42	0.0100	0.01858
8	RTV11® + 10 %SF1147	1.47	0.0086	0.00592
-	Silica filled base	0.379	0.0050	0.013
3	Silica filled base + 10% SF1154	0.305	0.0029	0.00952
6	Silica filled base + 10% DMSC15	0.433	0.0151	0.0348
7	Silica filled base + 10% SF1147	0.266	0.0095	0.035

Appendix 2.B Peel adhesion properties of topcoat formulations

Table 2.B.1 Peel adhesion properties of topcoat formulation

Tiecoat	Topcoat	Conditions	Peel adhesion(N/m)	Standard deviation
Mistcoat/J501	RTV11 + SF1147	dry	3205	234
Mistcoat/J501	RTV11 + SF1147	wet	35	19
Mistcoat/J501	RTV11 + DMSC15	dry	2927	93
Mistcoat/J501	RTV11 + DMSC15	wet	32	22
Mistcoat/J501	RTV11	dry	3593	87
Mistcoat/J501	RTV11	wet	41	27
Mistcoat/J501	RTV11 + SF1154	dry	3853	118
Mistcoat/J501	RTV11 + SF1154	wet	40	12
Mistcoat elimination/J501	RTV11 + SF1147	dry	3582	193
Mistcoat elimination/J501	RTV11 + SF1147	wet	3772	222
Mistcoat elimination/J501	RTV11 + DMSC15	dry	3026	269
Mistcoat elimination/J501	RTV11 + DMSC15	wet	3509	467
Mistcoat elimination/J501	RTV11	dry	3838	166
Mistcoat elimination/J501	RTV11	wet	3938	111
Mistcoat elimination/J501	RTV11 + SF1154	dry	4163	215
Mistcoat elimination/J501	RTV11 + SF1154	wet	3736	750
SEA/SCM	RTV11	wet	538	33
SEA/SCM	RTV11	dry	666	35
SEA/SCM	RTV11 + DMSC15	wet	400	34
SEA/SCM	RTV11 + DMSC15	dry	580	65
SEA/SCM	RTV11 + SF1147	wet	540	19
SEA/SCM	RTV11 + SF1147	dry	913	55
SEA/SCM	RTV11 + SF1154	wet	675	60
SEA/SCM	RTV11 + SF1154	dry	894	9
SEA/SCM/J501	RTV11 + SF1147	dry	842	5
SEA/SCM/J501	RTV11 + SF1147	wet	1009	32
SEA/SCM/J501	RTV11 + DMSC15	dry	836	18
SEA/SCM/J501	RTV11 + DMSC15	wet	660	19
SEA/SCM/J501	RTV11	dry	744	40
SEA/SCM/J501	RTV11	wet	884	61
SEA/SCM/J501	RTV11 + SF1154	dry	744	18
SEA/SCM/J501	RTV11 + SF1154	wet	1045	33
Mil III/Mistcoat elimination/J501	RTV11	dry	1774	693
Mil III/Mistcoat elimination/J501	RTV11	wet	3182	96
Mil III/Mistcoat elimination/J501	RTV11 + DMSC15	dry	2123	209
Mil III/Mistcoat elimination/J501	RTV11 + DMSC15	wet	2757	179
Mil III/Mistcoat/J501	RTV11	dry	2866	135
Mil III/Mistcoat/J501	RTV11	wet	3270	38
Mil III/Mistcoat/J501	RTV11 + DMSC15	dry	2323	147
Mil III/Mistcoat/J501	RTV11 + DMSC15	wet	2929	137
Amerlock 400/mistcoat/J501	RTV11 + DMSC15	dry	2417	94
Amerlock 400/mistcoat/J501	RTV11 + DMSC15	wet	1894	597
Amerlock 400/mistcoat/J501	RTV11	dry	3070	101
Amerlock 400/mistcoat/J501	RTV11	wet	841	30

Appendix 2.C Abrasion resistance of topcoat formulations

Table 2.C.1 Abrasion resistance of downselected topcoats over mistcoat/J501 system

DS #	Composition	Abrasion Results	Qualitative System Adhesion
1	Epoxy/J501/RTV11®	Control	Good
	Epoxy/J501/Silica filled base	Control	Good
2	Epoxy/J501/RTV11® + 10% SF1154	Worse than RTV11®	Good
3	Epoxy/J501/Silica filled base + 10%SF1154	Equivalent to Silica filled base	Very good
4	Epoxy/J501/RTV11® +10% DBE224	Worse than control	Good
5	Epoxy/J501/RTV11® + 10% DMSC15	Eorse than control	Marginal
6	Epoxy/J501/Silica filled base + 10% DMSC15	Equivalent to Silica filled base	Good
7	Epoxy/J501/Silica filled base + 10% SF1147	Equivalent to Silica filled base	Good
8	Epoxy/J501/ RTV11® + 10% SF1147	Better than RTV11®	Very good
10	Epoxy/J501/RTV1® + 10%ablative carbinol	Better than RTV11®	Good
11	Epoxy/J501/RTV11® + 10%ablative phenyl	Better than RTV1®	Bood

Table 2.C.2 Abrasion resistance of screening coatings over the mistcoat/J501 system

System Composition	Abrasion Results	Qualitative System Adhesion
Epoxy/J501 + 10% SF1147/RTV11®	Better than control	Delaminated J501/epoxy interface
Epoxy/J501 + 10 %PDV 0331/RTV11®	Better than control	Good
Epoxy/J501 + 10% 406/RTV11®	Better than control	Good
epoxy/J501 + 10% 563/RTV11®	better than control	Good
Epoxy/J501 + 10% DEB224 /RTV11®	Failure	Very poor: epoxy/tie failure
Epoxy/J501 + 10% DMSC15 type B capsules/RTV11®	Same as RTV11®	Good
Epoxy/J501 + 10% DMSC15/RTV11®	Aetter than control	Poor: epoxy/tie failure in places
Epoxy/J501 + 10% DMSC15/Silica filled base	Same as silica filled base	Good
Epoxy/J501 + 10% MCRC13/RTV11®	Worse than control	Good
Epoxy/J501 + 10% PDV0325/RTV11®	Wetter than control	Good/oil streaks to surface
Epoxy/J501 + 10% PDV0341/RTV11®	Same as RTV11®	Good
Epoxy/J501 + 10% PS835/RTV11®	Better than control	Delamination J501/epoxy interface
Epoxy/J501 + 10% SF1147/Silica filled base	Same as silica filled base	Delaminated J501/epoxy interface
Epoxy/J501 + 10% SF1154/Silica filled base	Same as silica filled base	Good
Epoxy/J501 + 10%CMS222/RTV11®	Better than control	Good
Epoxy/J501 + 10%CMS222/Silica filled base	Same as silica filled base	Delaminated J501/topcoat interface
Epoxy/J501 + 10%DBE224 /RTV511®	Worse than control	Very poor:epoxy/tiecoat failure
Epoxy/J501 + 10%DMSB31/Silica filled base	Same as silica filled base	Delaminated J501/topcoat interface
Epoxy/J501 + 10%MCRC13/Silica filled base	Same as silica filled base	Good
Epoxy/J501 + 10%PDV0325/RTV11®	Better than control	Good
Epoxy/J501 + 10%PDV0325/Silica filled base	Same as silica filled base	Good
Epoxy/J501 + 10%PDV0341/Silica filled base	Same as silica filled base	Good

Epoxy/J501 + 10%RTT1011/Silica filled base	Same as silica filled base	Good
Epoxy/J501 + 10%SF1154/RTV11®	Same as RTV11®	Good
Epoxy/J501 + 30% SF1154/RTV11®	Worse than control	Good-poor: epoxy/tie failure
Epoxy/J501 +10%PDV0331/Silica filled base	Same as silica filled base	Good
Epoxy/J501/ RTV11® + 10% PDV0331	Worse than control	Good
Epoxy/J501/ RTV11® + 10% SF1147	Better than control	Very good
Epoxy/J501/ RTV11® + 20% SF1154	Worse than control	Good
Epoxy/J501/ RTV11® + 30% SF1154	Worse than control	Good/ poor durability
Epoxy/J501/RTV11®	Same as RTV11®	Good
Epoxy/J501/RTV11®	Same as RTV11®	Good
Epoxy/J501/RTV11®	Same as RTV11®	Good
Epoxy/J501/RTV11® + 10% CMS222 (PS835)	Worse than control	Good
Epoxy/J501/RTV11® + 10% DBE224	Same as RTV11®	Good
Epoxy/J501/RTV11® + 10% DMSB31 (PS563)	Same as RTV11®	Good
Epoxy/J501/RTV11® + 10% DMSC15	Worse than control	Marginal
Epoxy/J501/RTV11® + 10% MCRSC13	Better than control	Good
Epoxy/J501/RTV11® + 10% PDV0325	Worse than control	good
Epoxy/J501/RTV11® + 10% PDV0341	Better than control	Good,oily surface
Epoxy/J501/RTV11® + 10% RTT1011(406)	Worse than control	Good
Epoxy/J501/RTV11® + 10% SF1154	Better than control	Good
Epoxy/J501/RTV11® + 10% SF1154	Worse than control	Good
Epoxy/J501/RTV11® + 10%ablative carbinol	Better than control	Good
Epoxy/J501/RTV11® + 10%ablative phenyl	Better than control	Good
Epoxy/J501/RTV11® + 10%DMSC25	Same as RTV11®	Good
Epoxy/J501/RTV11® + 10%FMS123	Better than control	Good/poor durability
Epoxy/J501/RTV11® + 10%Microcap C DMSC15	Same as RTV11®	Good adhesion/poor durability
Epoxy/J501/RTV11® + 10%SF1154 + talc	Same as RTV11®	Good
Epoxy/J501/RTV11® + 10%tethered carbinol	Better than control	Good
Epoxy/J501/RTV11® + 5%SF1154 + 5%DBE222	Same as RTV11®	Good
Epoxy/J501/RTV11® + 5%SF1154 + 5%MCRC13	Better than control	Good
epoxy/J501/RTV11® + 5%SF1154 +5%DMSC15	Same as RTV11®	Good
Epoxy/J501/RTV11® +10% DBE224	Worse than control	Good a
Epoxy/J501/RTV11® +10%SF1154 + kaolin	Worse than control	Good
Epoxy/J501/RTV11® +10%SF1154 +graphite	Failure	Good /poor durability
Epoxy/J501/RTV11® +10%SF1154 C capsules	Better than control	Good but weak topcoat
Epoxy/J501/RTV511	Worse than control	Good
Epoxy/J501/RTV511	Same as RTV11®	Good

Epoxy/J501/RTV511	Same as RTV11®	Good
Epoxy/J501/RTV511 + 10% DBE224	Worse than control	Good
Epoxy/J501/RTV511 + 10% SF1154	Same as RTV11®	Good
Epoxy/J501/RTV511 +10%DMSC15	worse than control	Good
Epoxy/J501/RTV511+10%SF96(350)	Failure	Very poor: top/tie failure (easily peels apart)
Epoxy/J501/Silica filled base	Same as silica filled base	Good
Epoxy/J501/Silica filled base	Same as silica filled base	Good
Epoxy/J501/Silica filled base + 10% DMSC15	Same as silica filled base	Good
Epoxy/J501/Silica filled base + 10% FMS123	Same as silica filled base	Good
Epoxy/J501/Silica filled base + 10% MCRC13	Same as silica filled base	Good /poor durability
Epoxy/J501/Silica filled base + 10% Microcap C DMSC15	Failure	Good /poor durability
Epoxy/J501/Silica filled base + 10% PDV0331	S as silica filled base	Good
Epoxy/J501/Silica filled base + 10% PDV0341	S as silica filled base	Good
Epoxy/J501/Silica filled base + 10% RTT1011	S as silica filled base	Good/very durable
Epoxy/J501/Silica filled base + 10% SF1147	S as silica filled base	Good
Epoxy/J501/Silica filled base + 10% SF1154 +macro.resin	Failure	Good /poor durability
Epoxy/J501/Silica filled base + 10%CMS222	S as silica filled base	Good
Epoxy/J501/Silica filled base + 10%DMSC25	Worse than control	Good
Epoxy/J501/Silica filled base + 10%PDV0325	As good as silica filled base	Good
Epoxy/J501/Silica filled base + 10%PDV0331	Same as silica filled base	Good
Epoxy/J501/Silica filled base + 10%PDV0341	Same as silica filled base	Good
Epoxy/J501/Silica filled base + 10%PS563	Same as silica filled base	Good
Epoxy/J501/Silica filled base + 10%SF1154	Same as silica filled base	Very good
Epoxy/J501/Silica filled base + 10%SF1154 +10%talc	Failure	Good
Epoxy/J501/Silica filled base + 20% SF1154	S as silica filled base	Good
Epoxy/J501+ 10% FMS123/RTV11®	Better than control	Good
Epoxy/J501+ 20% SF1154/RTV11®	S as RTV11®	Poor: epoxy/tie failure (easily peels apart)
Epoxy/J501+10%DBE224/Silica filled base	Failure	Very poor: epoxy/tie failure (easily peels apart)
Epoxy/J501+10%SF96(350) /RTV511	Failure	Good
J501/RTV11 + 10% SF1154 B microcapsules	Failure	Good
Epoxy/J501/RTV11 + 10% DMSC15 + 10% DMSC15 type C capsules	Same as RTV11®	Good
Epoxy/J501 + 10 % MCRC13/RTV11	Same as RTV11®	Good
Epoxy/J501/RTV11® + 10% CMS222	Worse than control	Good
Epoxy/J501/RTV11® + 10% DBE224	Same as RTV11®	Good
Epoxy/J501/RTV11® + 10%DMSC15	Worse than control	Good
Epoxy/J501/RTV11®+ 10%RTT1011	Same as RTV11®	Good
Epoxy/J501/Silica filled base + 10% SF1147	Same as silica filled base	Good

Appendix 2.D Critical surface tensions and energy descriptors for foul-release formulations

Table 2.D.1 Critical surface tensions and surface energy descriptors for pre exposure coatings

DS	Description	γc [mN/m]	γd [mN/m]	γp [mN/m]	γs [mN/m]	%γp	Observations
1	RTV11®	22.3	23.2	2.3	25.5	9%	All test fluids relatively stable on surface
2	RTV11® + 10% SF1154	22.7	22.8	3.8	26.6	14%	Naphthalenes unstable
3	Silica filled base + 10% SF1154	25.5	23.5	5.4	28.9	19%	All test fluids relatively stable on surface
4	RTV11® + 10% DBE224	21.5	21.7	4.1	25.8	16%	Polar fluids unstable
5	RTV11® + 10% DMSC15	21.6	21.8	9.4	31.2	30%	Rapid surface reactivity
6	Silica filled base + 10% DMSC15	27.5	24.2	17.4	41.6	42%	Polar fluids unstable
7	Silica filled base + 10% SF1147	24.6	23.8	3	26.8	11%	All test fluids relatively stable on surface
8	RTV11® + 10% SF1147	21.6	23.7	2.7	26.4	10%	Water unstable
9	RTV11® + 5% DBE224 + 5% SF1154	20.8	22.4	5.2	27.6	19%	Polar fluids/naphthalene unstable
10	RTV11® + 10% ablative carbinol	20.5	22	>12.2	>34.2	>36%	Only alkanes stable
11	RTV11® + 10% ablative phenyl	21	22.9	2.2	25.1	9%	Some polar fluids unstable
12	J501+CMS222/RTV11®	22.5	22.8	9.4	32.2	29%	All test fluids relatively stable on surface
13	J501+SEA-9-211/RTV11® + 10% DMSC15	21.3	22.6	7.5	30.1	25%	Rapid surface reactivity

* All topcoats over J501-alone, unless stated otherwise

γc: critical surface tension γd: dispersion component of surface free energy

γp: polar component of surface free energy

Table 2.D.2. Cumulative field notes; Freshwater sites in western New York State
DOWNSELECT SET #1

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY
										**topcoat slightly abraded before immersion*
1A	20aug97	28	100	100	SI,SL	80	No test	N, ---	No test	
23jul97	14sep97	53	100	95	SI,SL,IF	95	90	N, ---	No test	
Dunkirk	23jan98	184	100	100	SI,SL	100	No test	N, ---	No test	
	Removed									
1C*	20aug97	28	100	100	SI,SL	90	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	100	90	N, ---	No test	
Dunkirk	23jan98	184	50	100	SI,SL	20	No test	N, ---	No test	
	Removed									
1B*	13nov97	112	100	95	SI,SL,MOL	50	No test	Y, no test	No test	
24jul97	20mar98	239	100	100	SI,SL	90	No test	N, ---	>15	
Medina	12jun98	323	100	100	SI,SL	70	30	N, ---	18	
	11sep98	414	95	95	SI,SL,IF,BR	90	90	N, ---	3	
	11dec98	505	90	95	SI,SL,MOL	40	40	Y, N	12	
	22mar99	606	90	100	SI,SL	80	No test	N, no test	10	
1D	13nov97	112	100	95	SI,SL,MOL	60	No test	Y, no test	No test	
24jul97	20mar98	239	100	100	SI,SL	90	No test	N, ---	>15	
Medina	12jun98	323	95	100	SI,SL	90	80	N, ---	>30	
	11sep98	414	95	95	SI,SL,IF	80	80	N, ---	6	
	11dec98	505	95	90	SI,SL,MOL	60	40	Y, Y	21	
	22mar99	606	95	100	SI,SL	90	No test	N, no test	>20	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
2A	20aug97	28	100	100	SI,SL	80	No test	N, ---	No test	
23jul97	14sep97	53	100	95	SI,SL,IF	95	90	N, ---	No test	
Dunkirk	23jan98	184	100	95	SI,SL,AL	100	No test	N, ---	No test	
	Removed									
2C*	20aug97	28	100	100	SI,SL	100	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	100	90	N, ---	No test	
Dunkirk	23jan98	184	90	100	SI,SL	80	No test	N, ---	No test	
	Removed									
2B*	13nov97	112	100	95	SI,SL,MOL	60	No test	Y, no test	No test	
24jul97	20mar98	239	100	100	SI,SL	100	No test	N, ---	>15	
Medina	12jun98	323	100	95	SI,SL,IF	10	10	N, ---	18	
	11sep98	414	95	95	SISLIFBRMO	95	95	Y, Y	9	
	11dec98	505	90	95	SISLIFMOL	30	15	Y, Y	5	
	22mar99	606	85	100	SI,SL	90	No test	N, no test	7	
2D	13nov97	112	100	100	SI,SL	20	No test	N, ---	No test	
24jul97	20mar98	239	95	100	SI,SL	100	No test	N, ---	>15	
Medina	12jun98	323	95	95	SI,SL,IF	90	80	N, ---	18	
	11sep98	414	95	95	SI,SL,AL	60	60	N, ---	3	
	11dec98	505	95	95	SI,SL,MOL	95	45	Y, N	14	
	22mar99	606	95	100	SI,SL	90	No test	N, no test	14	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
3A	20aug97	28	100	100	SI,SL	70	No test	N, ---	No test	
23jul97	14sep97	53	100	95	SI,SL,AL	80	60	N, ---	No test	
Dunkirk	23jan98	184	30	100	SI,SL	60	No test	N, ---	No test	
	Removed									
3C*	20aug97	28	100	100	SI,SL	90	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	80	70	N, ---	No test	
Dunkirk	23jan98	184	-0-	100	SI,SL	No test	No test	N, ---	No test	
	Removed									
3B*	13nov97	112	100	95	SI,SL,MOL	70	No test	Y, no test	No test	
24jul97	20mar98	239	95	100	SI,SL	100	No test	N, ---	12	
Medina	12jun98	323	90	100	SI,SL	30	30	N, ---	12	
	11sep98	414	90	90	SSIFABRMO	100	100	Y, Y	6	
	11dec98	505	90	95	SI,SL,MOL	90	40	Y, N	7	
	22mar99	606	60	100	SI,SL	80	No test	N, ---	7	
3D	13nov97	112	100	95	SI,SL,MOL	50	No test	Y, no test	No test	
24jul97	20mar98	239	100	100	SI,SL	95	No test	N, ---	12	
Medina	12jun98	323	100	100	SI,SL	70	20	N, ---	15	
	11sep98	414	100	95	SI,SL,IF	5	5	N, ---	3	
	11dec98	505	95	100	SI,SL	100	80	N, ---	9	
	22mar99	606	95	100	SI,SL	90	No test	N, ---	7	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY
										**topcoat slightly abraded before immersion*
4A	20aug97	28	100	100	SI,SL	50	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	70	60	N, ---	No test	
Dunkirk	23jan98	184	90	100	SI,SL	50	no test	N, ---	No test	
	Removed									
4C*	20aug97	28	100	100	SI,SL	80	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	80	40	N, ---	No test	
Dunkirk	23jan98	184	95	100	SI,SL	80	no test	N, ---	No test	
	Removed									
4B*	13nov97	112	100	100	SI,SL	20	No test	N, ---	No test	
24jul97	20mar98	239	100	100	SI,SL	80	No test	N, ---	9	
Medina	12jun98	323	100	100	SI,SL	90	75	N, ---	12	
	11sep98	414	90	80	SI,SL,BR,MO	20	20	Y, Y	9	
	11dec98	505	90	90	SI,SLALMOL	85	40	Y, N	10	
	22mar99	606	90	100	SI, SL	40	No test	N, ---	>20	
4D	13nov97	112	100	100	SI,SL	20	No test	N, ---	No test	
24jul97	20mar98	239	95	95	SI,SL,IF	80	No test	N, ---	12	
Medina	12jun98	323	90	100	SI,SL	80	70	N, ---	18	
	11sep98	414	90	95	SISLALMOL	60	60	Y, Y	3	
	11dec98	505	90	95	SI,SL,MOL	100	75	Y, N	12	
	22mar99	606	80	100	SI,SL	60	No test	N, ---	5	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
5A	20aug97	28	100	100	SI,SL	90	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	90	60	N, ---	No test	
Dunkirk	23jan98	184	80	100	SI,SL	20	No test	N, ---	No test	
	Removed									
5C*	20aug97	28	100	100	SI,SL	95	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	50	40	N, ---	No test	
Dunkirk	23jan98	184	100	100	SI,SL	80	No test	N, ---	No test	
	Removed									
5B*	13nov97	112	95	100	SI,SL	<5	No test	N, ---	No test	
24jul97	20mar98	239	95	100	SI,SL	50	No test	N, ---	3	
Medina	12jun98	323	95	95	SI,SL,IF	100	90	N, ---	30	
	11sep98	414	95	70	SSIFBRMOL	70	60	Y, N	9	
	11dec98	505	90	95	SI,SL,ALMOL	95	25	Y, N	4	
	22mar99	606	85	100	SI,SL	90	No test	N, ---	>20	
5D	13nov97	112	100	100	SI,SL	20	No test	N, ---	No test	
24jul97	20mar98	239	100	100	SI,SL	70	No test	N, ---	3	
Medina	12jun98	323	95	100	SI,SL	70	40	N, ---	18	
	11sep98	414	90	100	SI,SL	70	70	N, ---	3	
	11dec98	505	90	95	SI,SL,ALMOL	90	20	Y, N	3	
	22mar99	606	90	100	SI,SL	60	No test	N, ---	1	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
6A	20aug97	28	100	100	SI,SL	90	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	90	80	N, ---	No test	
Dunkirk	23jan98	184	100	95	SI,SL,AL	100	No test	N, ---	No test	
	Removed									
6C*	20aug97	28	100	100	SI,SL	95	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	70	50	N, ---	No test	
Dunkirk	23jan98	184	90	95	SI,SL,AL	90	No test	N, ---	No test	
	Removed									
6B*	13nov97	112	100	95	SI,SL,MOL	40	No test	Y, no test	No test	
24jul97	20mar98	239	95	100	SI,SL	90	No test	N, ---	6	
Medina	12jun98	323	95	95	SI,SL,IF	100	50	N, ---	>30	
	11sep98	414	70	95	SI,SL,IF,BR	25	25	N, ---	6	
	11dec98	505	30	95	SI,SL,IF	95	90	N, ---	30	
	22mar99	606	30	100	SI,SL	100	No test	N, ---	>20	
6D	13nov97	112	100	95	SI,SL,MOL	<10	No test	Y, no test	No test	
24jul97	20mar98	239	100	100	SI,SL	80	No test	N, ---	9	
Medina	12jun98	323	95	95	SI,SL,IF,MOL	40	30	Y, N	30	
	11sep98	414	95	95	SI,SL,AL,BR	80	80	N, ---	6	
	11dec98	505	95	95	SI,SL,IF,MOL	100	85	Y, N	3	
	22mar99	606	80	100	SI,SL	70	No test	N, ---	6	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
7A	20aug97	28	100	100	SI,SL	90	No test	N, ---	No test	
23jul97	14sep97	53	100	95	SI,SL,IF	90	60	N, ---	No test	
Dunkirk	23jan98	184	95	100	SI,SL	90	No test	N, ---	No test	
	Removed									
7C*	20aug97	28	100	100	SI,SL	50	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	70	60	N, ---	No test	
Dunkirk	23jan98	184	80	100	SI,SL	90	No test	N, ---	No test	
	Removed									
7B*	13nov97	112	100	95	SI,SL,MOL	40	No test	Y, no test	No test	
24jul97	20mar98	239	100	100	SI,SL	100	No test	N, ---	6	
Medina	12jun98	323	95	95	SI,SL,MOL	20	10	Y, N	9	
	11sep98	414	95	95	SISL,AL	100	100	N, ---	6	
	11dec98	505	95	95	SI,SL,MOL	100	25	Y, N	3	
	22mar99	606	95	100	SI,SL	90	No test	N, ---	3	
7D	13nov97	112	100	100	SI,SL	40	No test	N, ---	No test	
24jul97	20mar98	239	100	100	SI,SL	90	No test	N, ---	6	
Medina	12jun98	323	100	100	SI,SL	10	10	N, ---	6	
	11sep98	414	100	95	SI,SL,IF	40	40	N, ---	15	
	11dec98	505	100	100	SI,SL	95	25	N, ---	5	
	22mar99	606	95	100	SI,SL	60	No test	N, ---	2	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
8A	20aug97	28	100	100	SI,SL	90	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	100	90	N, ---	No test	
Dunkirk	23jan98	184	95	100	SI,SL	90	No test	N, ---	No test	
	Removed									
8C*	20aug97	28	100	100	SI,SL	95	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	90	70	N, ---	No test	
Dunkirk	23jan98	184	90	100	SI,SL	40	No test	N, ---	No test	
	Removed									
8B*	13nov97	112	100	100	SI,SL	<5	No test	N, ---	No test	
24jul97	20mar98	239	100	100	SI,SL	70	No test	N, ---	6	
Medina	12jun98	323	100	100	SI,SL	95	85	N, ---	9	
	11sep98	414	95	100	SI,SL	50	50	N, ---	6	
	11dec98	505	95	95	SI,SL,MOL	90	15	Y, N	4	
	22mar99	606	90	100	SI,SL	30	No test	N, ---	3	
8D	13nov97	112	100	100	SI,SL	10	No test	N, ---	No test	
24jul97	20mar98	239	95	100	SI,SL	90	No test	N, ---	9	
Medina	12jun98	323	95	100	SI,SL	70	20	N, ---	9	
	11sep98	414	90	95	SI,SL,AL	20	20	N, ---	6	
	11dec98	505	90	100	SI,SL	90	25	N, ---	6	
	22mar99	606	90	100	SI,SL	40	No test	N, ---	3	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage Ppre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
9A	20aug97	28	100	100	SI,SL	80	No test	N, ---	No test	
23jul97	14sep97	53	100	95	SI,SL,IF	95	30	N, ---	No test	
Dunkirk	23jan98	184	90	100	SI,SL	20	No test	N, ---	No test	
	Removed									
9C*	20aug97	28	100	100	SI,SL	80	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	60	50	N, ---	No test	
Dunkirk	23jan98	184	95	100	SI,SL	90	No test	N, ---	No test	
	Removed									
9B*	13nov97	112	100	100	SI,SL	60	No test	N, ---	No test	
24jul97	20mar98	239	100	100	SI,SL	95	No test	N, ---	12	
Medina	12jun98	323	95	100	SI,SL	95	80	N, ---	18	
	11sep98	414	95	95	SI,SL,IF,AL	100	100	N, ---	3	
	11dec98	505	95	95	SI,SL,IFMOL	80	30	Y, N	10	
	22mar99	606	95	100	SI,SL	80	No test	N, ---	9	
9D	13nov97	112	100	95	SI,SL,MOL	50	No test	Y, no test	No test	
24jul97	20mar98	239	100	100	SI,SL	60	No test	N, ---	>15	
Medina	12jun98	323	100	100	SI,SL	90	50	N, ---	18	
	11sep98	414	100	95	SI,SL,IF	90	90	N, ---	9	
	11dec98	505	95	90	SI,SLALMOL	80	40	Y, N	15	
	22mar99	606	95	100	SI,SL	80	No test	N, ---	12	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
10A	20aug97	28	100	100	SI,SL	90	No test	N, ---	No test	
23jul97	14sep97	53	100	95	SI,SL,IF	100	90	N, ---	No test	
Dunkirk	23jan98	184	90	100	SI,SL	90	No test	N, ---	No test	
	Removed									
10C*	20aug97	28	100	100	SI,SL	60	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	100	90	N, ---	No test	
Dunkirk	23jan98	184	40	100	SI,SL	30	No test	N, ---	No test	
	Removed									
10B*	13nov97	112	100	95	SI,SL,MOL	50	No test	Y, no test	No test	
24jul97	20mar98	239	100	100	SI,SL	100	No test	N, ---	>15	
Medina	12jun98	323	100	100	SI,SL	50	40	N, ---	30	
	11sep98	414	95	95	SI,SL,BR	100	95	N, ---	3	
	11dec98	505	95	95	SI,SL,MOL	95	50	Y, N	>30	
	22mar99	606	95	100	SI,SL	90	No test	N, ---	11	
10D	13nov97	112	100	95	SI,SL,AL	50	No test	N, ---	No test	
24jul97	20mar98	239	100	95	SI,SL,IF	100	No test	N, ---	>15	
Medina	12jun98	323	95	100	SI,SL	70	40	N, ---	>30	
	11sep98	414	95	95	SI,SL,AL,BR	90	90	N, ---	3	
	11dec98	505	90	95	SI,SL,MOL	90	50	Y, N	>30	
	22mar99	606	50	100	SI,SL	90	No test	N, ---	10	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
11A	20aug97	28	100	100	SI,SL	80	No test	N, ---	No test	
23jul97	14sep97	53	100	95	SI,SL,IF	100	90	N, ---	No test	
Dunkirk	23jan98	184	100	100	SI,SL	100	no test	N, ---	No test	
	Removed									
11C*	20aug97	28	100	100	SI,SL	95	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	100	90	N, ---	No test	
Dunkirk	23jan98	184	90	100	SI,SL	60	No test	N, ---	No test	
	Removed									
11B*	13nov97	112	100	100	SI,SL	50	No test	N, ---	No test	
24jul97	20mar98	239	100	95	SI,SL,IF	95	No test	N, ---	12	
Medina	12jun98	323	100	95	SI,SL,IF	95	90	N, ---	>30	
	11sep98	414	95	95	SI,SL,BR	65	60	N, ---	9	
	11dec98	505	95	95	SI,SL,AL	90	40	N, ---	18	
	22mar99	606	95	100	SI,SL	90	No test	N, ---	>20	
11D	13nov97	112	100	95	SI,SL,MOL	70	No test	Y, no test	No test	
24jul97	20mar98	239	100	95	SI,SL,IFMOL	90	No test	Y, no test	15	
Medina	12jun98	323	95	100	SI,SL	95	30	N, ---	24	
	11sep98	414	95	80	SI,SL,BR	25	25	N, ---	9	
	11dec98	505	95	95	SI,SL,MOL	100	90	Y, N	20	
	22mar99	606	95	100	SI,SL	70	No test	N, ---	8	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
12A	20aug97	28	100	100	SI,SL	95	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	90	70	N, ---	No test	
Dunkirk	23jan98	184	95	100	SI,SL	80	No test	N, ---	No test	
	Removed									
12C*	20aug97	28	100	100	SI,SL	40	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	95	80	N, ---	No test	
Dunkirk	23jan98	184	90	100	SI,SL	50	no test	N, ---	No test	
	Removed									
12B*	13nov97	112	100	100	SI,SL	<5	No test	N, ---	No test	
24jul97	20mar98	239	100	100	SI,SL	70	No test	N, ---	6	
Medina	12jun98	323	95	100	SI,SL	90	90	N, ---	12	
	11sep98	414	95	95	SI,SL,BR	50	50	N, ---	9	
	11dec98	505	95	95	SI,SL,MOL	90	30	Y, Y	>30	
	22mar99	606	95	100	SI,SL	30	No test	N, ---	3	
12D	13nov97	112	100	100	SI,SL	40	No test	N, ---	No test	
24jul97	20mar98	239	100	100	SI,SL	60	No test	N, ---	9	
Medina	12jun98	323	100	100	SI,SL	90	80	N, ---	9	
	11sep98	414	100	100	SI,SL	30	30	N, ---	9	
	11dec98	505	95	95	SI,SL,MOL	80	40	Y, N	8	
	22mar99	606	95	100	SI,SL	70	No test	N, ---	3	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
13A	20aug97	28	100	100	SI,SL	70	No test	N, ---	No test	
23jul97	14sep97	53	100	95	SI,SL,IF	90	<5	N, ---	No test	
Dunkirk	23jan98	184	100	100	SI,SL	40	No test	N, ---	No test	
	removed									
13C*	20aug97	28	100	100	SI,SL	<5	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	20	20	N, ---	No test	
Dunkirk	23jan98	184	50	100	SI,SL	<5	No test	N, ---	No test	
	removed									
13B*	13nov97	112	100	100	SI,SL	20	No test	N, ---	No test	
24jul97	20mar98	239	95	100	SI,SL	30	No test	N, ---	12	
Medina	12jun98	323	95	100	SI,SL	30	30	N, ---	18	
	11sep98	414	95	95	SI,SL,IF	100	100	N, ---	6	
	11dec98	505	95	95	SI,SL,MOL	80	10	Y, N	6	
	22mar99	606	95	100	SI,SL	60	No test	N, ---	3	
13D	13nov97	112	100	100	SI,SL	10	No test	N, ---	No test	
24jul97	20mar98	239	95	100	SI,SL	40	No test	N, ---	12	
Medina	12jun98	323	95	95	SI,SL,IF	80	70	N, ---	>30	
	11sep98	414	95	100	SI,SL	50	50	N, ---	6	
	11dec98	505	95	95	SI,SL,AL	95	30	N, ---	6	
	22mar99	606	95	100	SI,SL	40	No test	N, ---	7	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
AFA	20aug97	28	100	100	SI,SL	100	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	90	90	N, ---	No test	
Dunkirk	23jan98	184	100	100	SI,SL	100	No test	N, ---	No test	
	Removed									
AFC*	20aug97	28	100	100	SI,SL	90	No test	N, ---	No test	
23jul97	14sep97	53	100	100	SI,SL	90	90	N, ---	No test	
Dunkirk	23jan98	184	95	100	SI,SL	100	No test	N, ---	No test	
	Removed									
AFB*	13nov97	112	100	90	SI,SL,MOL	40	No test	Y, no test	No test	
24jul97	20mar98	239	100	95	SI,SL,MOL	70	No test	Y, no test	9	
Medina	12jun98	323	100	90	SI,SL,IFMOL	100	80	Y, N	>30	
	11sep98	414	100	95	SI,SL,MOL	75	75	Y, Y	9	
	11dec98	505	100	95	SI,SL,MOL	85	50	Y, Y	9	
	22mar99	606	100	100	SI,SL	70	No test	N, ---	>20	
AFD	13nov97	112	100	95	SI,SL,MOL	50	No test	Y, no test	No test	
24jul97	20mar98	239	100	95	SI,SL,MOL	70	No test	Y, no test	9	
Medina	12jun98	323	100	90	SI,SL,MOL	100	50	Y, Y	>30	
	11sep98	414	100	95	SI,SL,IF	80	80	N, ---	9	
	11dec98	505	100	95	SI,SL,MOL	85	80	Y, Y	9	
	22mar99	606	100	100	SI,SL	80	No test	N, ---	17	

DOWNSELECT SET #2

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*

14A*	12jun98	84	100	95	SI,SL,IFMOL	60	40	Y, Y	15	
20mar98	11sep98	175	100	90	SI,SL,IF	80	70	N, ---	9	
Medina	11dec98	266	100	95	SI,SLALMOL	95	90	Y, N	30	
	22mar99	367	100	100	SI,SL	90	No test	N, ---	>20	
14B*	12jun98	84	100	90	SI,SL,IFMOL	70	40	Y, Y	>30	
20mar98	11sep98	175	100	80	SI,SL,IF	80	80	N, ---	9	
Medina	11dec98	266	100	95	SI,SL,MOL	95	60	Y, N	21	
	22mar99	367	100	95	SI,SL,MOL	100	No test	Y, no test	9	
14C	12jun98	84	100	95	SI,SL,IFMOL	95	80	Y, N	15	
20mar98	11sep98	175	100	95	SI,SL,IF	75	75	N, ---	6	
Medina	11dec98	266	100	95	SI,SL,MOL	80	30	Y, Y	15	
	22mar99	367	100	100	SI,SL	90	No test	N, ---	8	
14D	12jun98	84	100	90	SI,SL,MOL	80	60	Y, Y	24	
20mar98	11sep98	175	100	90	SI,SL,IF	90	80	N, ---	9	
Medina	11dec98	266	100	95	SI,SL,MOL	95	80	Y, Y	30	
	22mar99	367	100	95	SI,SL,MOL	90	No test	Y, no test	>20	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
15A*	12jun98	84	100	80	SI,SL,AL	30	No test	N, ---	No test	
20mar98	11sep98	175	100	90	SSALBRMOL	90	90	Y, Y	6	
Medina	11dec98	266	100	95	SI,SL,MOL	70	40	Y, N	10	
	22mar99	367	100	100	SI,SL	90	No test	N, ---	>20	
15B*	12jun98	84	100	100	SI,SL	40	No test	N, ---	No test	
20mar98	11sep98	175	100	90	SI,SL,BR	70	50	N, ---	3	
Medina	11dec98	266	100	95	SI,SL,IFMOL	40	20	Y, N	21	
	22mar99	367	95	100	SI,SL	90	No test	N, ---	10	
15C	12jun98	84	100	100	SI,SL	50	No test	N, ---	No test	
20mar98	11sep98	175	100	90	SSALBRMOL	80	80	Y, N	9	
Medina	11dec98	266	100	95	SI,SL,MOL	50	30	Y, N	9	
	22mar99	367	100	100	SI,SL	80	No test	N, ---	15	
15D	12jun98	84	100	95	SI,SL,MOL	40	30	Y, N	9	
20mar98	11sep98	175	100	90	SI,SL,AL	70	70	N, ---	21	
Medina	11dec98	266	100	100	SI,SL	90	50	N, ---	6	
	22mar99	367	100	100	SI,SL	70	No test	N, ---	9	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
										Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*
16A*	12jun98	84	100	95	SI,SL,IFMOL	95	80	Y, N	15	
20mar98	11sep98	175	100	95	SI,SL,IF	40	40	N, ---	12	
Medina	11dec98	266	100	95	SI,SL,MOL	90	70	Y, Y	>30	
	22mar99	367	100	100	SI,SL	100	No test	N, ---	>20	
16B*	12jun98	84	100	95	SI,SL,IFMOL	95	70	Y, N	9	
20mar98	11sep98	175	100	95	SI,SL,IF	75	70	N, ---	18	
Medina	11dec98	266	100	95	SI,SL,MOL	90	40	Y, N	21	
	22mar99	367	100	100	SI,SL	80	No test	N, ---	>20	
16C	12jun98	84	100	95	SI,SL,MOL	70	50	Y, Y	15	
20mar98	11sep98	175	100	80	SI,SL,IF	90	80	N, ---	>30	
Medina	11dec98	266	100	95	SI,SL,MOL	90	70	Y, Y	>30	
	22mar99	367	100	100	SI,SL	90	No test	N, ---	>20	
16D	12jun98	84	100	95	SI,SL,IFMOL	100	95	Y, N	9	
20mar98	11sep98	175	100	100	SI,SL	60	60	N, ---	21	
Medina	11dec98	266	100	95	SI,SL,MOL	70	70	Y, Y	15	
	22mar99	367	100	100	SI,SL	60	No test	N, ---	>20	

Panel and Date Deployed	Inspection Date	# Days Immersed	Physical Condition Score	Fouling Resist. Score	Fouling Types	Silt/Slime Coverage (Pre-clean)	Silt/Slime Coverage after Low Pressure Rinse	Mussels Present? After Rinse?	Brush Test # Strokes to Remove all Visible Fouling	
Fouling scores & tests are for areas of intact topcoat ONLY **topcoat slightly abraded before immersion*										
For Panel Series #18, observations & test results are for the UNNUMBERED side of each panel.										
18A*	12jun98	84	100	100	SI,SL	100	No test	N, ---	No test	
20mar98	11sep98	175	100	95	SI,SLBRMOL	80	80	Y, Y	15	
Medina	11dec98	266	100	95	SI,SL,IFMOL	30	20	Y, N	9	
	22mar99	367	100	100	SI,SL	90	No test	N, ---	>20	
18B*	12jun98	84	100	100	SI,SL	50	No test	N, ---	No test	
20mar98	11sep98	175	100	90	SI,SL,BR	80	80	N, ---	3	
Medina	11dec98	266	100	95	SI,SL,IFMOL	70	70	Y, N	12	
	22mar99	367	100	100	SI,SL	95	No test	N, ---	>20	
18C	12jun98	84	100	95	SI,SL,IFMOL	50	50	Y, N	9	
20mar98	11sep98	175	100	95	SI,SL,IF	80	75	N, ---	18	
Medina	11dec98	266	100	95	SI,SL,MOL	90	60	Y, N	15	
	22mar99	367	100	100	SI,SL	90	No test	N, ---	7	
18D	12jun98	84	100	95	SI,SL,IF	100	70	N, ---	9	
20mar98	11sep98	175	100	100	SI,SL	70	70	N, ---	12	
Medina	11dec98	266	100	95	SI,SL,MOL	30	30	Y, N	2	
	22mar99	367	100	100	SI,SL	70	No test	N, ---	7	

Table 2.D.2 Brush abrasion on first downselect panels (over J501)

Number	Sample	Average cummulative wear (microns)			
		20K brush	50K	90K	145K
1	RTV11	0	20.32	45.72	68.58
2	RTV11 + SF1154	12.7	20.32	45.72	81.28
3	Silica filled base + SF1154	20.32	43.18	71.12	96.52
4	RTV11 + DBE224	0	17.78	45.72	55.88
5	RTV11 + DMSC15	17.78	63.5	132.08	na
6	Silica filled base + DMSC15	30.48	81.28	83.82	121.92
7	Silica filled base + SF1147	20.32	38.1	43.18	76.2
8	RTV11 + SF1147	0	25.4	43.18	55.88
9	RTV11 + DBE224 +SF1154	0	38.1	38.1	50.8
10	RTV11 + Abl carbinol	0	17.78	38.1	58.42
11	RTV11+ Abl phenyl	0	0	20.32	30.48
12	J501 + CMS222/RTV11	0	7.62	20.32	38.1
13	SEA-9-211 in J501/RTV11	25.4	33.02	88.9	165.1

Appendix 2.E Application trip reports

2.E.1
To: Jim Cella, Biff Williams
From: Tim Burnell, John Carpenter, Owen Harblin

Subject: DARPA Test Patch Application to USS Nevada, Silverdale, Washington

cc: Ken Carroll, Judy Stein, Judy Serth-Guzzo, Katy Truby, Jim Resue

Date: 8/26/97-8/28/97

Highlights

Three test foul-release compositions were applied to 100 ft^2 areas on the USS Nevada at the Trident Refit Facility in Silverdale, Washington on August 26-28th, 1997. The compositions consisted of an Amerlock 400 anti-corrosion epoxy, a "mist coat", Silgan J-501, and RTV11® with 10% oil additives. The additives consisted of General Electric Silicones' SF1154 methylphenyl siloxane fluid, DMS-C15, a carbinol terminated poly(dimethylsiloxane), and DBE-224, a dimethylsiloxane-ethylene oxide block copolymer. The test patch utilizing RTV11® plus 10% SF1154 fluid was separated into two areas. One side contained a standard mil P 24441 Type III epoxy while the other half was coated with Amerlock 400. Previous test results have indicated that there may be an adhesion problem with the duplex system when a Type III epoxy is used.

A 3 ft x 3 ft area and a 2 ft x 2 ft area were also tested in an attempt to eliminate the "mist coat" application. On the 3 ft x 3 ft patch, a coat of Amerlock 400 plus 20% SCM501C was applied prior to the application of J-501. The J-501 was applied 2-3 hours later to a tacky epoxy. On the smaller patch, Amerlock 400 with no additive was applied. J-501 was then applied 2-3 hours later to a tacky, but partially cured epoxy. RTV11® + 10% DMS-C15 additive was applied over the J-501 on these patches.

Application of Anti-Corrosive Epoxy

Prior to our arrival at the refit facility, 3 (A,B,C) x 10 ftx10ft (100 ft^2) areas were sandblasted and then coated with a Formula 150 series Type III epoxy. In addition, 2 smaller patches; 4 ft^2 (D) and 2 ft^2 (E) were also blasted and coated with the Type III epoxy. Amerlock 400 FD was applied to the three 100 ft^2 areas. In section A, only half (divided vertically) was coated in an attempt to determine if there is a difference between Type III epoxy and Amerlock 400 FD. Atotal of 5-7 mils (Dry Film Thickness (DFT)) were applied to these areas using a standard airless pump (19:1) with a 417 tip size. On the smaller test patches, D and E, the epoxy was rolled on. Section E contained Amerlock 400 FD (6-8 mils DFT), and D contained Amerlock 400 FD + 20 % SCM501C additive. This additive contains gamma aminopropyl trimethoxy silane (GAP), which is being utilized as an adhesion promoter in this system. The goal with these 2 smaller patches is to test the feasibility of eliminating the "mist coat" currently used in

the duplex coating system. Test patches A, B, and C, were allowed to cure overnight prior to the application of the silicone coatings, while D and E were coated just prior to application of the silicone topcoats.

Duplex Coating over Test Patches A, B, C

Test patches A, B, and C were all prepared similarly with the exception of the additive into RTV11®. The mist coat was prepared by first mixing Epon 828 resin with Versamid 140 cure (55/45) for 15 minutes, then adding 100% butanol and stirring to form an emulsion. This was mixed for 1-1 ½ hours until the emulsion went clear, at which time, the mixture was applied at 1-3 mils (Wet Film Thickness (WFT)) using a standard airless pump (19:1) with a 415 tip.

Approximately 45 minutes after the application of the mist coat, Silgan J-501 was prepared and applied. SF 69 (10%) and naphtha (5%) was added to Silgan J-501 and was mixed by hand. The mixture was then applied over a tacky mist coat at 10-12 mils (WFT) using a 43-1 airless pump with a 515 tip.

Approximately 45 minutes after the application of the tiecoat (Silgan J-501), RTV11® plus 10% additives was applied at 16-20 mils (WFT) using a 74:1 airless pump with a 619 tip (5-10% naphtha was added to aid in spraying). Test patch A was coated with RTV11® + 10% SF1154 silicone oil. Test patch B was coated with RTV11® + 10% DMSC15 (poly(dimethylsiloxane), carbinol terminated). Test patch C was coated with RTV11® + 10% DBE224 ((dimethylsiloxane)-ethylene oxide) block copolymer).

Duplex Coating over Test Patches D, E

Silgan J-510 was applied directly over a tacky epoxy approximately 2 ½ hours after the epoxies were applied to test patches D and E; no mist coat was applied. These were followed a half an hour later with RTV11® + 10% DMSC15 topcoat.

2.E.2

APPLICATION OF GE DUPLEX FOUL RELEASE COATING SYSTEM ON USS NEVADA (SSBN 733)

In August 1998, a duplex foul release coating system, manufactured by General Electric Company, was applied to a test area on the hull of USS NEVADA (SSBN 733) during refit #40. The application was performed at the Trident Refit Facility, Bangor, Washington. The test area is located about mid-ship on the port side and measures about 100 ft^2 (10 ft x 10 ft).

Surface preparation for all test areas consisted of slurry blasting the surface to a near white metal finish (SSPC-SP-10 according to "Standards of Surface Finish" published by the Steel Structures Painting Council). The blast media, consisting of 80% Kleenblast copper slag and 20% Blastox (to encapsulate lead paint), was mixed with water and sprayed at high pressure to abrasively remove paint and leave a profile. Rust-Lick B (ITW Fluid Products Group) rust inhibitor was injected into the blast stream to prevent flash rusting. The complete coating system beginning with the first coat applied to the steel hull is shown in Table 2.E.2.1 below.

Table 2.E.2.1.. Foul-release coating system (August 1998)

Coat	Coating System	Recommended DFT (mils)
1st-4th	MIL-P-24441, Type III	8-16
5th	Mist coat (two components) Epon 828 epoxy resin Miller-Stephenson Chemical Co. Batch number - 02-YHJ-47 Versamid 140 Miller-Stephenson Chemical Co. Batch number - 7M8789	2-3
6th	RTV Silicone Dispersion J501 Wacker Silicones Corp. Lot number - Z6NK-005, with approximately 5% SF69 oil	10-12
Topcoat	RTV11 Silicone Rubber Compound GE Silicones Batch number - HE817, with approximately 10% DMSC15 oil	14-18

Wet and dry bulb temperatures were measured using a sling psychrometer prior to application of all paints. The dew point was calculated from the wet and dry bulb temperatures. Surface temperature was measured using a surface temperature thermometer. The dew points, corresponding surface temperatures, and relative humidities are shown in Table 2.E.2.2 below.

Table 2.E.2.2. Dew points, surface temperatures, and relative humidities.

Date	Time	Coating	Dew Point (^{o}F)	Surface Temperature (^{o}F)	Relative Humidity (%)
11 August	1755	Mil-P-24441, Type III, Formula 151	59	65	73
12 August	1255	Mist Coat	56	74 *	63
"	1400	J501 with 5% SF69	58	64	64
"		RTV11 with 10% DMSC15 oil	60	69	60

*Test area was in direct sunlight.

Table 2.E.2.2 shows that the surface temperature always exceeded the dew point. This means that no moisture was present on the surface during paint application.

The three coats of MIL-P-24441, Type III epoxy were applied by TRF Shop 71A personnel under the direction of Dan Kolda and Kevin Jones, Shop 71A Foremen. All coats were strained after mixing and were applied using airless spray equipment (Graco 45:1 pump, 725 tip, 80-100 psi pressure at the pump). Wet film thickness was measured by the applicator to ensure proper thickness.

In all test areas, all coatings beyond the first three coats of MIL-P-24441, Type III epoxy, were applied by Owen Harblin, a General Electric Co. technical representative. Tim Burnell and Larry Wichelns, General Electric Co. and technical representatives, were also on-site during the application.

Mixing of Epon 828 resin with the Versamid 140 curing agent, performed by General Electric Co. personnel, was a meticulous and time-consuming process. When first mixed, then thinned by 50% with butanol, the solution is milky rather than clear and transparent. It is essential that the solution be clear before application. Frequent mixing and lengthy waiting periods were required for the solution to become clear. For this application, the mixing/waiting period was about 1 hour and 30 minutes. This lengthy procedure would definitely present a problem in a shipyard production environment.

The Epon 828/Versamid 140 mist coat was applied using an electric 30:1 pump and a 315 tip. RTV Silicone Dispersion J501 with about 5% SF69 oil was applied using 43:1 pump with 100 psi pressure at the pump, 50 ft of line with 3/8 in. inside diameter (ID), and a 417 spray tip were used. The RTV11® topcoat with 10% DMSC15 oil was applied using a 74:1 pump with 100 psi pressure at the pump, 50 ft. of line with 1/2 in ID, and a 613 spray tip were used. Application of the RTV11® topcoat with 10% DMSC15 oil was characterized by spray tip clogs. A possible solution for spray tip clogging is a larger tip size or variable orifice size.

Dry film thickness was measured to document final coating thickness. A magnetic DFT gauge, calibrated to 40 mils was used. Table 2.E.2.3, below, shows results of the DFT survey.

Table 2.E.2.3. DFT data

	#Readings (mils)	**Average (mils)**	**Standard Deviation**	**Maximum (mils)**	**Minimum (mils)**
Complete System	100	35.5	4.8	46	26

Table 2.E.2.1, presented earlier in the report, shows the minimum recommended DFT for the total system to be 34 mils. DFT data shows that, on the average, 35.5 mils were applied for the total system.

Personnel from General Electric Co. and NSWCCD inspected the 100 ft^2 test area the day following final coat application. The finished coating system had the appearance of extensive runs. Overall, the coating system was considered to be in good condition and ready for exposure testing.

Panels for adhesion testing and bilge keel panels for real-time shipboard exposure testing were prepared at the same times as coating applications on the submarine hull.

A Standard Coating Application Form, developed to facilitate increased Quality Assurance (QA), was completed.

2.E.3
To: Biff Williams, Jim Cella, Judy Stein
From: Kathryn Truby, Owen Harblin, Tim Burnell, John Carpenter
Date: 3 June 1998

Subject: Trip report on the painting of the FIT fouling-release testing boat

The opportunity to apply the Duplex fouling release coating system to Florida Institute of Technology's (FIT) testing boat came about during discussions at the DARPA review meeting held in Melbourne, Florida at the end of March 1998. The need for an intermediate-scale real-world application became clear, not only for additional evaluation of the fouling release properties of the best-performing topcoat, but also for the ability to evaluate the physical properties of this system in a carefully-controlled environment. Dr. Geoff Swain offered the use of FIT's 21 ft long fiberglass boat to carry out power trials, drag evaluations, hydrodynamic testing, and barnacle adhesion measurements on the coating system.

In addition to using this intermediate-scale application for topcoat performance evaluation, this application opportunity was used to compare the adhesion performance of the mistcoat-containing Duplex system and the new mistcoat-free coating system. The mistcoat elimination formulation that has shown the best adhesion performance in the lab, Amerlock 400 epoxy containing 20 vol% GE SCM501C, was applied in place of the mistcoat on the port side of the hull. The current Duplex system was applied to the starboard side of the hull.

Sandblasting of the boat hull to remove the existing coatings was performed at a marina in Melbourne one week before the GE team arrived for the application. A repair to the fiberglass on the keel just forward of the first block shift repair patch was also done by FIT prior to the arrival of the GE team. The sandblasting pitted the surface of the fiberglass; about 5% of the surface was damaged below the protective gel coat, exposing raw fiberglass. Even though the fiberglass will not corrode on contact with water, there was concern that one-coat coverage of the epoxy anticorrosive paint would not sufficiently fill the pitted surface. Water will cause fiberglass to swell, which could subsequently cause delamination. Therefore, two base coats of unaltered epoxy were applied to the entire hull.

The application took place inside a building owned by FIT that is usually used for storage and the development of alternative-fuel cars. The application conditions and additives for each layer of the coating system are shown in Figure 2.E.3.1. Before the application of each epoxy layer, the entire hull was wiped down with naphtha to remove dust and moisture. The first epoxy base coat, ivory Amerlock 400, was applied on the first day and allowed to cure overnight before application of the second coat, pearl gray Amerlock 400, on the second day.

Table 2.E.3.1 Application formulations and conditions of the Duplex fouling release coating system and mistcoat-free system as applied to the FIT testing boat

Application Layer	Date	Temp. (°F)	RH (%)	WFT (mil)
5 gal Amerlock 400 ivory + 1 pt Ameron #65 solvent	5/26	88	56	22-24
2 gal Amerlock 400 pearl gray + 1 pt Ameron #65 solvent	5/27	77	72	14-16
4 gal Amerlock 400 pearl gray + 1 gal GE SCM501C	5/28	85	67	12-14 (Port side)
½ gal Shell Versamid + ½ gal Shell Epon 828 + 1 gal butanol	5/28	85	67	2-3 (Stbd side)
5 gal Wacker J-501 + 1 gal GE SF69	5/28	85	67	18-20
5 gal GE RTV11 + ½ gal DMSC15 + ½ gal naphtha + 30 ml DBTDL	5/28	85	67	16-20
500 g GE SEA210A + 16 ml GE SCM501C	5/29	85	65	2-3 Brushed
450 ml Wacker J-501 + 50 ml GE SF69	5/29	85	65	16-20 Brushed
3500 ml GE RTV11® + 350 ml DMSC15 + 10 ml DBTDL	5/29	85	65	18-20 Brushed

Insufficient amounts of epoxy were available to complete application of the experimental mistcoat-free system on the morning of the third day, so application did not start until that afternoon when a pearl gray Amerlock 400 was obtained from a local source. A curtain of plastic sheeting was hung along the length of the keel with vinyl tape to allow the spraying of the experimental formulation and mistcoat on the same day. The experimental system, Amerlock 400 containing 20 vol% GE SCM501C, was applied to the port side at about 1:00 pm; after approximately one hour, mixing of the mistcoat was begun (to ensure sufficient cure on the mistcoat-free side). The mistcoat was applied to the starboard side at 2:30 pm; the masking was then carefully removed and mistcoat was rolled along the keel (to an approximate 2-3 mil wet film thickness) so no repair between the two adhesion systems was necessary. Amerlock 400 + 20% SCM501C sprayed very well and had a 2-1/2 hour window for the subsequent application of J-501; the mistcoat was tack-free in twenty minutes and required the immediate application of J-501.

At 3:00 pm, J501 was applied to the entire hull; the first coat across the boat was sprayed to a wet film thickness of 16-18 mils, and a second light coat was applied 20 minutes later to ensure that any pinholes remaining from the fiberglass pitting were well-filled. The inclusion of SF69 in the J501 continues to make J501 easy to spray at high ambient temperatures.

RTV11® was cured with only one tube (30 ml) of dibutyltin dilaurate catalyst to five gallons (a typical application requires 2-3 tubes). The same batch of RTV11® as was shipped for this

application was used to prepare exposure panels before this trip. The RTV11®, which was mixed with two tubes of catalyst, had cured in only 45 minutes and clogged the pump. Discussion with Bob Smith, the product chemist at GE Silicones who developed RTV11®, revealed that as little as ¾ of a tube (~21 ml, 0.1 wt%) of DBTDL will sufficiently cure five gallons of RTV11®. With the dilution of added oil and naphtha, the RTV11® sprayed easily in Melbourne (using a 619 tip and 74:1 air pressure ratio pump), coated the J501 well, and was cured by the next morning. "Gel balls" appeared in the spray for the first five minutes, making coverage uneven, but then the spray smoothed out and produced uniform coverage via two coats across the entire hull. Drips at edges on the hull were smoothed with a roller.

The GE SEA210A/GE SCM501C repair package with J501 and RTV11® was used to repair the block shift patches the next day. Only four small patches needed to be repaired: two at the keel and one on each side, about halfway back, where the boat had rested on supports. Each spot was wiped down with naphtha and brushed with a thin layer of SEA210A/SCM501C. After the silicone was tack-free, J501 was brushed over the areas of epoxy that had had no J501. When the J501 was cured all the way through (not merely skinned over), RTV11® was brushed on and any drips were smoothed.

The coating system was allowed to cure for at least one week before the boat was launched. Although dock damage to the hull coating is not an issue (the boat bumps the dock at a high enough point that the lower hull never makes contact), it has been agreed to occasionally reverse the boat's docking position to avoid fouling bias due to differences in light on either side of the boat. Power trials are expected to take place in September or October 1998.

Many thanks to the FIT team (Geoff, Brett, Ronan, and Bill), who were a terrific help with everything from the masking to obtaining epoxy to handling the chemical waste and packing up the heavy spraying equipment.

2.E.4
To: Biff Williams, Greg Gillette
From: Christina Darkangelo-Wood
Date: 1 February 2000

Subject: Trip report on the application of the GE/Sigma fouling release system

Summary

A 19 ft private vessel anchored at FIT anchorage was chosen as the second small-scale validation/demonstration platform for DARPA sponsored fouling release program. The objective of the application was validation of the adhesion of the fouling release system to the hull prior to the large-scale validation scheduled for fall 2000. The application occurred Jan 17-22 in Melbourne, Florida. The Sigma/GE silicone fouling release coating was applied to the 19' McKee power boat by the GE CRD team (Christina Darkangelo-Wood, Owen Harblin, Judy Stein, with the assistance by a representative from NSWC (Tom Radacovich). In addition, Mike Winter from Sigma Paint was present during application of the epoxy paint. A summary of the application conditions, wet film thickness (WFT) and application parameters are given in Tables 2.E.4.1 and 2.E.4.2. The coating adhesion and performance will be monitored by the owner and our team at FIT over the next few months.

Detailed Summaries

Before arrival of the application team, Tom Hayman (the boat owner) sandblasted the hull to remove the existing coating in preparation for the coating application.

Day 1: Boat Preparation and Sigma primer application.

The boat was hung from a crane and turned over, so that, application was simplified and blocks were not necessary. Sandblasting of the hull had not completely removed all the anti corrosion paint. Spot scraping and hand sanding with course sandpaper removed the remaining antifouling paint. Grit and dust were removed using a stream of compressed air. Areas of the boat which were not scheduled to be painted were protected from overspray by masking. (Figure 2.E.4.1)

Figure 2.E.4.1. The boat prior to application

After masking was complete, the Sigma primer was applied. The metallic green primer was mixed according to the Sigma Tech Sheets (3:1 base to hardener ratio with 5 % Sigma 91-92 solvent) and then applied using airless spray equipment (Figure 2.E.4.2). This layer was allowed to dry overnight.

Figure 2.E.4.2. The boat after application of Sigma primer

Day 2: Application of the Sigma Multiguard and on-site determination of optimum catalyst concentration for the GE topcoat.

Overnight dew formed on the coating; this moisture was wiped off with clean rags and the boat was allowed to air dry before the next layer of coating was applied. The Sigma Multiguard was mixed according to Sigma Tech sheets (3.22 gal of base to 1 gal hardener (mixed whole kit) + 5 % Sigma 91-92 solvent) with assistance from Mike Winter (Sigma staff) on site for the day. The Multiguard was applied with airless spray equipment and allowed to cure over night. The application plan was discussed with Mike Winter who recommended a 24 hour overcoat interval for the tielayer to ensure adhesion of tielayer to epoxy based on data received from Sigma (Europe). Another consideration was the short application window each day. The team decided that one coating per day would be the most prudent plan.

Previous laboratory experiments showed that the bulk curing rate of the topcoat was significantly shorter than the tack free time of thin films. In addition, the tack free time of the topcoat was increased when the topcoat was applied over the Sigma tiecoat relative to application over bare aluminum. The optimum catalyst level in which potlife was maximized and tack free time was minimized was determined at the application site.

A summary of all on site catalyst concentration testing can be found in Table 2.E.4.3.

Figure 2.E.4.3. The boat after application of the Sigma Multiguard

Day 3: Application of Sigma Tielayer and further catalyst testing.

Moisture, which had settled overnight on the boat, was removed and the surface allowed to air dry before application of the tielayer. The tielayer was mixed according to Sigma Tech sheets (93:7 base: hardener (one 5 gal kit was used) + 5 % Sigma 21-20 solvent). The tielayer was applied using a 40:1 airless pump (Figure 4). A tarp was suspended over the boat to protect the coating overnight.

Additional catalyst concentration experiments were performed to determine the appropriate catalyst level to provide a 3-4 hour cure time over Sigma Tielayer with a pot life of 30-40 minutes.

Figure 2.E.4.4. The boat after application of the Sigma tielayer

Day 4: Application of GE topcoat.

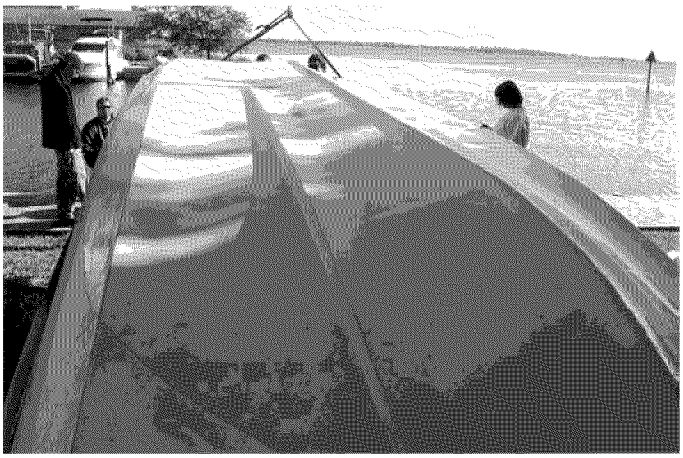
The tarp was removed and the surface was wiped and allowed to dry. The RTV11® formulation and catalyst loading was tested to determine the pot life under the current conditions. The chosen catalyst concentration of 3.4 ounces/5 gallons gave a work window of 30 minutes. Five

gal of RTV11® was mixed with ½ gal of SF1147 oil and 1 gal of naphtha followed by 3.4 ounces of catalyst and mixed for 4-5 minutes. The pump was then primed with naphtha and the coating formulation placed in the feed tank. The coating was applied with a 45: 1 airless pump (Figure 2.E.4.5). The tarp was redeployed over the coating to protect from any rain or debris.

Figure 2.E.4.5. The boat after application of GE RTV11® + SF1147

Day 5: Masking removal.

The tarp was removed and the masking stripped from the boat (Figures 2.E.4.6 and 2.E.4.7). The coating was allowed to cure for 7 days prior to redeployment.



Figures 2.E.4.6. and 2.E.4.7. Complete coating application after the removal of the masking

Table 2.E.4.1. Environmental conditions and wet film thickness for coating layer

	Surface	**Relative**	**Wft**

		Dew Point (°F)	Temp (°F)	Humidity (%)	(mils)
Day 1	Sigma Green Primer	55	74	65	5-6
Day 2	Sigma Red-brown epoxy	57	79	50	5-6
Day 3	Sigma Tiecoat	62	70	90	10-12
Day 4	RTV11®	64	80	81	13-14

Table 2.E.4.2. Airless spray equipment used for each coating layer

		Tip Size (in.)	Pump Ratio	Line Specs (Length; Inside Diameter (ID))
Day 1	Sigma Green Primer	0.019	30:1	50 ft.; 3/8 in. ID
Day 2	Sigma Red-brown epoxy	0.019	30:1	50 ft.; 3/8 in. ID
Day 3	Sigma Tielayer	0.019	40:1	50 ft.; 3/8 in. ID
Day 4	RTV11®	0.017	45:1	50 ft.; 1/2 in. ID

On site testing for the determination of cure speeds of RTV11® topcoat

On 1/18 the Sigma Tielayer was mixed according to tech sheets (93 ml base with 7 ml hardener + 5 ml Sigma 21-20 solvent) and applied to metal coupons with drawdown cards (doctor blades) to a wft of 10-12 mils. The overcoat interval was 2 hours and 24 hours. The cure times of the topcoat were not changed by the difference in the overcoat interval.

Table 2.E.4.3 . Summary of the cure experiments carried out on site

Date	RTV11® ml	SF1147 ml	Naphtha ml	DBTDL catalyst µl	Time to gel min	Tack free over metal	Tack free over tielayer
1/18	50	5	2.5	250	45	2 hr 50 min	5 hr
1/18	50	5	2.5	370	30	2 hr 20 min	4 hr 15 min
1/19	50	5	10	300	40		4 hr 30 min
1/19	50	5	10	370	40		3 hr 30 min
1/20	30	3	6	180	45		

2.E.5

To: Biff Williams, Greg Gillette
From: Christina Darkangelo Wood
Date: 4 August 2000
Subject: Trip report small-scale validation (July 24-28)

Summary

A 24 ft private vessel at FIT anchorage was chosen as a small scale validation/demonstration platform for DARPA sponsored fouling release program. The objective of the application was validation of the adhesion of the fouling release system to the hull prior to the large-scale validation scheduled for fall 2000. The application took place the week of July 24-28 in Melbourne, Florida. The "new" GE silicone fouling release coating was applied to the 24 ft Oldfield power boat by the GE CRD team (Christina Darkangelo Wood, Owen Harblin, Jim Resue) with assistance from a representative from NSWC (Tom Radacovich). A summary of the application conditions, wet film thickness (wft) and application parameters are given in Tables 1 and 2. The boat will be deployed by its owner 7 days after the application of the topcoat. The owner and our team at FIT will monitor the coating adhesion and performance over the next few months.

Detailed Summaries

A GE fouling release coating was applied to this boat in June 2000. The coating adhesion was questionable and it was decided that the team would strip the old coating, blast the surface, and then apply a new coating which would consist of 1 layer of epoxy, the SEA/SCM tiecoat and the RTV11 + 10% SF1147 topcoat

Day 1: Surface Preparation and masking

The boat placed on blocks and supported by a crane. The team pulled off loosely adhering areas of SEA/SCM tiecoat and RTV11 topcoat (Figure 2.E.5.1). The remaining small areas of tightly adhering SEA/SCM tiecoat and RTV11 topcoat were removed by hand scraping and wiping with toluene. The entire hull was then hand wiped with toluene. This was followed by sand blasting with course sand to remove or roughen the topcoat of epoxy paint. Spot hand sanding with 50 grit sandpaper feathered isolated areas of "deeper blasting". The entire underwater hull was then hand wiped with toluene again. The boat was masked, to protect areas that were not being coated, starting at the waterline (Figure 2.E.5.2).

Figure 2.E.5.1. The boat after removal of old coating and masking

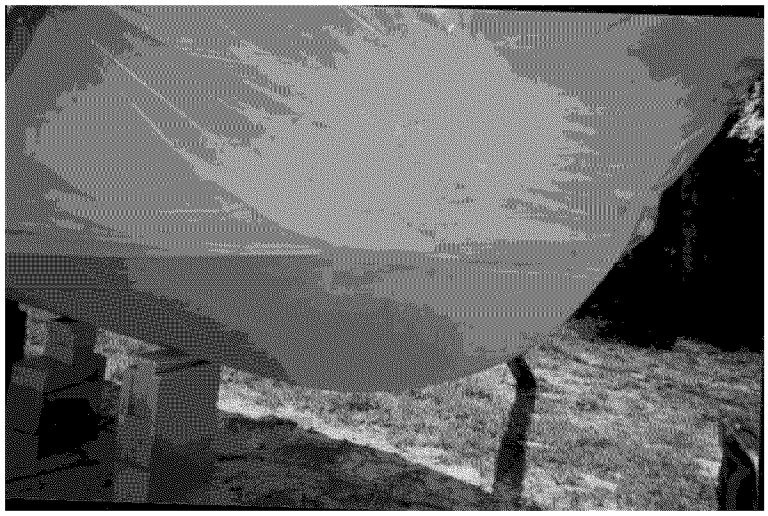


Figure 2.E.5.2. The boat after sand blasting and toluene surface preparation

Day 2: Application of the epoxy layer

The surface of the boat inspected to ensure that the surface was free from moisture. The Amerlock 400FD gray epoxy was mixed according to the Tech Sheets (1:1 base to hardener ratio with 5 % lacquer thinner) and then applied using airless spray equipment (Figure 2.E.5.3). This layer was allowed to dry overnight.

Figure 2.E.5.3. The boat after application of the gray epoxy

Day 3: Application of GE Tiecoat

The surface of the boat inspected to ensure that the surface was free from moisture prior to the application of the next layer of coating. Small-scale mixing tests were performed for the SEA/SCM tiecoat (Table 2.E.5.3). The SEA/SCM tiecoat, was mixed in two batches due to the hot weather and the short pot life of the coating. The tielayer was applied using a 40:1 airless pump (Figure 2.E.5.4). A tarp was strung over the boat after the coating was applied to protect it from the elements (rain). The tiecoat was tackfree in 1 hr.

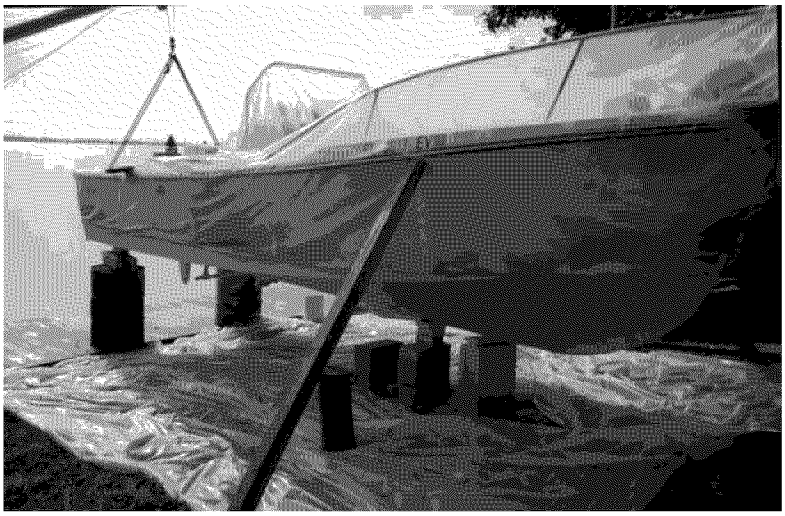


Figure 2.E.5.4. The boat after application of the GE tiecoat

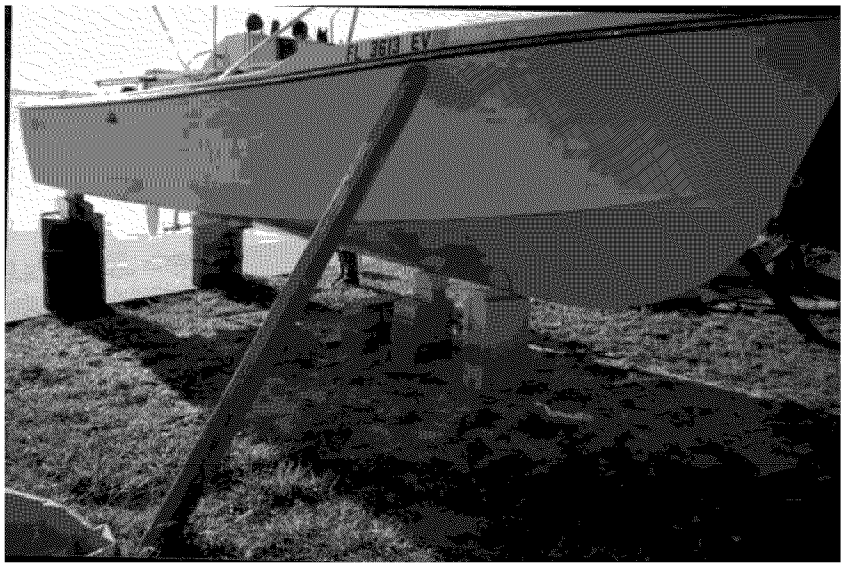
Day 4: Application of GE topcoat

The tarp was removed and the surface of the boat inspected to ensure that the surface was free from moisture prior to the application of the next layer of coating. Small-scale mixing tests were performed to confirm the pot life of the RTV11. The chosen catalyst concentration of 1.7

ounces/4 gallons gave a work window of 60 minutes. 4 gal of RTV11 was mixed with 0.4 gal of SF1147 oil and 0.8 gal of naphtha followed by 1.7 ounces of catalyst and mixed for 4-5 minutes. The pump was then primed with naphtha and the coating formulation filtered and poured into the feed tank. The coating was applied with a 74: 1 airless pump.

Day 5: Masking removal

The masking was removed from the boat. No block shifts were done on this boat (Figure 2.E.5.5). The coating was allowed to cure for 7 days and then the boat will be deployed and the adhesion and coating performance will be monitored by the owner and personnel at FIT.



Figures 2.E.5.5. Complete coating application after the removal of the masking

Table 2.E.5.1. Environmental conditions and wet film thickness for coating layer

		Dew Point (°F)	Surface Temp (°F)	Relative Humidity (%)	Wft (mils)
Day 2	Amerlock 400 (gray)	81	94 / 88*	87	10-12
Day 3	SEA/SCM Tie Coat	78	91 / 88*	85	16-18
Day 4	RTV-11 + 10% SF1147	75	93 / 80*	89	16-18

* - The first temperature is for sunny surfaces. The second is for surfaces in the shade.

Table 2.E.5.2 Airless spray equipment used for each coating layer

		Tip Size (in.)	Pump Ratio	Line Specs (Length; Inside Diameter (ID))
Day 2	Amerlock 400 (gray)	0.019	30:1	50 ft.; 3/8 in. ID
Day 3	SEA/SCM Tie coat	0.021	40:1	50 ft.; 3/8 in. ID
Day 4	RTV-11 + 10% SF1147	0.017	74:1	50 ft; 1/2 in. ID + 6 ft; 3/8 in. ID (whip)

Table 2.E.5.3. Pot life of SEA/SCM tiecoat

	Retarder %	Pot life (min)	Temp ^{o}F	Humidity (%RH)
Sample 1	20	35	90	89
Sample 2	25	40	90	89

2.E.6
From: Christina Darkangelo Wood
Date: 3 September 2001

Subject: Trip report full scale application of repair and recoat package (July 30-Aug 1)

Summary
A 19 ft T-Craft operated by Geoff Swain's group at FIT was chosen as a demonstration platform for the GE repair and recoat package. The objective of the application was demonstrate the use of the repair and recoat package over an older fouling release coating. The T-Craft had been coated with the GE/NRL duplex system with RTV11® + DMSC15 topcoat in 1998. The repair and recoat application took place July 30-Aug 1, 2001 in Melbourne, Florida. The boat was deployed 5 days after the application of the topcoat. The team at FIT will monitor the coating adhesion and performance over the next few months.

Detailed Summaries

A GE fouling release coating was applied to this boat in June 1998. This coating performed well, however there has been some decrease in the topcoat performance. This platform allowed us to validate the recoat and repair package and applied the GE downselected topcoat. The coating that was applied over the existing coating consisted of the SEA210A/SCM501C repair and recoat (tiecoat) and the RTV11® + 10% SF1147 topcoat. Three days prior to the application the boat was removed from the water and pressure washed.

Day 1: Surface preparation, masking, and application of repair and recoat package.

The boat placed on blocks and the waterline masked. The older coating showed some cuts to the epoxy, fish bites, and J501 however 95% of the topcoat was still intact (Figure 2.E.6.1). Next, the old coating was wiped with V M & P Naphtha to further clean the surface. The repair and recoat package was mixed. SEA210A was combined with 20% by weight Sherwin Williams Retarder thinner and 15% by weight V M & P Naphtha. The V M & P Naphtha was colored with solvent blue pigment to enhance the contrast and ensure good coverage. SCM501C at 3% by weight was added to the SEA210 after the solvents had been incorporated. The final mixture was applied to the boat using standard paint rollers with ¼" nap (Figure 2.E.6.2). The wet film thickness of this layer was 8-12 mils.

Figure 2.E.6.1. The boat prior to the application of the repair and recoat system.

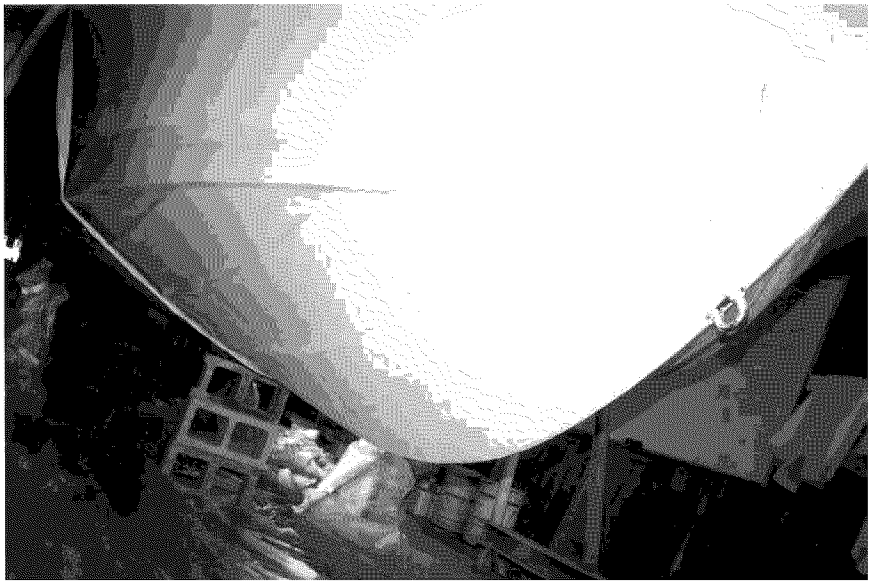


Figure 2.E.6.2. The boat after the application of the repair and recoat package

Day 2: Application of the topcoat.

The surface of the boat inspected to ensure that the repair and recoat package had cured overnight. The RTV11® was mixed with 10% by volume of SF1147 oil and 5% by volume V M & P Naphtha followed by 0.5% by volume. The coating was applied with standard paint rollers with ¼" nap (Figure 2.E.6.3). The wet film thickness of the topcoat was 10-12 mils.

Figure 2.E.6.3. Application of the topcoat

Day 3: Block shifts.

The boat was shifted on the blocks allowing for the coating under the blocks to be recoated. The repair and recoat was prepared as described above and applied using 2" brushes. The coating was allowed to cure until it was tackfree (1 hr and 30 min). Then the topcoat was mixed as described above and applied with a brush. The boat was then placed back on the trailer and will be allowed to cure for 5 days before being deployed.

Figure 2.E.6.4. Complete coating application

Appendix 2.F Reports from hydrodynamic boat trails

CCBC-99-GE-TCRAFT-1 March 1999

The performance of the 21 foot T-Craft coated with GE RTV11 + DMSC15 and DBTDL fouling-release bottom coat.

Exposure Period: June 1998 to February 1999

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Executive Summary

In May 1998, the 22 ft T-Craft power boat (operated by the Center for Corrosion and Biofouling Control, Florida Institute of Technology) was coated with the General Electric RTV11® + 10% DMSC15 oil Duplex fouling release coating. The boat was placed in the water on 15 June of 1998, and monitored for biofouling and powering efficiency.

The coating performed very well. The fouling communities which developed on this coating were much reduced when compared to normal non-toxic surfaces. Slime fouling was fairly heavy around the waterline and would require regular cleaning with a brush to keep clean. Most of the marine growth became detached when the boat reached high speeds (28 knots).

Performance penalties due to fouling were measured during the powering trials. The maximum percent increase in propeller rpm (compared to the clean hull condition) measured due to fouling was about 14%. This was reduced to less than 6% after the boat had run for a short period at high speed and self cleaned.

Cleaning and maintenance of the boat hull were extremely easy, with all forms of fouling being easily removed by a light brush. The overall physical condition of the coating was excellent, however, the coating had received some cuts in the bow area during launching and retrieval with the boat trailer.

Acknowledgments

We would like to acknowledge the support of General Electric and the Defense Advanced Research Agency for their support of this work. We would offer especial thanks to Kathryn Truby, Owen Harblin, Tim Burnell, and John Carpenter who came to Florida and provided such an excellent coating for our boat.

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1.0 Background

The Center for Corrosion and Biofouling Control at the Florida Institute of Technology (FIT) uses a 22' T-Craft power boat for its operations in the Indian River Lagoon, Florida (Figure 2.F.1.1.1). In March 1998, it was decided to use this vessel as a test platform for the RTV11 + 10% DMSC15 oil fouling-release coating developed by General Electric (GE). The boat was removed from the water in May 1998 and the hull sand blasted to remove the existing copper based antifouling system. The boat was washed and moved under cover where a team from GE applied the fouling release coating according to the specification shown in Table 2.F.1.1.1. The coating was applied between 26 to 28 May 1998. The coating was allowed to cure and the boat launched 15 June 1998.

Figure 2.F.1.1.1 22 T-Craft with GE fouling-release bottom coat.

The fouling release performance of this coating had been evaluated at the Florida Institute of Technology Static Immersion Site and the hard fouling adhesion properties are shown in Table 2.F.1.1.2.

Table 2.F.1.1.1 Coating specifications for the T-craft

Application Layer	Date	Temp. (°F)	RH (%)	WFT (mil)
Barrier Coats				
5 gal Amerlock 400 ivory + 1 pt naphtha	5/26	88	56	22-24
2 gal Amerlock 400 pearl gray + 1 pt naphtha	5/27	77	72	14-16
Mist Coats (port and starboard side were different)				
4 gal Amerlock 400 pearl gray + 1 gal GE SCM501C (port side)	5/28	85	67	12-14 (port)
½ gal Shell Versamid + ½ gal Shell Epon 828 + 1 gal butanol (starboard side)	5/28	85	67	2-3 (stbd)
Tie Coat				
5 gal Wacker J-501 + 1 gal GE SF69	5/28	85	67	18-20
Fouling – Release Coat				
5 gal GE RTV11® + ½ gal DMSC15 + ½ gal naphtha + 30 ml DBTDL	5/28	85	67	16-20
Patch Coats				
500 g GE SEA210A + 6 ml GE SCM501C	5/29	85	65	2-3
450 ml Wacker J-501 + 50 ml GE SF69	5/29	85	65	16-20
3500 ml GE RTV11® + 350 ml DMSC15 + 10 ml DBTDL	5/29	85	65	18-20

Table 2.F.1.1.2Hard fouling adhesion data obtained from panels immersed at the FIT static immersion site.

Organism	Average (psi)	SD (psi)	n
Balanus eburneus	3.53	2.43	87
Hydroides sp.	22.93	8.36	52
Oyster	13.78	3.49	43

2.0 Instrumentation

The boat was instrumented to measure speed over the ground, speed through the water, engine revolutions per minute (rpm), and engine fuel consumption in gallons per minute (gpm) using the instrumentation shown in Table 2.F.1.2.1.

Table 2.F.1.2.1 Instrumentation for power trials.

Data	Item	Model #
Speed over the ground	Garmin GPS III	403850
Speed through the water	West Marine Speed 100 Speed/Log/Temp	266827
Engine rpm and fuel consumption	FloScan Series 8000 Fuel Computer	8000-264-1P

3.0 Method

The following procedure was used to assess the skin friction and fouling release properties of the coating. Power trials were only performed on days when the wind speed was less than 5 knots.

- Fill fuel tanks to capacity.
- Motor at less than 4 knots to power trial area (less than two miles).
- Perform underwater video inspection of hull.
- Run power trials, starting at about 2 knots. Maintain speed for 2 minutes. Monitor speed, rpm and gpm. Increase speed and repeat data collection up to speeds of about 25 knots.
- Run the boat at top speed (about 28 knots) for 10 minutes.
- Perform underwater video inspection of hull.
- Run power trials, starting at about 2 knots. Maintain speed for 2 minutes. Monitor speed, rpm and gpm. Increase speed and repeat data collection up to speeds of about 25 knots.
- Analyze the video data to estimate biofouling cover.
- Analyze the boat power data to estimate drag.

4.0 Boat Operating History

The boat is used for regular research activities in the Indian River Lagoon. Table 2.F.1.4.1 summarizes the operating schedule over the past 6 months.

Table 2.F.1.4.1 Boat operating schedule since GE coating application

Date	Activity
6/15/98	Boat launched.
6/23/98	Hull cleaned and first power trial.
6/25/98	Foil testing, run for 4 hours (0 to 25 knots).
7/1/98	Foil testing, run for 4 hours (0 to 25 knots).
7/2/98	Panel inspection and cage maintenance. 1 hour (20 knots).
7/9/98	Out of water inspection of boat.
7/17/98	Power trials.
8/4/98	Foil testing, run for 4 hours (0 to 25 knots).
8/7/98	Foil testing, run for 4 hours (0 to 25 knots).
8/22/98	Attempted power trials, postponed due to weather.
9/1/98	Attempted power trials, camera flooded.
9/10/98	Attempted power trials, postponed due to weather.
10/9/98	Inspection and cage maintenance. 1 hour (20 knots).
10/30/98	Power trials and platform maintenance.
11/20/98	Panel inspection and cage maintenance. 1 hour (20 knots).
11/23/98	Boat maintenance. 20 minutes (25 knots).
12/22/98	Panel, boat and cage inspection. 1 hour (20 knots).
12/23/98	Take boat out of water for outboard service.
1/13/99	Return boat to water.
1/29/99	Inspection and cage maintenance. 1 hour (20 knots).
2/18/98	Remove boat from water for hull modifications to improve foil data collection.

5.0 Boat Powering and Biofouling Data

There have been three successful power trials since the GE fouling release coating was applied at the end of May 1998. These are as follows:

- 23 June 1998, clean hull baseline power data.
- 17 July 1998, fouled hull and hydrodynamically self cleaned hull power data.
- 30 October 1998, fouled hull and hydrodynamically self cleaned hull power data.

Boat powering data are presented as propeller revolutions per minute (rpm) versus boat speed (knots). The data obtained for the 23 June clean hull run was used as the baseline from which to compare the performance of the hull in the fouled and hydrodynamically self cleaned conditions. Third order polynomials were run on the rpm vs. boat speed curves. From the curve fit equations the performance data are presented as percentage change in rpm from the clean hull condition. Because the boat is a planing hull, there will rarely be an exact match of rpm and boat speed, however, the data clearly show differences in performance due to biofouling.

The biofouling data were obtained by analyzing the underwater videos of the boat hull. The videos were taken in combination with a measuring tape and so the exact location on the hull was known. The video was made along the length of the hull for each of the four chines per side and the water line. Biofouling was assessed for every one-foot length of hull. The light and heavy slime films were assessed as percent cover. The final figures represent the average percent cover of the hull surface. The barnacle and tubeworm cover were assessed by estimating the number of individuals present. The final data are presented as estimated total numbers of individuals at each foot along the hull. It must be emphasized that the biofouling data are estimates and not exact numbers.

5.1 23 June 1998

On 23 June 1998, the hull was totally cleaned, and a baseline power trial run. The power curve is shown in Figure 2.F.1.5.1 and provides the baseline from which further power trials are compared.

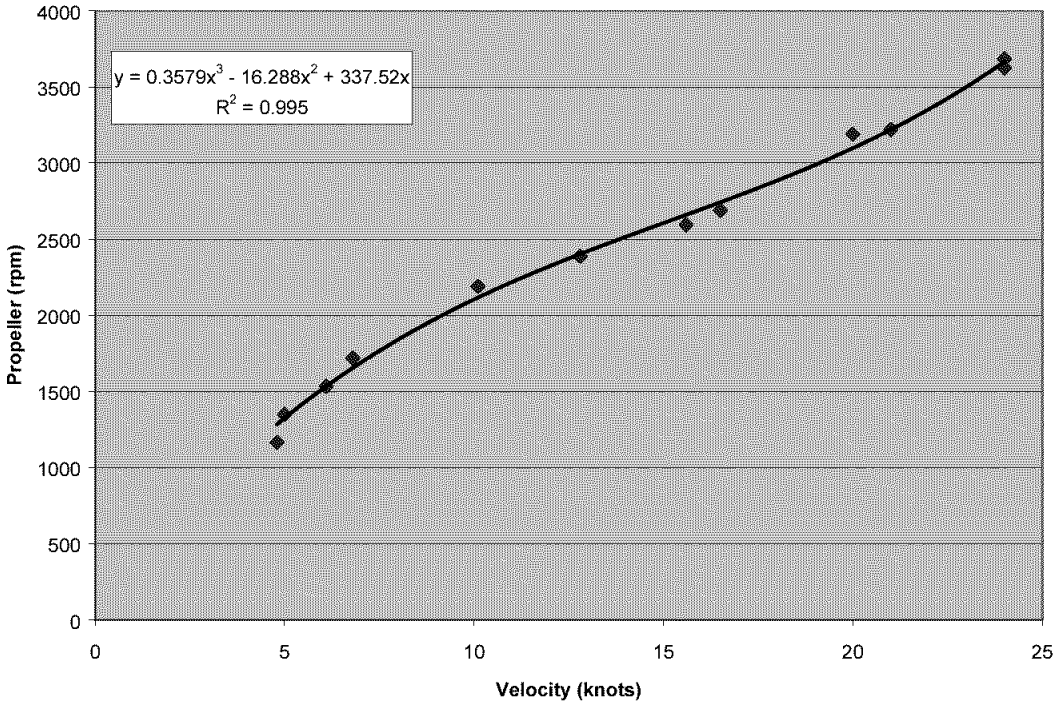

Figure 2.F.1.5.1 Power data (23 June 1998)

5.2 17 July 1998

On 17 July 1998, the first power trial was run with a lightly fouled hull (Figures 2.F.1.5.2 and 2.F.1.5.3). The fouling consisted of light and heavy slime films, tubeworms and a few barnacles (Figures 2.F1.5.4 to 2.F1.5.11). The biofilms resulted in an increase in drag. After running the boat at 28 knots for 10 minutes, most of the fouling had been removed by hydrodynamic forces and the power required for propulsion returned to that of the clean boat.

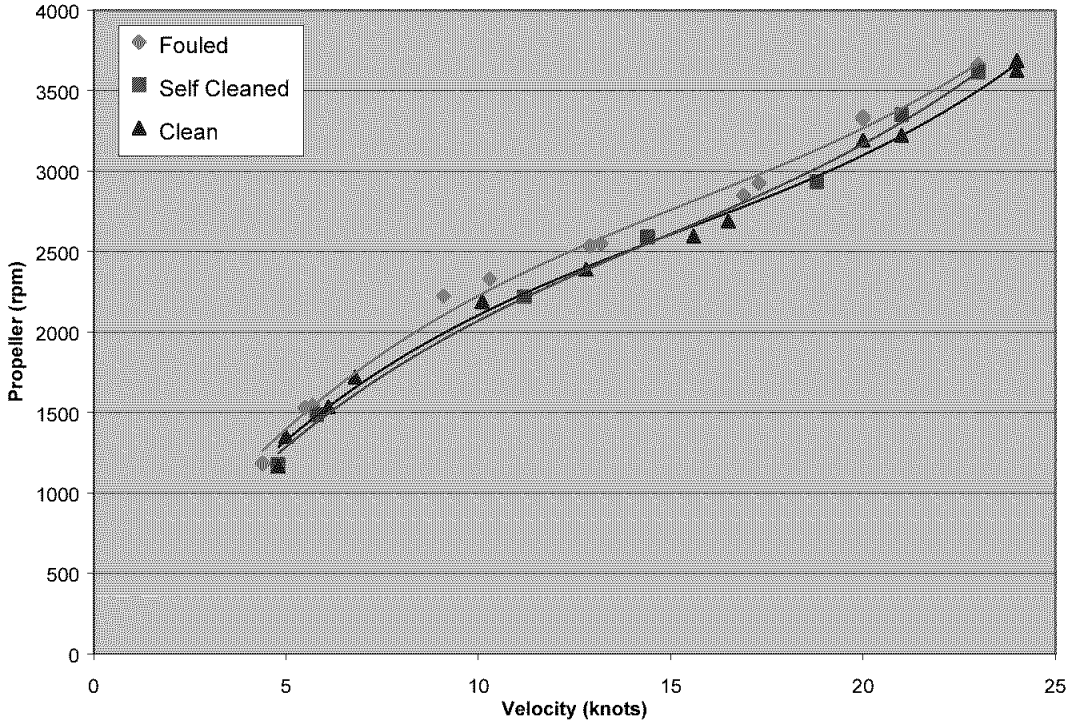

Figure 2.F.1.5.2 Power data (17 July 1998).

Table 2.F.1.5.1 Third order polynomial regression data

Hull Condition	3rd Order Polynomial Regression	R^2
Fouled	$y = 0.3598x^3 - 16.712x^2 + 353.71x$	0.9944
Self Cleaned	$y = 0.3455x^3 - 15.226x^2 + 324.67x$	0.9964
Clean	$y = 0.3579x^3 - 16.288x^2 + 337.52x$	0.995

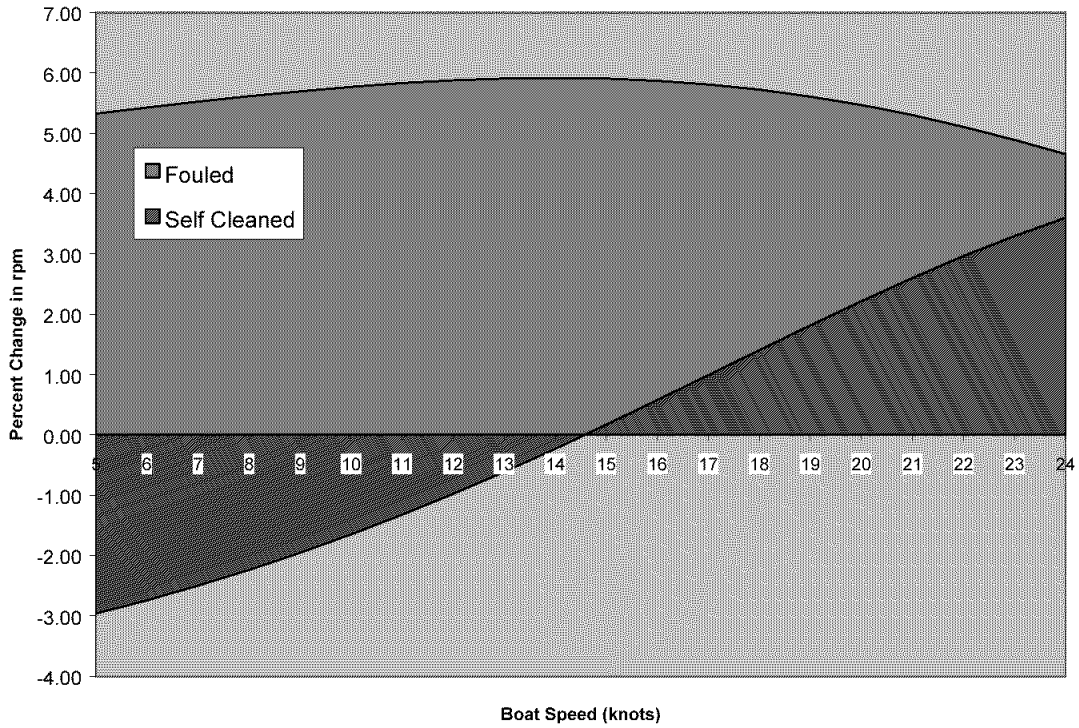

Figure 2.F.1.5.3 Percent change in rpm from the clean hull condition.

The biofouling communities that had become established on the hull were mainly comprised of light slime films with some heavier slime films near the waterline. Both these showed a greater than 50% reduction after the boat had run at 28 knots for ten minutes. There were small numbers of both tubeworms and barnacles. Tubeworms were only observed on the underwater areas of the hull and only a few were removed by high speed water velocity. This would correlate to the relatively high adhesion strengths of these organisms to the hull. Barnacles were fewer in number than the tubeworms. In the fully submerged areas, there was evidence for hydrodynamic removal of barnacles. Hydrodynamic removal of barnacles towards the stern in the waterline areas was less effective.

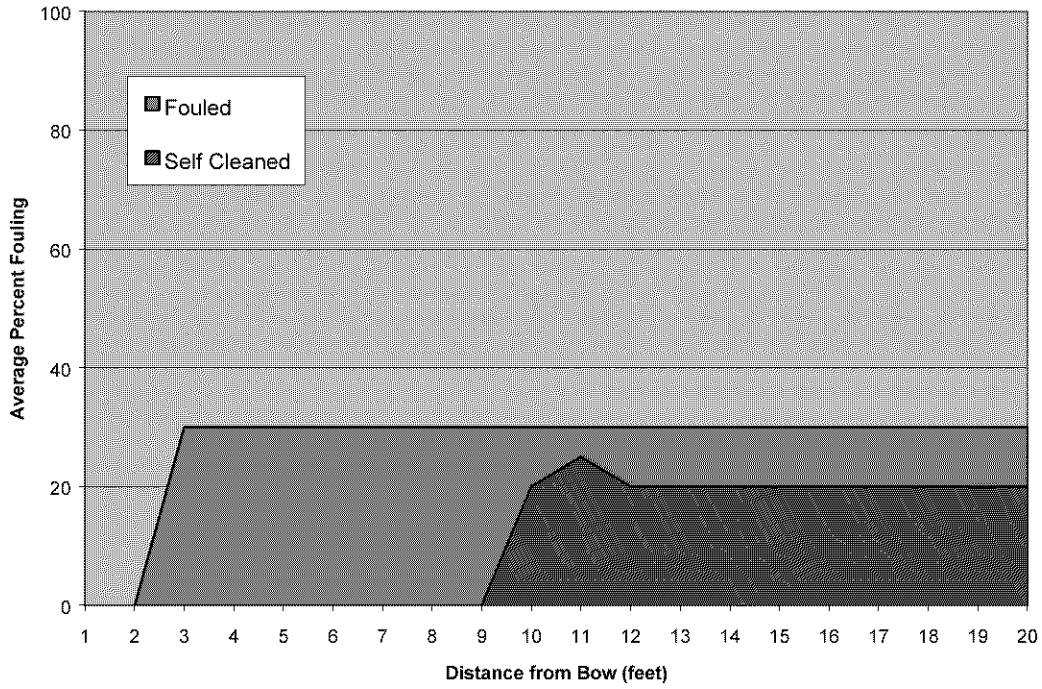

Figure 2.F.1.5.4 Light slime film fouling, waterline (17 July 1998).

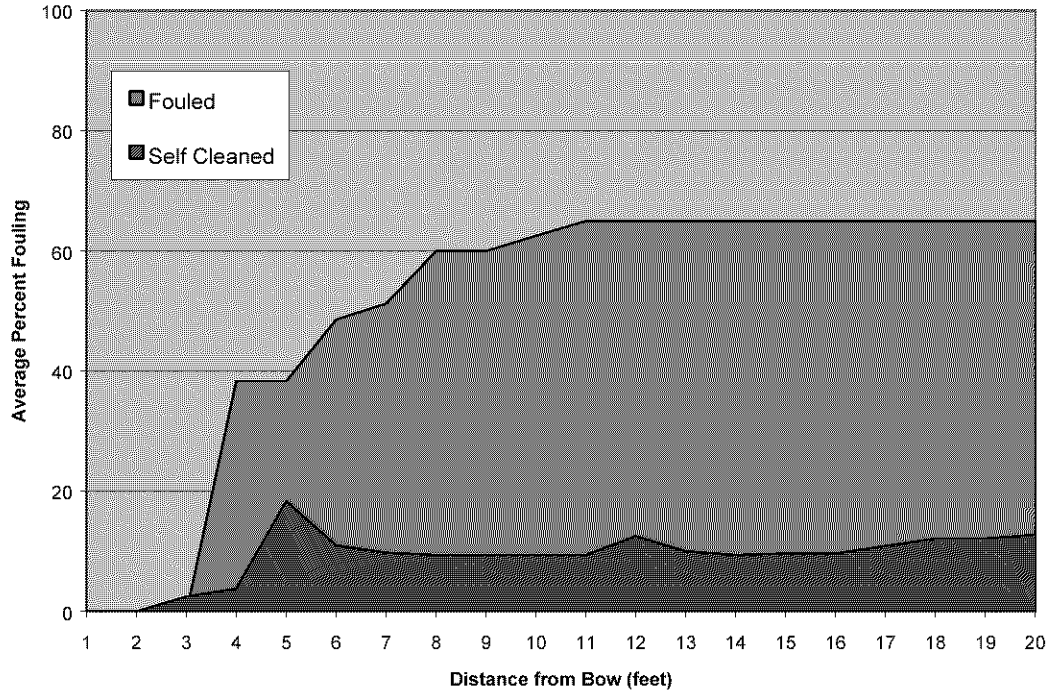

Figure 2.F.1.5.5 Light slime film fouling, underwater areas (17 July 1998).

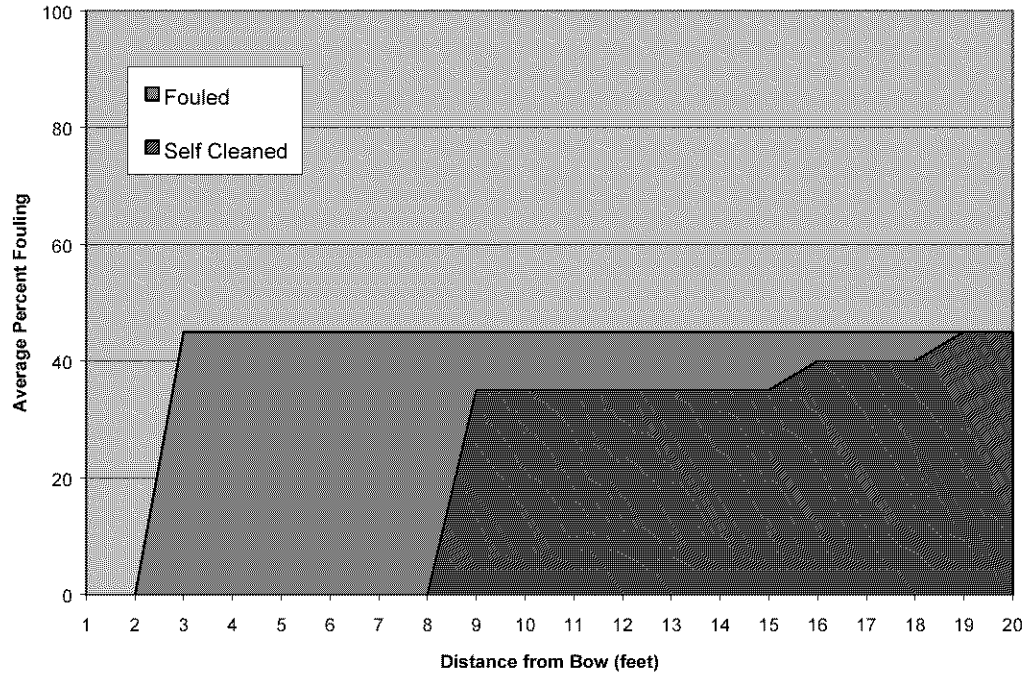

Figure 2.F.1.5.6 Heavy slime film fouling, waterline (17 July 1998).

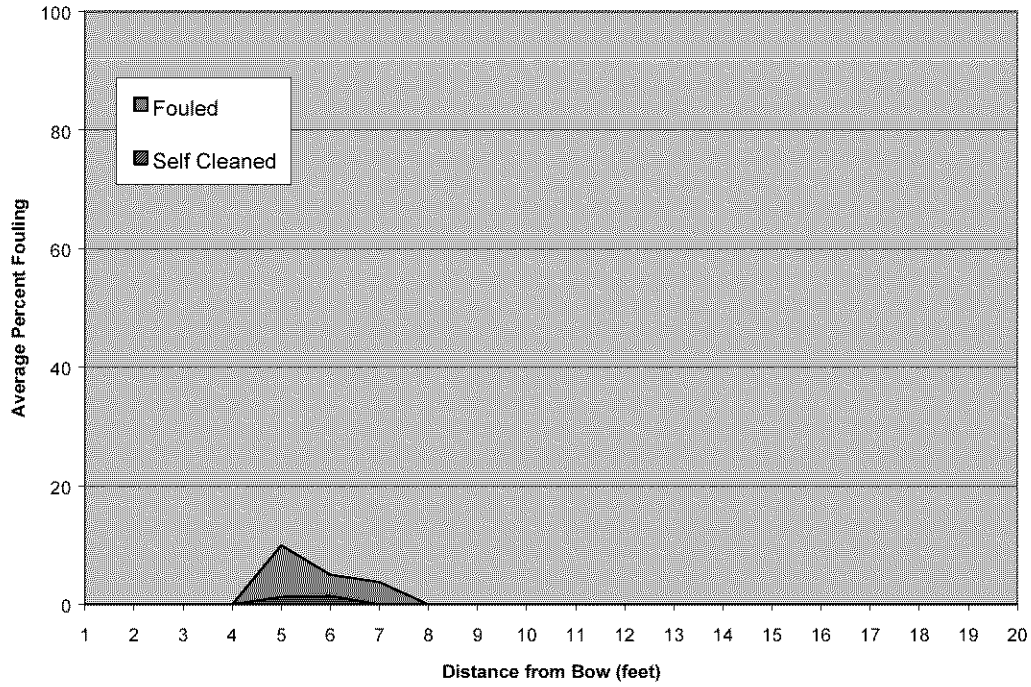

Figure 2.F.1.5.7 Heavy slime film fouling, underwater areas (17 July 1998).

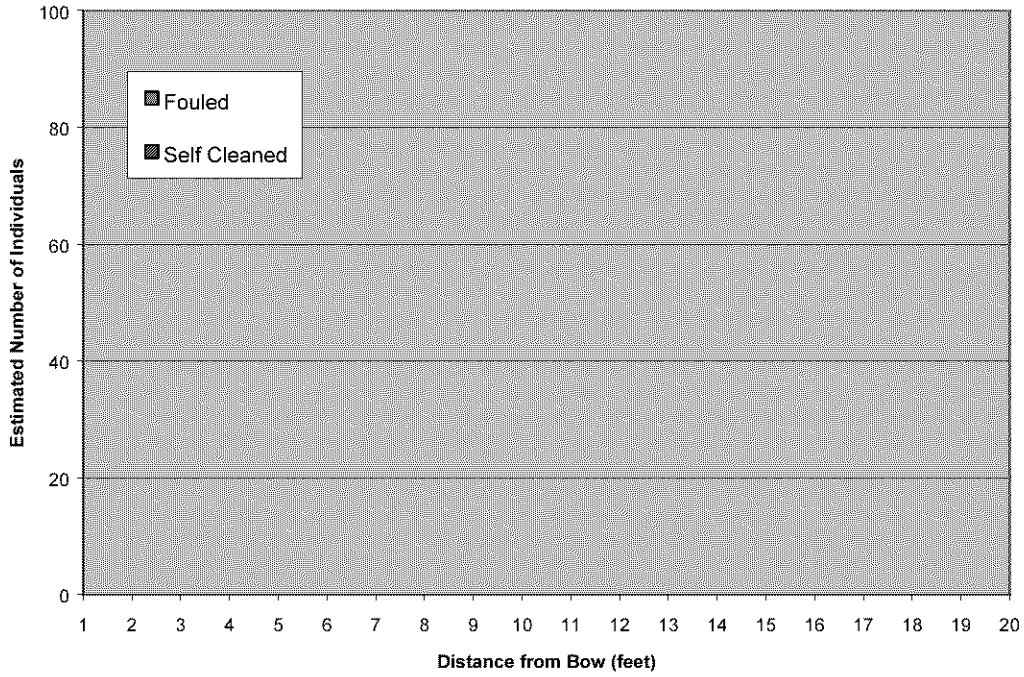

Figure 2.F.1.5.8 Tubeworm fouling, waterline (17 July 1998).

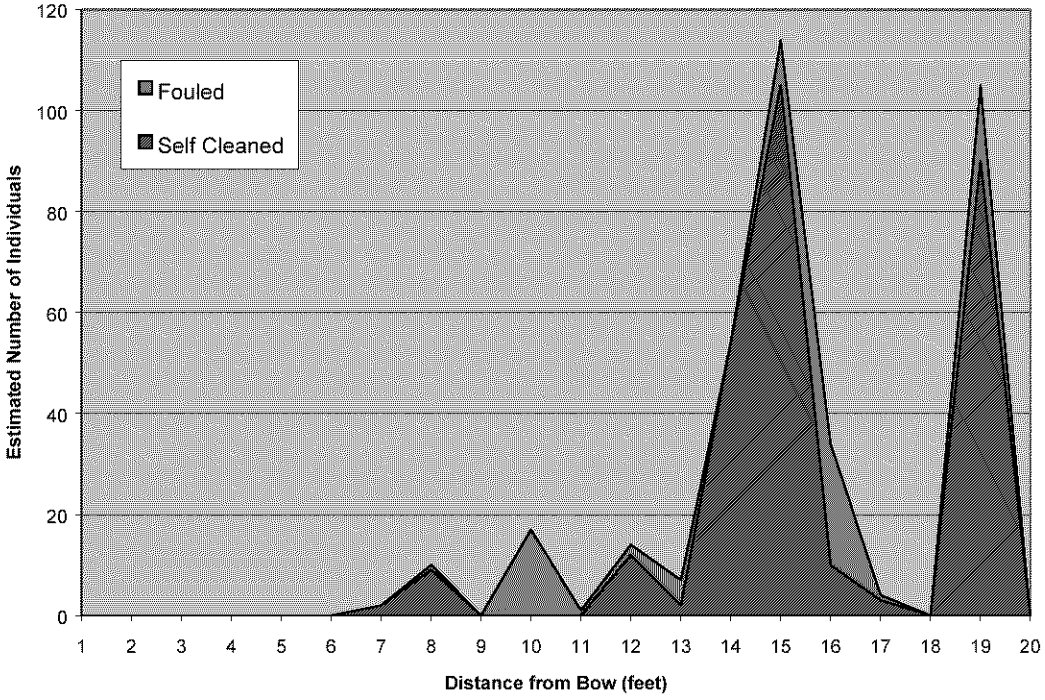

Figure 2.F.1.5.9 Tubeworm fouling, underwater areas (17 July 1998).

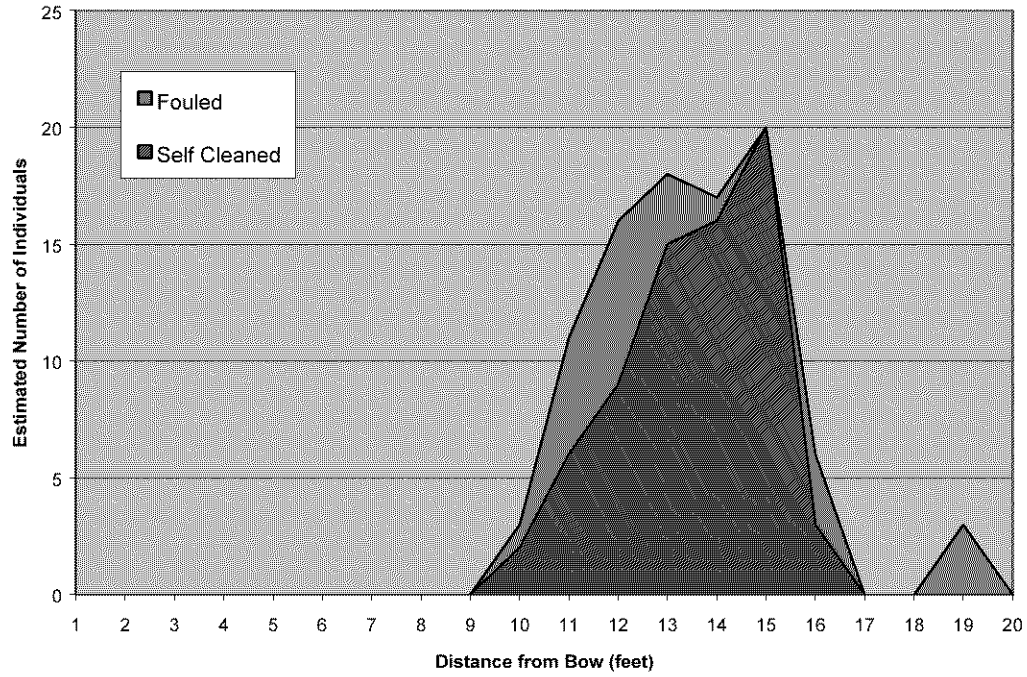

Figure 2.F.1.5.10 Barnacle fouling, waterline (July 1998).

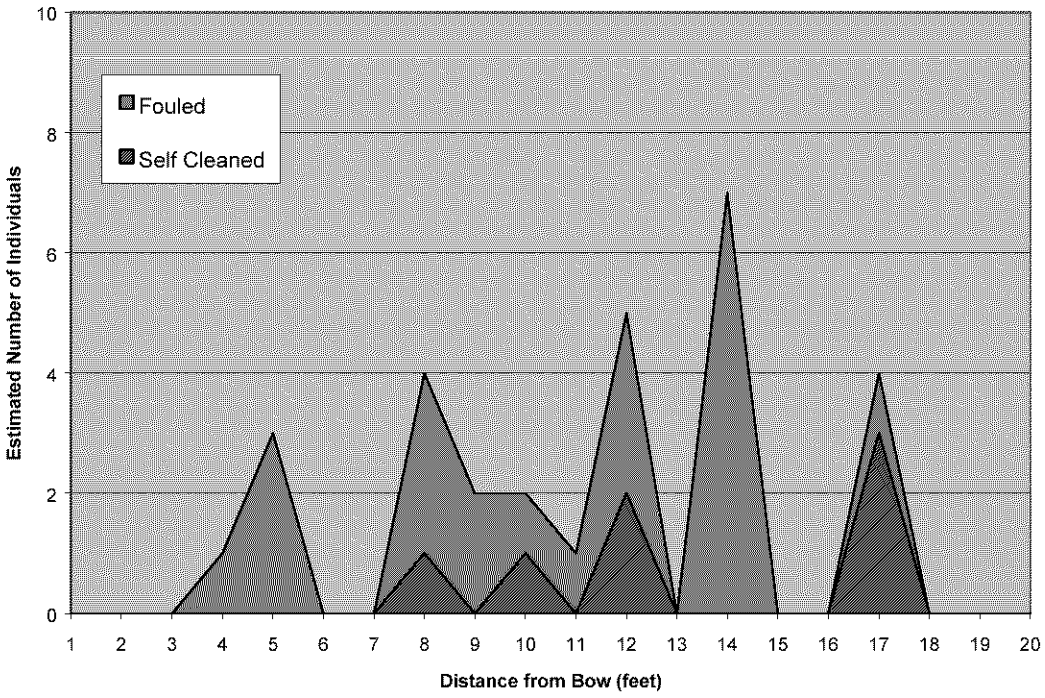

Figure 2.F.1.5.11 Barnacle fouling, underwater areas (July 1998).

5.2 30 October 1998

On 30 October 1998, a second power trial was run (Figures 2.F.1.5.8 and 2.F.1.5.9). The hull was more heavily fouled than the July power trials (Figures 2.F.1.5.12 to 2.F.1.5.21). The fouling consisted of light and heavy slime films, tubeworms and a few barnacles. The biofilms resulted in an increase in drag. After running the boat at 28 knots for 10 minutes some of the fouling had been removed by hydrodynamic forces. However, the power required for propulsion did not return to that of the clean boat, and a penalty due to biofouling remained.

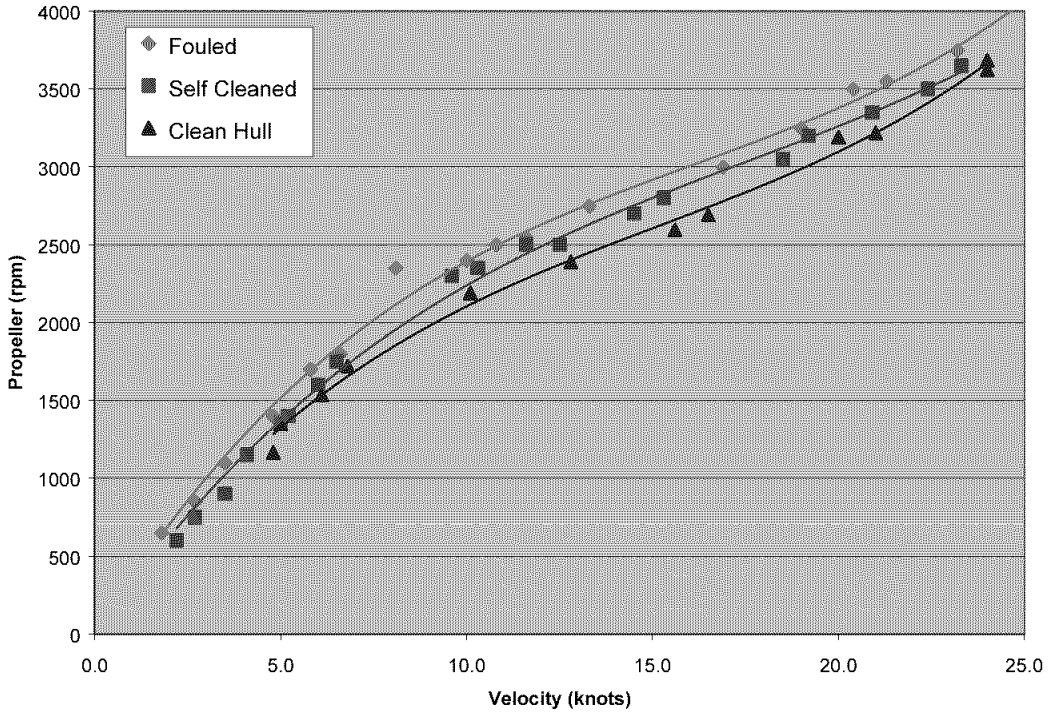

Figure 2.F.1.5.12 Powering data (30 October 1998).

Table 2.F.1.5.2 Third order polynomial regression data

Hull Condition	3rd Order Polynomial Regression	R^2
Fouled	$y = 0.3853x^3 - 18.599x^2 + 386.85x$	0.9941
Self Cleaned	$y = 0.2706x^3 - 14.197x^2 + 338.77x$	0.996
Clean	$y = 0.3579x^3 - 16.288x^2 + 337.52x$	0.995

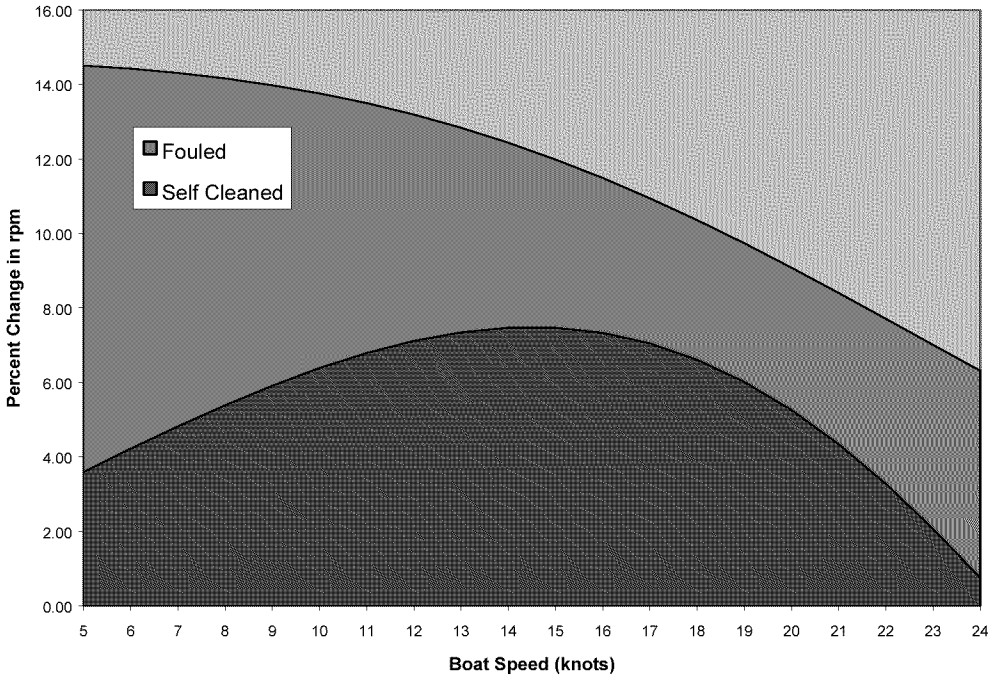

Figure 2.F.1.5.13 Percent change in rpm from the clean hull condition.

The biofouling communities that had become established on the hull by October were mainly comprised of light and heavy slime films, with an increase in the number of tubeworms plus a few barnacles. There was a reduction in slime film cover after the boat had run at 28 knots for ten minutes. The increase in light slime film, shown at the waterline (Figure 2.F.1.5.14), was due to the heavy slime film (Figure 2.F.1.5.16) being cleaned back to a light cover. Both the tubeworms and barnacles were partially removed by high- speed water velocity. Hydrodynamic removal of hard fouling towards the stern in the waterline areas was less effective.

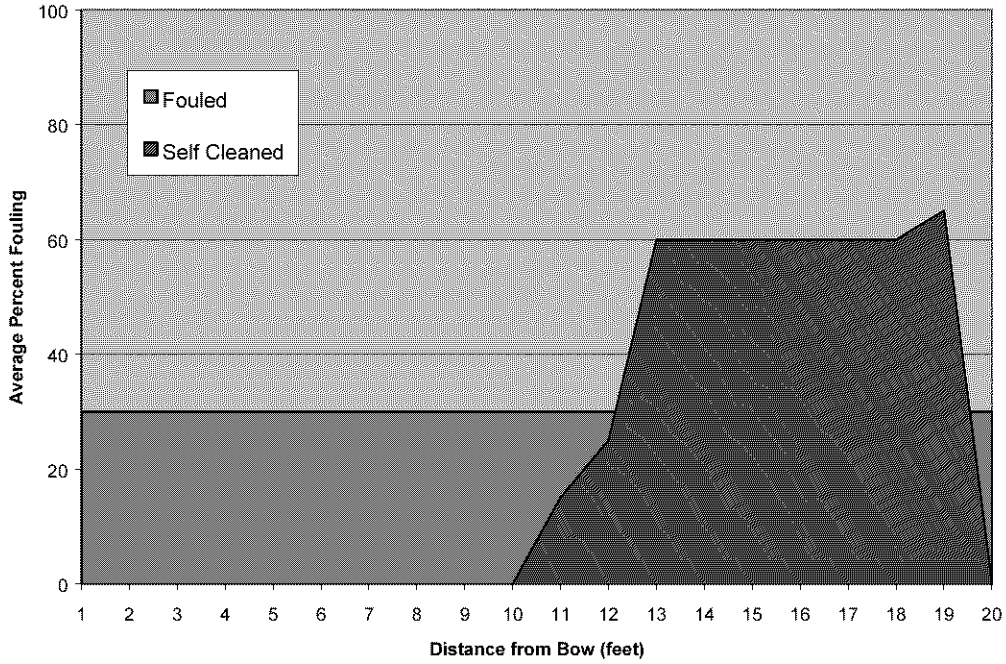

Figure 2.F.1.5.14 Light slime film fouling, waterline (30 October 1998).

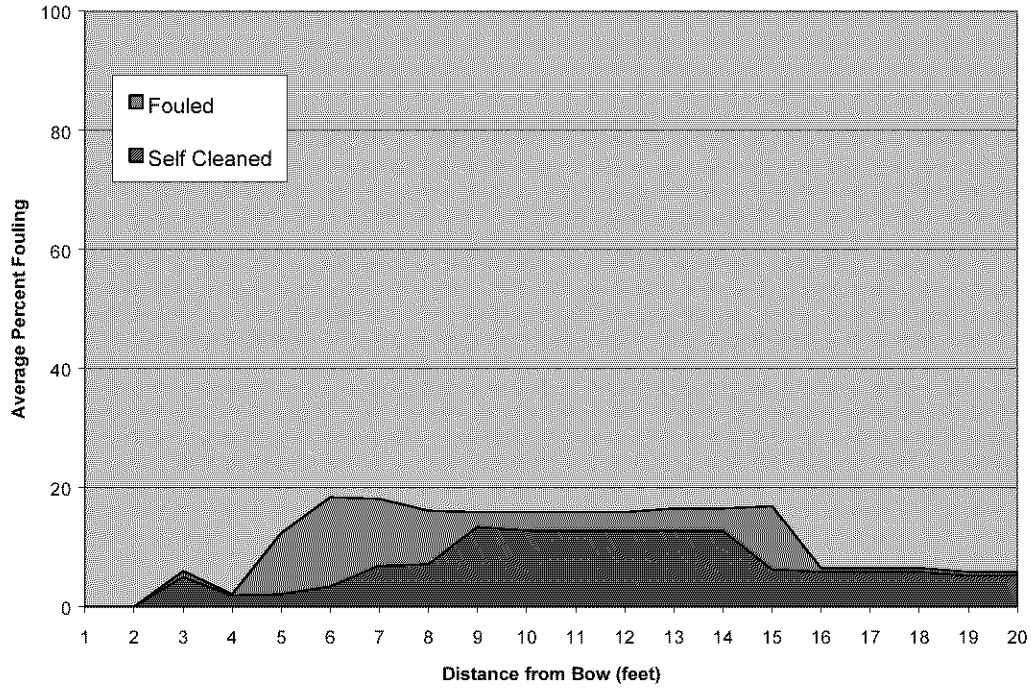

Figure 2.F.1.5.15 Light slime film fouling, underwater areas (30 October 1998).

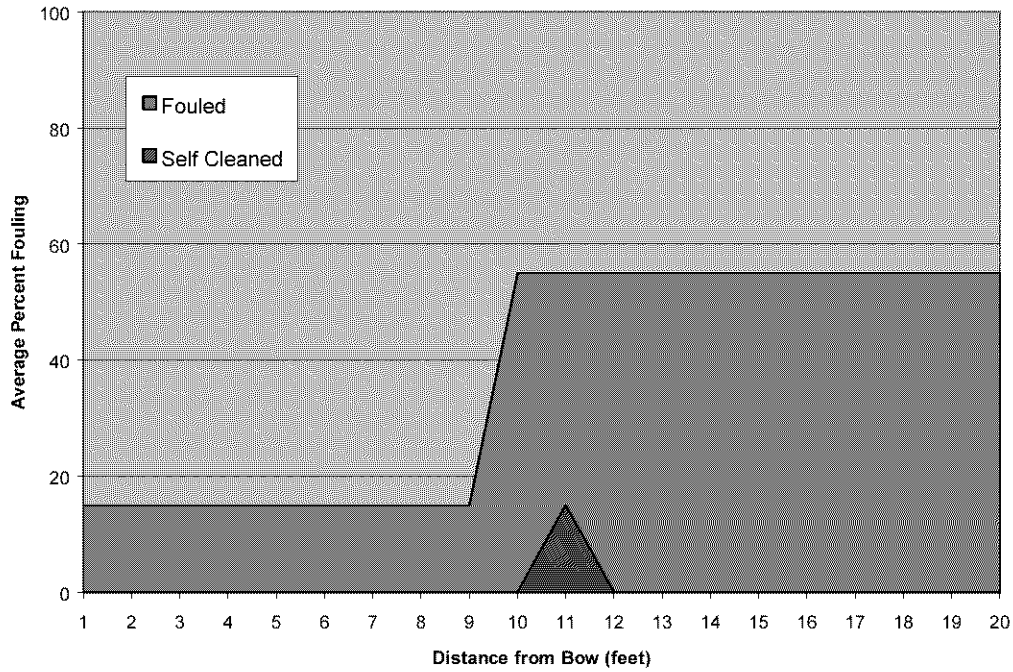

Figure 2.F.1.5.16 Heavy slime film fouling, waterline (30 October 1998).

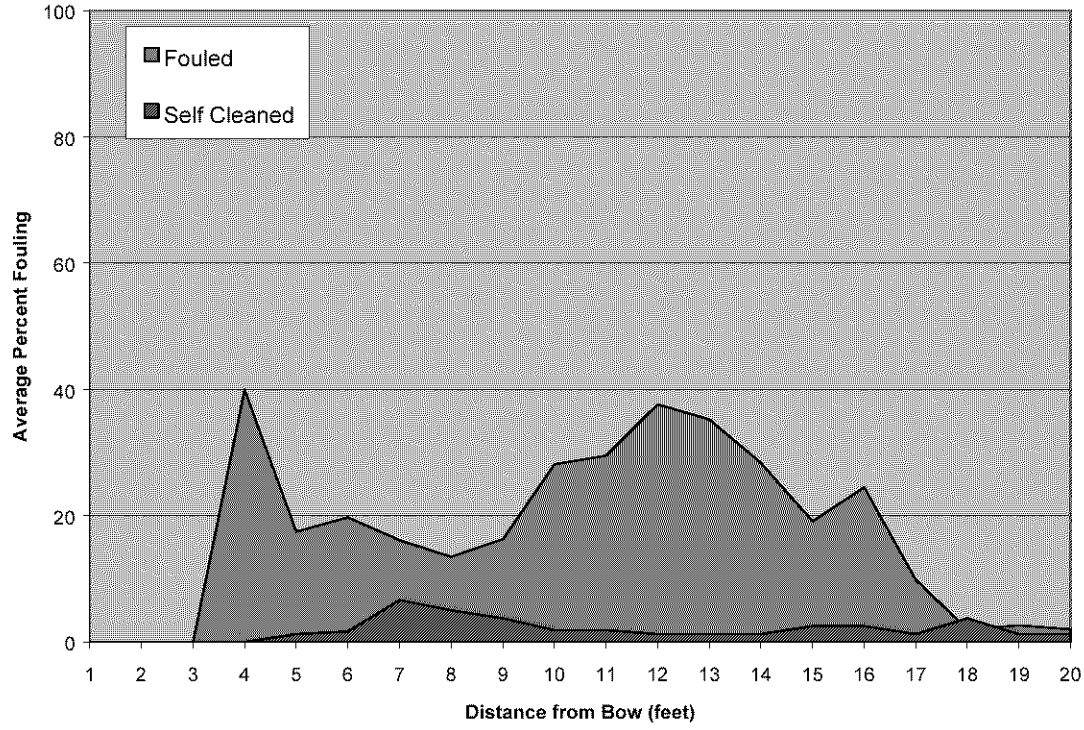

Figure 2.F.1.5.17 Heavy slime film fouling, underwater areas (30 October 1998).

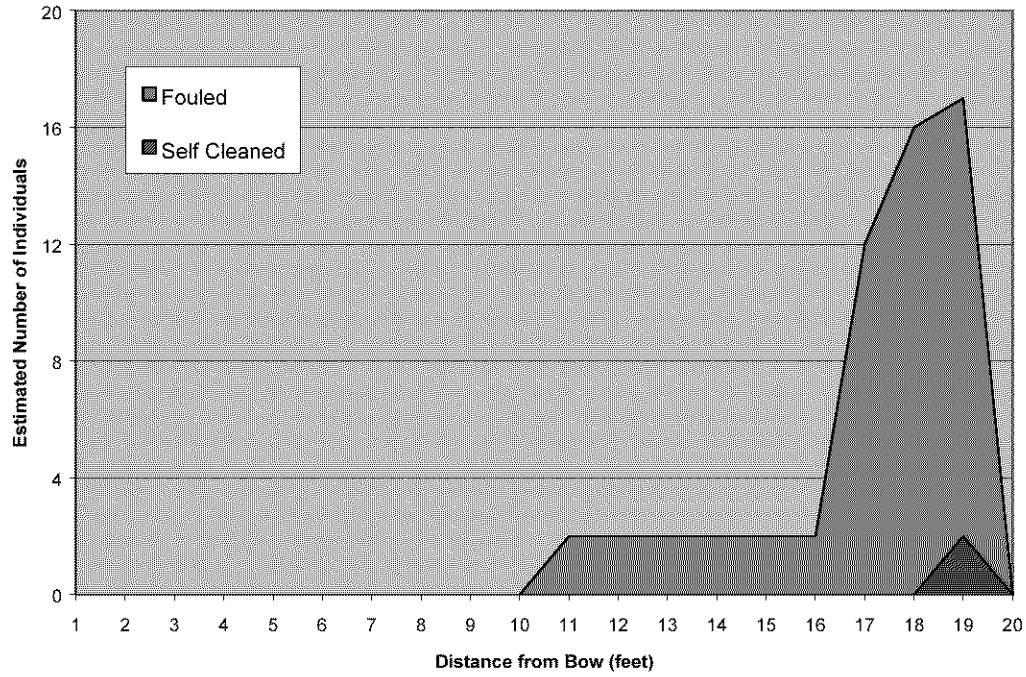

Figure 2.F.1.5.18 Tubeworm fouling, waterline (30 October 1998).

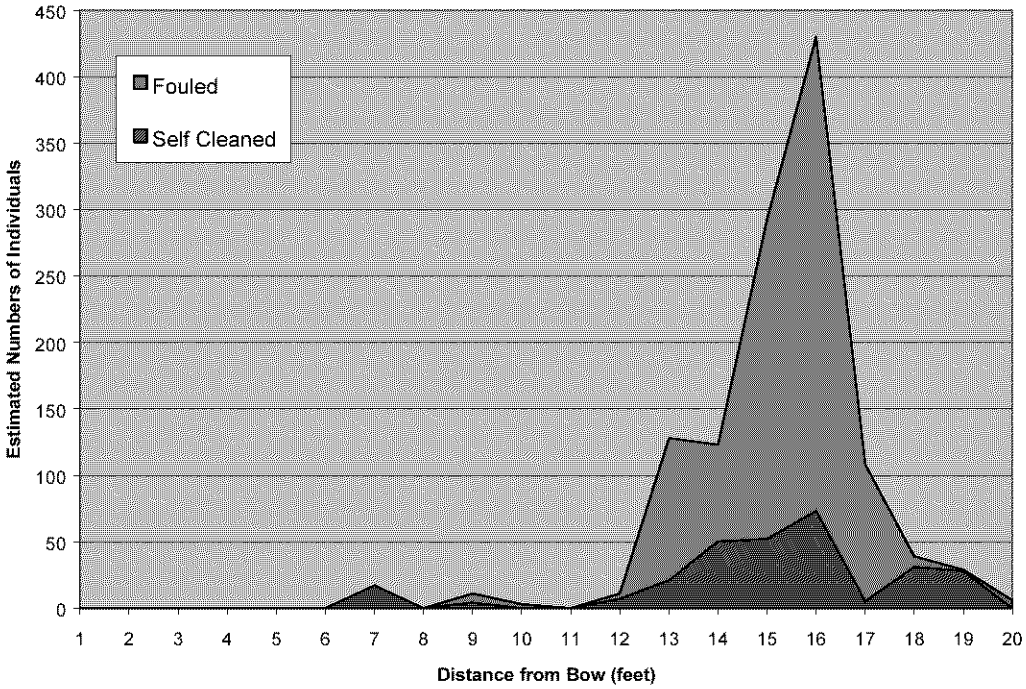

Figure 2.F.1.5.19 Tube worm fouling, underwater areas (30 October 1998).

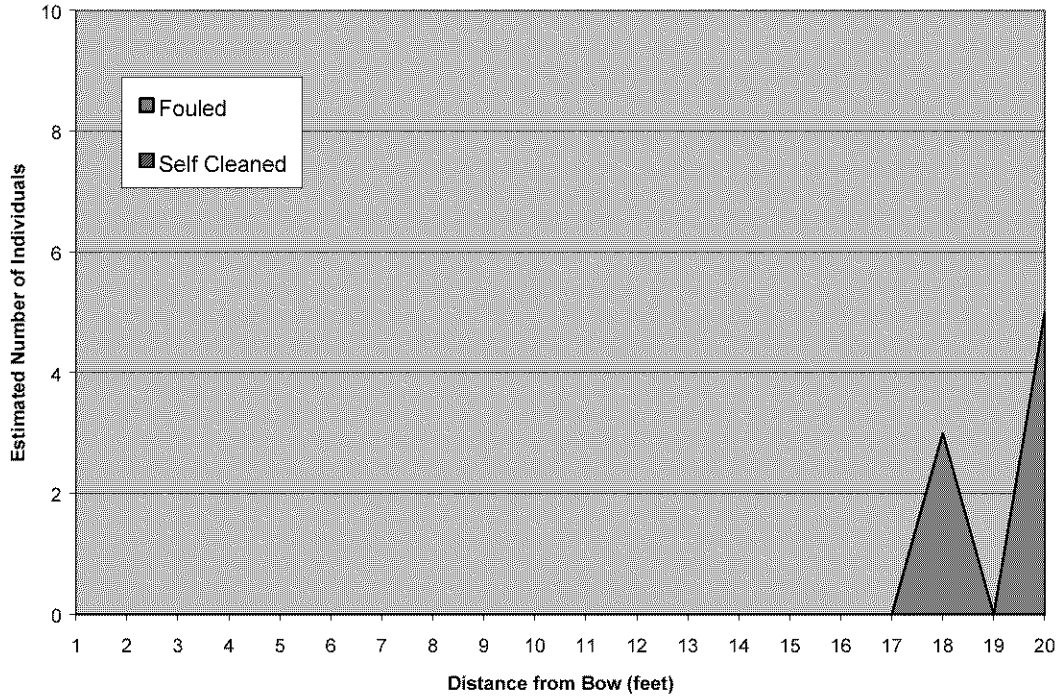

Figure 2.F.1.5.20 Barnacle fouling, waterline (30 October 1998).

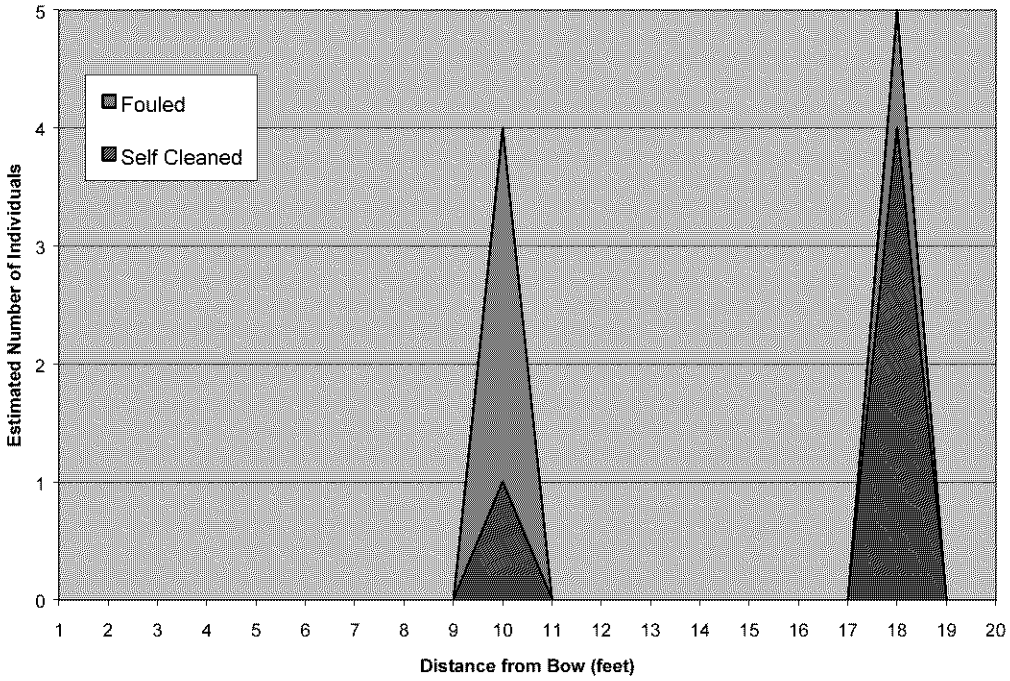

Figure 2.F.1.5.21 Barnacle fouling, underwater areas (30 October 1998).

6.0 Physical Condition

The overall physical condition of the coating is excellent, with no signs of blistering or delamination. There has been some mechanical damage to the bow area of the coating due to launching and retrieval of the boat onto the boat trailer. This occurs when the boat moves off the bow rollers and hits the metal supports on the trailer. The damage is in the form of long cuts that have shown no signs of spreading.

7.0 Summary

The RTV11® + 10% DMSC15 oil fouling release coating has shown good performance characteristics. The fouling communities, which developed on this coating, were much reduced when compared to normal non-toxic surfaces. This may be due to fish grazing the surface and due to loss of fouling when the boat was underway. Slime fouling was fairly heavy around the waterline and would require regular cleaning with a brush to keep clean.

Performance penalties due to fouling were measured during the powering trials. The maximum percent increase in propeller rpm (compared to the clean hull condition) measured due to fouling was about 14%. This was reduced to less than 6% after the boat had run for a short period at high speed and self cleaned. Most of the marine growth became detached when the boat reached high speeds (28 knots), however, slime films and some of the hard fouling remained. This would suggest that the coating would require some supplementary in water cleaning. Cleaning and maintenance of the boat hull were extremely easy, with all forms of fouling being easily removed by a light brush.

The overall physical condition of the coating was excellent. The coating had received cuts in the bow area during launch and retrieval with the boat trailer.

Appendices

1 Power Data

2. Biofouling Data

Appendix 1 Power Data

Date	Hull Condition	Speed	Fuel	
		(knots)	(gph)	RPM
6/23/98	Clean	4.8	2.1	1165
6/23/98	Clean	5.0	2.3	1350
6/23/98	Clean	6.1	3.1	1535
6/23/98	Clean	6.8	3.7	1720
6/23/98	Clean	10.1	4.5	2190
6/23/98	Clean	12.8	5.3	2390
6/23/98	Clean	15.6	6.1	2595
6/23/98	Clean	16.5	6.6	2690
6/23/98	Clean	20	8.2	3190
6/23/98	Clean	21	9	3220
6/23/98	Clean	24	10.9	3625
6/23/98	Clean	24	11.4	3685
7/17/98	Fouled	4.4	3	1180
7/17/98	Fouled	4.4	2.8	1185
7/17/98	Fouled	5.5	3.5	1530
7/17/98	Fouled	5.7	3.5	1545
7/17/98	Fouled	9.1	5.3	2225
7/17/98	Fouled	10.3	6	2330
7/17/98	Fouled	13.2	7	2550
7/17/98	Fouled	12.9	6.6	2535
7/17/98	Fouled	16.9	8.7	2850
7/17/98	Fouled	17.3	8.4	2925
7/17/98	Fouled	20	10	3325
7/17/98	Fouled	20	10.6	3340
7/17/98	Fouled	23	11.2	3665
7/17/98	Fouled	23	11.3	3650
7/17/98	Self Cleaned	4.8	0.9	1175
7/17/98	Self Cleaned	5.8	0.5	1485
7/17/98	Self Cleaned	11.2	5	2220
7/17/98	Self Cleaned	14.4	7	2590
7/17/98	Self Cleaned	18.8	8.7	2935
7/17/98	Self Cleaned	21	8.7	3350
7/17/98	Self Cleaned	23	10	3615
10/30/98	Fouled	1.8	1.9	650
10/30/98	Fouled	2.7	2.8	850
10/30/98	Fouled	3.5	2.4	1100
10/30/98	Fouled	4.8	2.5	1400
10/30/98	Fouled	5.8	3.6	1700
10/30/98	Fouled	6.6	4.1	1800
10/30/98	Fouled	8.1	5.7	2350

10/30/98	Fouled	10.0	6.0	2400
10/30/98	Fouled	10.8	6.2	2500
10/30/98	Fouled	11.6	6.7	2550
10/30/98	Fouled	13.3	7.2	2750
10/30/98	Fouled	16.9	8.0	3000
10/30/98	Fouled	19.0	9.0	3250
10/30/98	Fouled	20.4	10.0	3500
10/30/98	Fouled	21.3	9.6	3550
10/30/98	Fouled	23.2	12.8	3750
10/30/98	Fouled	25.0	14.9	
10/30/98	Self Cleaned	2.2	1.9	600
10/30/98	Self Cleaned	2.7	4.1	750
10/30/98	Self Cleaned	3.5	4.3	900
10/30/98	Self Cleaned	4.1	2.1	1150
10/30/98	Self Cleaned	5.0	5.2	1350
10/30/98	Self Cleaned	5.2	3.2	1400
10/30/98	Self Cleaned	6.0	3.4	1600
10/30/98	Self Cleaned	6.5	4.7	1750
10/30/98	Self Cleaned	9.6	7.8	2300
10/30/98	Self Cleaned	10.3	7.8	2350
10/30/98	Self Cleaned	11.6	6.4	2500
10/30/98	Self Cleaned	12.5	6.1	2500
10/30/98	Self Cleaned	14.5	7.9	2700
10/30/98	Self Cleaned	15.3	8.6	2800
10/30/98	Self Cleaned	18.5	10.5	3050
10/30/98	Self Cleaned	19.2	11.7	3200
10/30/98	Self Cleaned	20.9	10.8	3350
10/30/98	Self Cleaned	22.4	10.3	3500
10/30/98	Self Cleaned	23.3	11.4	3650

Appendix 2 Biofouling Data

17 July 1998, Fouling Data

Organism	Side	Inspection	Location	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Lt Slime	Port	Fouled	1 Chine	0	0	0	0	0	0	60	60	60	60	60	60	60	60	60	60	60	60	60	60
Lt Slime	Stbd	Fouled	1 Chine	0	0	0	0	0	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Lt Slime	Port	Fouled	2 Chine	0	0	0	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
Lt Slime	Stbd	Fouled	2 Chine	0	0	0	0	0	50	60	60	60	80	80	80	80	80	80	80	80	80	80	80
Lt Slime	Port	Fouled	3 Chine	0	0	0	70	70	70	70	70	70	70	90	90	90	90	90	90	90	90	90	90
Lt Slime	Stbd	Fouled	3 Chine	0	0	0	30	30	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
Lt Slime	Port	Fouled	4 Chine	0	0	0	0	0	0	0	70	70	70	70	70	70	70	70	70	70	70	70	70
Lt Slime	Stbd	Fouled	4 Chine	0	0	0	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70
Lt Slime	Ave	Fouled	Chine	0	0	0	38.3	38.3	48.6	51.3	60	60	62.5	65	65	65	65	65	65	65	65	65	65
Lt Slime	SD	Fouled	Chine	0	0	0	33.1	33.1	25.4	24.2	13.1	13.1	14.9	17.7	17.7	17.7	17.7	17.7	17.7	17.7	17.7	17.7	17.7
Lt Slime	Port	Fouled	Water Line	0	0	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
Lt Slime	Stbd	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Lt Slime	Ave	Fouled	Water Line	0	0	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Lt Slime	Port	S Cleaned	1 Chine	0	0	0	0	0	8	8	5	5	5	5	5	5	5	5	5	5	5	5	5
Lt Slime	Stbd	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	2	2	2	2	2
Lt Slime	Port	S Cleaned	2 Chine	0	0	0	0	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Lt Slime	Stbd	S Cleaned	2 Chine	0	0	0	0	5	5	5	5	5	5	5	30	10	5	5	5	5	5	5	10
Lt Slime	Port	S Cleaned	3 Chine	0	0	0	0	60	30	20	20	20	20	20	20	20	20	20	20	30	40	40	40
Lt Slime	Stbd	S Cleaned	3 Chine	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Lt Slime	Port	S Cleaned	4 Chine	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Lt Slime	Stbd	S Cleaned	4 Chine	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Lt Slime	Ave	S Cleaned	Chine	0	0	2.5	3.75	18.3	11	9.75	9.38	9.38	9.38	9.38	12.5	10	9.38	9.63	9.63	10.9	12.1	12.1	12.8
Lt Slime	SD	S Cleaned	Chine	0	0	3.54	2.5	22.7	11.9	10	10.2	10.2	10.2	10.2	12.2	10	10.2	9.91	9.91	11.8	14.4	14.4	14.2
Lt Slime	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	40	50	40	40	40	40	40	40	40	40	40
Lt Slime	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Lt Slime	Ave	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	20	25	20	20	20	20	20	20	20	20	20
Hvy Slime	Port	Fouled	1 Chine	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	Fouled	1 Chine	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	Fouled	2 Chine	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	Fouled	2 Chine	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	Fouled	3 Chine	0	0	0	0	20	0	30	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	Fouled	3 Chine	0	0	0	0	20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Hvy Slime	Port	Fouled	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	Fouled	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Ave	Fouled	Chine	0	0	0	0	10	5	3.75	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	SD	Fouled	Chine	0	0	0	0	11.5	5.35	10.6	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	Fouled	Water Line	0	0	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Hvy Slime	Stbd	Fouled	Water Line	0	0	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80
Hvy Slime	Ave	Fouled	Water Line	0	0	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45
Hvy Slime	Port	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	S Cleaned	1 Chine	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	S Cleaned	3 Chine	0	0	0	0	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Ave	S Cleaned	Chine	0	0	0	0	1.25	1.43	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	SD	S Cleaned	Chine	0	0	0	0	2.5	3.78	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	10	10	10	10	10
Hvy Slime	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	70	70	70	70	70	70	70	70	70	80	80
Hvy Slime	Ave	S Cleaned	Water Line	0	0	0	0	0	0	0	0	35	35	35	35	35	35	35	40	40	45	45
Tubeworms	Port	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	Fouled	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0
Tubeworms	Stbd	Fouled	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	9	6	0	0	0	0
Tubeworms	Port	Fouled	3 Chine	0	0	0	0	0	0	0	0	0	17	1	0	7	50	105	28	0	0	0
Tubeworms	Stbd	Fouled	3 Chine	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	Fouled	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0	105	0
Tubeworms	Stbd	Fouled	4 Chine	0	0	0	0	0	0	0	10	0	0	0	14	0	0	0	0	0	0	0
Tubeworms	Totl	Fouled	Chine	0	0	0	0	0	0	2	10	0	17	1	14	7	54	114	34	4	0	105	0
Tubeworms	Ave	Fouled	Chine	0	0	0	0	0	0	0.25	1.25	0	2.13	0.13	1.75	0.88	6.75	14.3	4.25	0.5	0	13.1	0
Tubeworms	SD	Fouled	Chine	0	0	0	0	0	0	0.71	3.54	0	6.01	0.35	4.95	2.47	17.5	36.8	9.82	1.41	0	37.1	0
Tubeworms	Port	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Tot	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	4	5	6	0	0	0	0

Tubeworms	Stbd	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	2	50	100	4	0	0	0
Tubeworms	Stbd	S Cleaned	3 Chine	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	90
Tubeworms	Stbd	S Cleaned	4 Chine	0	0	0	0	0	0	0	9	0	0	0	12	0	0	0	0	0	0	0
Tubeworms	Tot	S Cleaned	Chine	0	0	0	0	0	0	2	9	0	0	0	12	2	54	105	10	3	0	90
Tubeworms	Ave	S Cleaned	Chine	0	0	0	0	0	0	0.25	1.13	0	0	0	1.5	0.25	6.75	13.1	1.25	0.38	0	11.3
Tubeworms	SD	S Cleaned	Chine	0	0	0	0	0	0	0.71	3.18	0	0	0	4.24	0.71	17.5	35.1	2.38	1.06	0	31.8
Tubeworms	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Tot	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	Fouled	1 Chine	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	0	0	3	0	2	0	0	0	0	0
Barnacles	Port	Fouled	2 Chine	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	Fouled	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	5	0	0	0	0	0
Barnacles	Port	Fouled	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	Fouled	3 Chine	0	0	0	0	0	0	0	3	0	1	1	0	0	0	0	0	0	0	0
Barnacles	Port	Fouled	4 Chine	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0	4	0	0
Barnacles	Stbd	Fouled	4 Chine	0	0	0	1	3	0	0	0	0	1	0	0	0	0	0	0	0	0	0
Barnacles	Totl	Fouled	Chine	0	0	0	1	3	0	0	4	2	2	1	5	0	7	0	0	4	0	0
Barnacles	Ave	Fouled	Chine	0	0	0	0.13	0.38	0	0	0.5	0.25	0.25	0.13	0.63	0	0.88	0	0	0.5	0	0
Barnacles	SD	Fouled	Chine	0	0	0	0.35	1.06	0	0	1.07	0.71	0.46	0.35	1.19	0	1.81	0	0	1.41	0	0
Barnacles	Port	Fouled	Water Line	0	0	0	0	0	0	0	0	0	3	11	16	18	17	20	6	0	0	3
Barnacles	Stbd	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Tot	Fouled	Water Line	0	0	0	0	0	0	0	0	0	3	11	16	18	17	20	6	0	0	3
Barnacles	Port	S Cleaned	1 Chine	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0	3	0	0
Barnacles	Stbd	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
Barnacles	Tot	S Cleaned	Chine	0	0	0	0	0	0	0	1	0	1	0	2	0	0	0	0	3	0	0
Barnacles	Ave	S Cleaned	Chine	0	0	0	0	0	0	0	0.13	0	0.13	0	0.25	0	0	0	0	0.38	0	0
Barnacles	SD	S Cleaned	Chine	0	0	0	0	0	0	0	0.35	0	0.35	0	0.71	0	0	0	0	1.06	0	0
Barnacles	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	2	6	9	15	16	20	3	0	0	0

Barnacles	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Tot	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	2	6	9	15	16	20	3	0	0	0

30 October, Fouling Data

Organism	**Side**	**Inspection**	**Location**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Lt Slime	Port	Fouled	1 Chine	0	0	0	0	0	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Lt Slime	Stbd	Fouled	1 Chine	0	0	0	0	80	80	80	80	80	80	80	80	80	80	80	0	0	0	0	0
Lt Slime	Port	Fouled	2 Chine	0	0	0	0	0	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Lt Slime	Stbd	Fouled	2 Chine	0	0	0	0	0	20	20	2	0	0	0	0	0	0	0	0	0	0	0	0
Lt Slime	Port	Fouled	3 Chine	0	0	0	5	5	5	5	5	5	5	5	5	10	10	10	10	10	10	10	10
Lt Slime	Stbd	Fouled	3 Chine	0	0	0	0	0	0	0	5	5	5	5	5	5	5	5	5	5	5	0	0
Lt Slime	Port	Fouled	4 Chine	0	0	0	0	2	2	5	2	2	2	2	2	2	2	5	2	2	2	2	2
Lt Slime	Stbd	Fouled	4 Chine	0	0	12	12	12	10	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Lt Slime	Ave	Fouled	Chine	0	0	6	2.13	12.4	18.4	18.1	16.1	15.9	15.9	15.9	15.9	16.5	16.5	16.9	6.5	6.5	6.5	5.88	5.88
Lt Slime	SD	Fouled	Chine	0	0	8.49	4.36	27.6	26	26	26.5	26.6	26.6	26.6	26.6	26.4	26.4	26.2	6.72	6.72	6.72	7.1	7.1
Lt Slime	Port	Fouled	Water Line	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
Lt Slime	Stbd	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Lt Slime	Ave	Fouled	Water Line	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Lt Slime	Port	S Cleaned	1 Chine	0	0	0	0	0	0	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Lt Slime	Stbd	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	50	50	50	50	50	50	0	0	0	0	0	0
Lt Slime	Port	S Cleaned	2 Chine	0	0	0	0	0	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Lt Slime	Stbd	S Cleaned	2 Chine	0	0	0	0	0	0	10	10	10	5	5	5	5	5	0	0	0	0	0	0
Lt Slime	Port	S Cleaned	3 Chine	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Lt Slime	Stbd	S Cleaned	3 Chine	0	0	0	0	0	0	0	5	5	5	5	5	5	5	5	5	5	5	0	0
Lt Slime	Port	S Cleaned	4 Chine	0	0	0	0	2	2	5	2	2	2	2	2	2	2	5	2	2	2	2	2
Lt Slime	Stbd	S Cleaned	4 Chine	0	0	10	10	10	10	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Lt Slime	Ave	S Cleaned	Chine	0	0	5	1.88	2.13	3.38	6.88	7.13	13.4	12.8	12.8	12.8	12.8	12.8	6.25	5.88	5.88	5.88	5.25	5.25
Lt Slime	SD	S Cleaned	Chine	0	0	7.07	3.72	3.64	4.44	6.51	6.24	15.8	16.1	16.1	16.1	16.1	16.1	6.41	6.58	6.58	6.58	6.9	6.9
Lt Slime	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	30	50	50	50	50	50	50	50	50	0
Lt Slime	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	70	70	70	70	70	70	80	0
Lt Slime	Ave	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	15	25	60	60	60	60	60	60	65	0
Hvy Slime	Port	Fouled	1 Chine	0	0	0	0	0	50	30	30	30	30	30	60	50	10	5	10	10	10	10	5
Hvy Slime	Stbd	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	Fouled	2 Chine	0	0	0	0	0	15	15	15	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	Fouled	2 Chine	0	0	0	0	0	3	3	30	60	80	80	80	80	80	80	60	0	0	0	0
Hvy Slime	Port	Fouled	3 Chine	0	0	0	0	0	80	20	7	5	0	1	1	2	2	2	15	3	1	1	1

Hvy Slime	Stbd	Fouled	3 Chine	0	0	0	0	0	0	0	20	20	50	60	60	90	80	60	60	60	0	0	0
Hvy Slime	Port	Fouled	4 Chine	0	0	0	60	5	5	60	5	5	5	5	50	10	5	5	50	5	5	5	5
Hvy Slime	Stbd	Fouled	4 Chine	0	0	0	20	30	5	1	1	10	60	60	50	50	50	1	1	1	0	5	5
Hvy Slime	Ave	Fouled	Chine	0	0	0	40	17.5	19.8	16.1	13.5	16.3	28.1	29.5	37.6	35.3	28.4	19.1	24.5	9.88	2	2.63	2
Hvy Slime	SD	Fouled	Chine	0	0	0	28.3	17.7	29.4	20.9	12.2	20.5	31.8	32.9	32.2	37.2	35.8	31.9	27.3	20.5	3.66	3.7	2.51
Hvy Slime	Port	Fouled	Water Line	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Hvy Slime	Stbd	Fouled	Water Line	0	0	0	0	0	0	0	0	0	80	80	80	80	80	80	80	80	80	80	80
Hvy Slime	Ave	Fouled	Water Line	15	15	15	15	15	15	15	15	15	55	55	55	55	55	55	55	55	55	55	55
Hvy Slime	Port	S Cleaned	1 Chine	0	0	0	0	0	0	30	30	20	5	5	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	S Cleaned	2 Chine	0	0	0	0	0	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Hvy Slime	Stbd	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	S Cleaned	3 Chine	0	0	0	0	5	0	0	0	0	0	0	0	0	0	0	10	0	0	0	0
Hvy Slime	Stbd	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	S Cleaned	4 Chine	0	0	0	0	0	3	10	0	0	0	0	0	0	0	10	0	0	10	0	0
Hvy Slime	Stbd	S Cleaned	4 Chine	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	10	0	0
Hvy Slime	Ave	S Cleaned	Chine	0	0	0	0	1.25	1.63	6.63	5	3.75	1.88	1.88	1.25	1.25	1.25	2.5	2.5	1.25	3.75	1.25	1.25
Hvy Slime	SD	S Cleaned	Chine	0	0	0	0	2.5	3.54	10.4	10.7	7.44	3.72	3.72	3.54	3.54	3.54	4.63	4.63	3.54	5.18	3.54	3.54
Hvy Slime	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	30	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Ave	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	15	0	0	0	0	0	0	0	0	0
Tubeworms	Port	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	2
Tubeworms	Stbd	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	5	20	20	2	2
Tubeworms	Port	Fouled	2 Chine	0	0	0	0	0	0	0	0	10	0	0	10	61	115	200	300	80	4	0	0
Tubeworms	Stbd	Fouled	2 Chine	0	0	0	0	0	0	0	0	1	0	0	1	60	6	30	60	5	4	4	0
Tubeworms	Port	Fouled	3 Chine	0	0	0	0	0	0	0	0	0	3	0	0	0	0	60	60	0	0	0	0
Tubeworms	Stbd	Fouled	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	5	2	2	5	3	1	1	0
Tubeworms	Port	Fouled	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	Fouled	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0	10	20	2
Tubeworms	Totl	Fouled	Chine	0	0	0	0	0	0	0	0	11	3	0	11	128	123	293	430	108	39	29	6
Tubeworms	Ave	Fouled	Chine	0	0	0	0	0	0	0	0	1.38	0.38	0	1.38	16	15.4	36.6	53.8	13.5	4.88	3.63	0.75
Tubeworms	SD	Fouled	Chine	0	0	0	0	0	0	0	0	3.5	1.06	0	3.5	27.5	40.3	69.5	103	27.7	7	6.76	1.04
Tubeworms	Port	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	2	2	2	2	2	2	12	16	17	0
Tubeworms	Tot	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	2	2	2	2	2	2	12	16	17	0
Tubeworms	Port	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Tubeworms	Port	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	4	0	0	7	21	45	50	50	5	0	0	0
Tubeworms	Stbd	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	5	2	23	0	2	0	0
Tubeworms	Port	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	8	0	0
Tubeworms	Port	S Cleaned	4 Chine	0	0	0	0	0	0	15	0	0	0	0	0	0	0	0	0	0	15	0	0
Tubeworms	Stbd	S Cleaned	4 Chine	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	6	28	0
Tubeworms	Tot	S Cleaned	Chine				0	0	0	17	0	4	0	0	7	21	50	52	73	5	31	28	0
Tubeworms	Ave	S Cleaned	Chine	0	0	0	0	0	0	2.13	0	0.5	0	0	0.88	2.63	6.25	6.5	9.13	0.63	3.88	3.5	0
Tubeworms	SD	S Cleaned	Chine	0	0	0	0	0	0	5.25	0	1.41	0	0	2.47	7.42	15.8	17.6	18.4	1.77	5.46	9.9	0
Tubeworms	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0
Tubeworms	Tot	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0
Barnacles	Port	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	Fouled	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	Fouled	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	Fouled	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	Fouled	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0
Barnacles	Port	Fouled	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0
Barnacles	Stbd	Fouled	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Totl	Fouled	Chine	0	0	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	5	0	0
Barnacles	Ave	Fouled	Chine	0	0	0	0	0	0	0	0	0	0.5	0	0	0	0	0	0	0	0.63	0	0
Barnacles	SD	Fouled	Chine	0	0	0	0	0	0	0	0	0	1.41	0	0	0	0	0	0	0	1.41	0	0
Barnacles	Port	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	5
Barnacles	Stbd	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Tot	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	5
Barnacles	Port	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	0	0
Barnacles	Stbd	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
Barnacles	Tot	S Cleaned	Chine	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	4	0	0
Barnacles	Ave	S Cleaned	Chine	0	0	0	0	0	0	0	0	0	0.13	0	0	0	0	0	0	0	0.5	0	0
Barnacles	SD	S Cleaned	Chine	0	0	0	0	0	0	0	0	0	0.35	0	0	0	0	0	0	0	1.41	0	0

Barnacles	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Tot	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

CCBC-99-GE-TCRAFT-2 August 1999

The performance of the 21 foot T-Craft coated with GE RTV11 + DMSC15 and DBTDL fouling-release bottom coat.

Exposure Period: June 1998 to July 1999

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Executive Summary
In May 1998, the 22 ft T-Craft power boat (operated by the Center for Corrosion and Biofouling Control, Florida Institute of Technology) was coated by personnel from General Electric (GE) with the General Electric RTV11® + 10% DMSC15 oil Duplex fouling release coating. The boat was placed in the water on 15 June of 1998, and monitored for biofouling and powering efficiency in June, July and October of 1998. The data from these tests are presented in a report submitted to GE, "The performance of the 21 foot T-Craft coated with GE RTV11 + DMSC15® and DBTDL fouling-release bottom coat". CCBC-99-GE-TCRAFT on1 March 1999.

The boat was removed from the water during February 1999 to facilitate the construction of a wet well in the stern of the boat. This feature was built to enable the drag and fouling-release testing of GE down select panels. The boat was returned to the water in April 1999 and new power trial and fouling data were obtained in July 1999.

The coating is performing very well. The fouling communities, which developed on this coating, were much reduced when compared to normal non-toxic surfaces. Slime fouling was fairly heavy around the waterline and would require regular cleaning with a brush to keep clean. Most of the marine growth became detached when the boat reached high speeds (28 knots).

Performance penalties due to fouling were measured during the powering trials. The maximum percent increase in propeller rpm (compared to the clean hull condition) measured due to fouling was about 22%. This was reduced to less than 10% after the boat had run for a short period at high speed and self cleaned.

Cleaning and maintenance of the boat hull were extremely easy, with all forms of fouling being easily removed by a light brush. The overall physical condition of the coating was excellent, however, the coating had received some cuts in the bow area during launching and retrieval with the boat trailer.

Acknowledgments
We would like to acknowledge the support of General Electric and the Defense Advanced Research Agency for their support of this work. We would offer especial thanks to Kathryn Truby, Owen Harblin, Tim Burnell, John Carpenter who came to Florida and provided such an excellent coating for our boat and to Christina Darkangelo- Wood who provided technical and material support during the boat trial operations.

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1.0 Background

The Center for Corrosion and Biofouling Control at the Florida Institute of Technology (FIT) uses a 22 ft T-Craft power boat for its operations in the Indian River Lagoon, Florida (Figure 2.F.2.1.1). In March 1998 it was decided to use this vessel as a test platform for the RTV11 + 10% DMSC15 oil fouling-release coating developed by General Electric (GE). The boat was removed from the water in May, 1998 and the hull sand blasted to remove the existing copper based antifouling system. The boat was washed and moved under cover where a team from GE applied the fouling release coating according to the specification shown in Table 2.F.2.1.1. The coating was applied between 26 to 28 May 1998. The coating was allowed to cure and the boat launched 15 June 1998.

Figure 2.F.2.1.1 22 T-Craft with GE fouling-release bottom coat.

The fouling-release performance of this coating had been evaluated at the Florida Institute of Technology Static Immersion Site and the hard fouling adhesion properties are shown in Table 2.F.2.1.2.

Table 2.F.2.1.1 Coating specifications for the T-Craft.

Application Layer	Date	Temp. (°F)	RH (%)	WFT (mil)
Barrier Coats				
5 gal Amerlock 400 ivory + 1 pt naphtha	5/26	88	56	22-24
2 gal Amerlock 400 pearl gray + 1 pt naphtha	5/27	77	72	14-16
Mist Coats (port and starboard side were different)				

4 gal Amerlock 400 pearl gray + 1 gal GE SCM501C (port side)	5/28	85	67	12-14 (port)
½ gal Shell Versamid + ½ gal Shell Epon 828 + 1 gal butanol (starboard side)	5/28	85	67	2-3 (stbd)
Tie Coat				
5 gal Wacker J-501 + 1 gal GE SF69	5/28	85	67	18-20
Fouling – Release Coat				
5 gal GE RTV11 + ½ gal DMSC15 + ½ gal naphtha + 30 ml DBTDL	5/28	85	67	16-20
Patch Coats				
500 g GE SEA210A + 6 ml GE SCM501C	5/29	85	65	2-3
450 ml Wacker J-501 + 50 ml GE SF69	5/29	85	65	16-20
3500 ml GE RTV11® + 350 ml DMSC15 + 10 ml DBTDL	5/29	85	65	18-20

Table 2.F.2.1.2 Hard fouling adhesion data obtained from panelsimmersed at the FIT static immersion site.

Organism	Average (psi)	SD (psi)	n
Balanus eburneus	3.53	2.43	87
Hydroides sp.	22.93	8.36	52
Oyster	13.78	3.49	43

2.0 Instrumentation

The boat was instrumented to measure speed over the ground, speed through the water, engine revolutions per minute (rpm) and engine fuel consumption in gallons per minute (gpm) using the instrumentation shown in Table 2.F.2.2.1.

Table 2.F.2.2.1 Instrumentation for power trials.

Data	Item	Model #
Speed over the ground	Garmin GPS III	403850
Speed through the water	West Marine Speed 100 Speed/Log/Temp	266827
Engine rpm and fuel consumption	FloScan Series 8000 Fuel Computer	8000-264-1P

3.0 Method

The following procedure was used to assess the skin friction and fouling release properties of the coating. Power trials were only performed on days when the wind speed was less than 5 knots.

- Fill fuel tanks to capacity.
- Motor at less than 4 knots to power trial area (less than two miles).
- Perform underwater video inspection of hull.
- Run power trials, starting at about 2 knots. Maintain speed for 2 minutes. Monitor speed, rpm and gpm. Increase speed and repeat data collection up to speeds of about 25 knots.
- Run the boat at top speed (about 28 knots) for 10 minutes.

- Perform underwater video inspection of hull.
- Run power trials, starting at about 2 knots. Maintain speed for 2 minutes. Monitor speed, rpm and gpm. Increase speed and repeat data collection up to speeds of about 25 knots.
- Analyze the video data to estimate biofouling cover.
- Analyze the boat power data to estimate drag.
- Obtain adhesion values for organisms remaining on hull after power trial.

4.0 Boat Operating History

The boat is used for regular research activities in the Indian River Lagoon. Table 2.F.2.4.1 summarizes the operating schedule over the past months.

Table 2.F.2.4.1 Boat operating schedule since GE coating application.

Date	Activity
6/15/98	Boat launched.
6/23/98	Hull cleaned and first power trial.
6/25/98	Foil testing, run for 4 hours (0 to 25 knots).
7/1/98	Foil testing, run for 4 hours (0 to 25 knots).
7/2/98	Panel inspection and cage maintenance. 1 hour (20 knots).
7/9/98	Out of water inspection of boat.
7/17/98	Power trials.
8/4/98	Foil testing, run for 4 hours (0 to 25 knots).
8/7/98	Foil testing, run for 4 hours (0 to 25 knots).
8/22/98	Attempted power trials, postponed due to weather.
9/1/98	Attempted power trials, camera flooded.
9/10/98	Attempted power trials, postponed due to weather.
10/9/98	Inspection and cage maintenance. 1 hour (20 knots).
10/30/98	Power trials and platform maintenance.
11/20/98	Panel inspection and cage maintenance. 1 hour (20 knots).
11/23/98	Boat maintenance. 20 minutes (25 knots).
12/22/98	Panel, boat and cage inspection. 1 hour (20 knots).
12/23/98	Take boat out of water for outboard service.
1/13/99	Return boat to water.
1/29/99	Inspection and cage maintenance. 1 hour (20 knots).
2/18/99	Remove boat from water for hull modifications to improve foil data collection.
4/13/99	Launch boat with wet well and try out "new foil"
4/15/99	Tested boat/foil system in harbor
4/19/99	Panel inspection and cage maintenance. Foil run
5/5/99	Panel inspection and cage maintenance. Foil run.
5/24/99	Pulled boat.
6/3/99	Launched boat after patch repair. Panel inspection and cage maintenance. 1 hour (20 knots).
6/4/99	Power boat trial- baseline with through hull.
6/15/99	Panel inspection and cage maintenance. 1 hour (20 knots).
6/21/99	Panel inspection and cage maintenance. 1 hour (20 knots).
6/29/99	Panel inspection and cage maintenance. Hydro Panel testing.
7/1/99	Thru Hull Foil Testing failed, platform to drop off panels
7/20/99	Power Trials.
7/21/99	Panel inspection and cage maintenance. 1 hour (20 knots).
7/27/99	Ran panel S1 to completion + three calibration curves.
7/30/99	Panel inspection and cage maintenance. 1 hour (20 knots).

8/4/99	Thru Hull Testing
8/13/99	Panel inspection and cage maintenance. Foil Test.
8/18/99	Panel inspection and cage maintenance. 1 hour (20 knots).
8/23/99	Gear in starter replaced
8/24/99	Panel inspection and cage maintenance. 1 hour (20 knots).

5.0 Boat Powering and Biofouling Data

There have been four successful power trials since the GE fouling-release coating was applied at the end of May 1998. These are as follows:

- 23 June 1998, clean hull baseline power data.
- 17 July 1998, fouled hull and hydrodynamically self cleaned hull power data.
- 30 October 1998, fouled hull and hydrodynamically self cleaned hull power data.
- 20 July 1999, fouled hull, hydrodynamicallly self cleaned hull and clean hull power data.

The data obtained for the 23 June clean hull run was not used as the baseline from which to compare the performance of the hull in the fouled and hydrodynamically self-cleaned conditions for the July, 1999 power trials. This was due to changes in the hull geometry with the addition of the wet well.

Boat powering data are presented as propeller revolutions per minute (rpm) versus boat speed (knots). Third order polynomials were run on the rpm vs. boat speed curves. From the curve fit equations, the performance data are presented as percentage change in rpm from the clean hull condition. Because the boat is a planing hull, there will rarely be an exact match of rpm and boat speed, however, the data clearly show differences in performance due to biofouling.

The biofouling data were obtained by analyzing the underwater videos of the boat hull. The videos were taken in combination with a measuring tape and so the exact location on the hull was known. The video was made along the length of the hull for each of the four chines per side and the water line. Biofouling was assessed for every one-foot length of hull. The light and heavy slime films were assessed as percent cover. The final figures represent the average percent cover of the hull surface. The barnacle and tubeworm cover were assessed by estimating the number of individuals present. The final data are presented as estimated total numbers of individuals at each foot along the hull. It must be emphasized that the biofouling data are estimates and not exact numbers.

5.1 20 July 1999 Power Trials

On 20 July 1999, a third fouled power trial was run (Figures 2.F.2.5.1 and 2.F.2.5.2). The fouling consisted of light and heavy slime films, tubeworms and barnacles. The biofilms resulted in an increase in drag. After running the boat at 28 knots for 10 minutes some of the fouling had been removed by hydrodynamic forces. However, the power required for propulsion did not return to that of the clean boat, and a penalty due to biofouling remained.

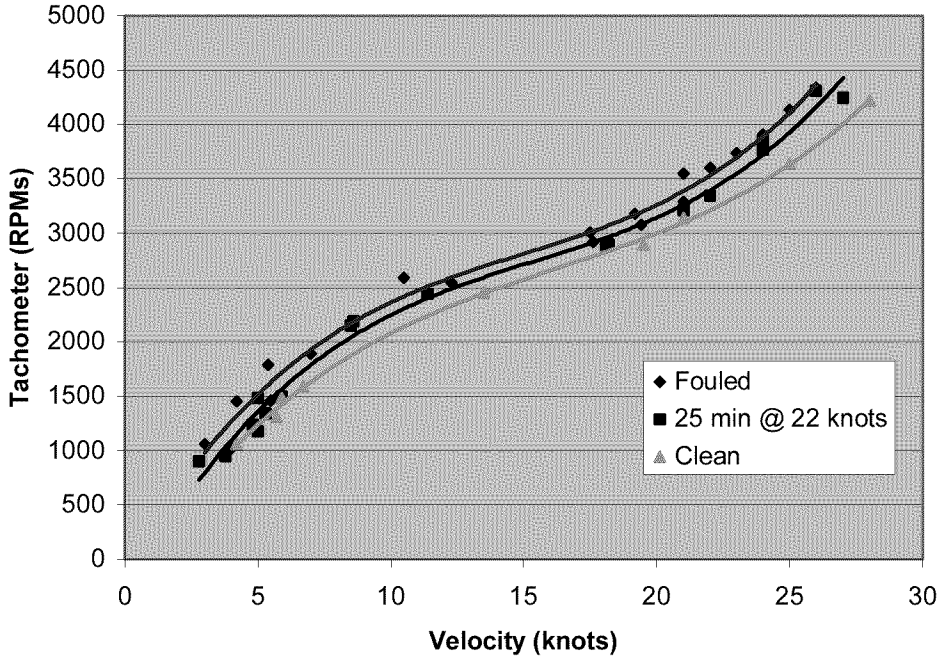

Figure 2.F.2.5.1 Powering data (20 July 1999).

Table 2.F.2.5.1 Third order polynomial regression data.

Hull Condition	**3rd Order Polynomial Regression**	**R^2**
Fouled	$y = 0.533x^3 - 23.953x^2 + 435.19x$	0.989
Self Cleaned	$y = 0.5183x^3 - 24.023x^2 + 447.53x$	0.990
Clean	$y = 0.3714x^3 - 18.134x^2 + 375.96x$	0.999

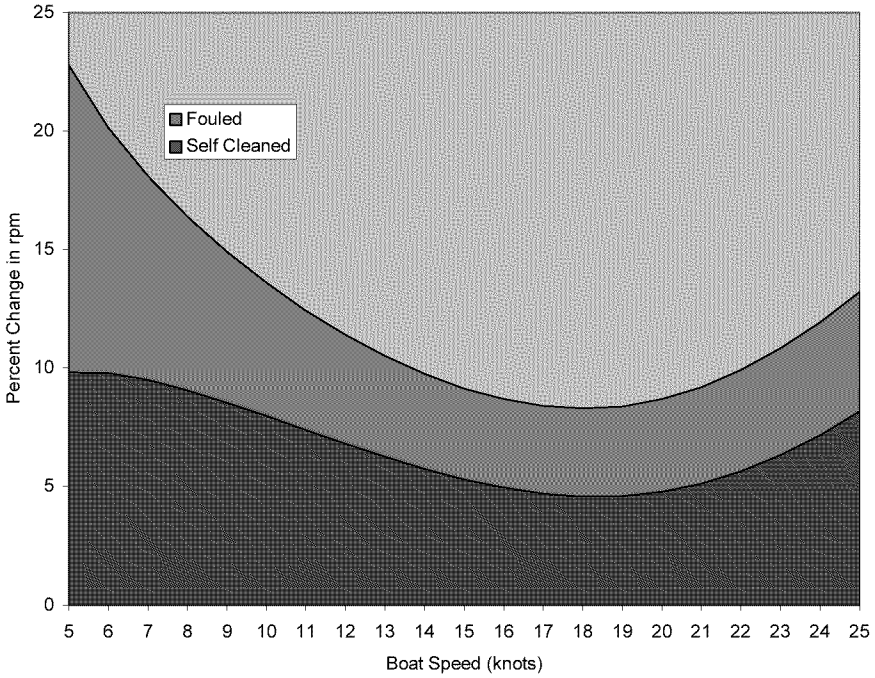

Figure 2.F.2.5.2 Percent change in rpm from the clean hull condition.

The biofouling communities that had become established on the hull by July were mainly comprised of light and heavy slime films, tubeworms and barnacles. No tubeworms were present on the waterline. There was a reduction in slime film cover after the boat had run at 28 knots for ten minutes. Barnacles were partially removed at the water line and mostly removed underwater by high-speed water velocity. Few of the underwater tubeworms were removed by high-speed water velocity. Hydrodynamic removal of hard fouling towards the stern in the waterline areas was less effective.

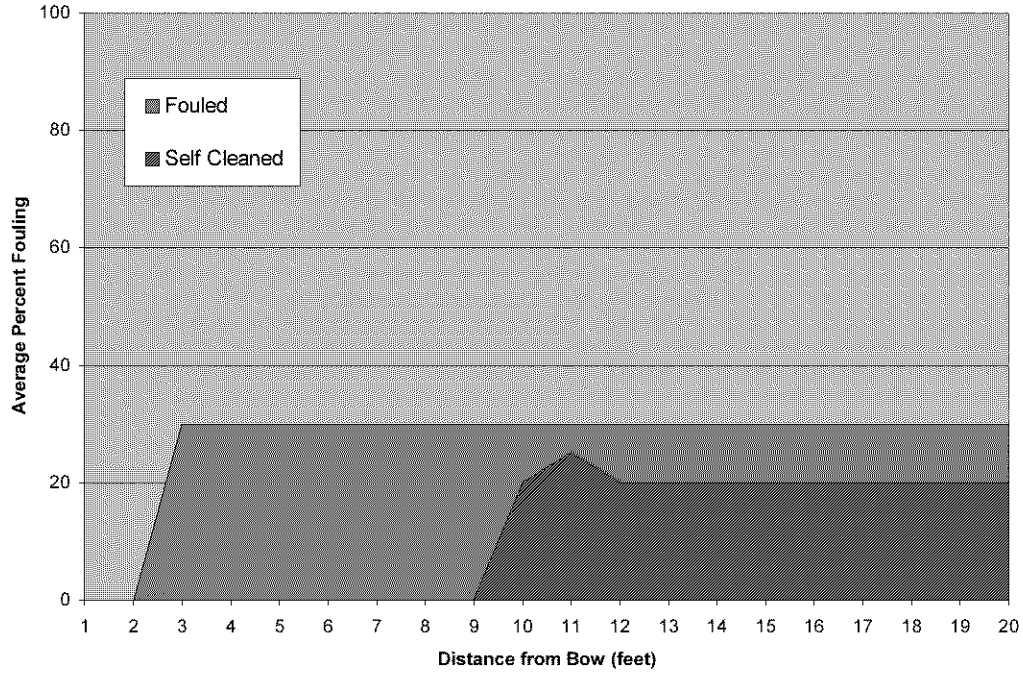

Figure 2.F.2.5.3 Light slime film fouling, waterline (20 July 1999).

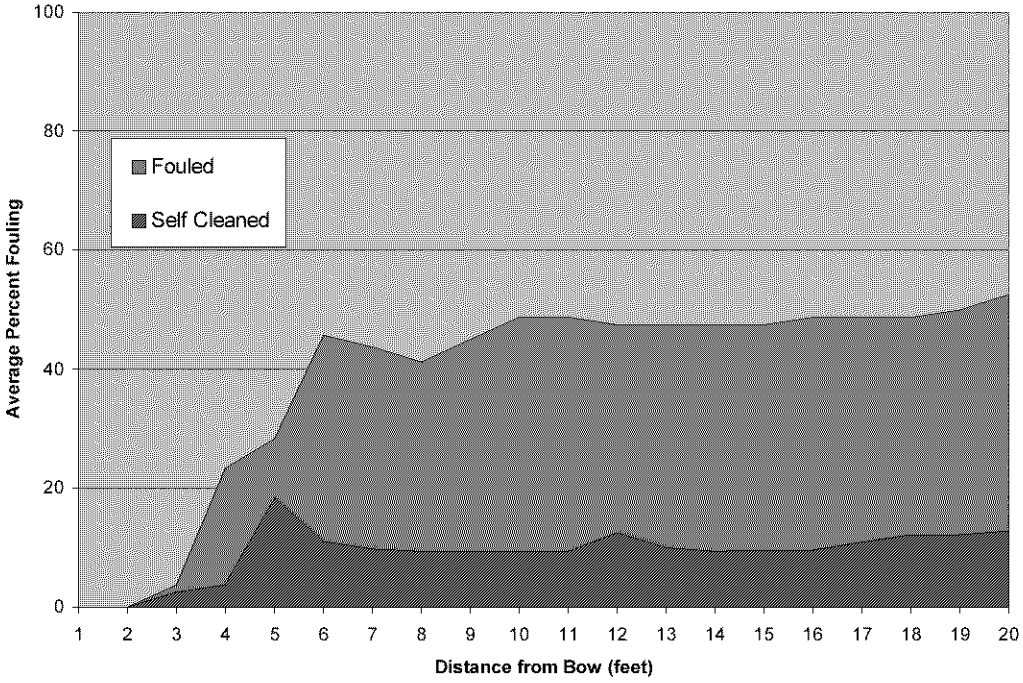

Figure 2.F.2.5.4 Light slime film fouling, underwater areas (20 July 1999).

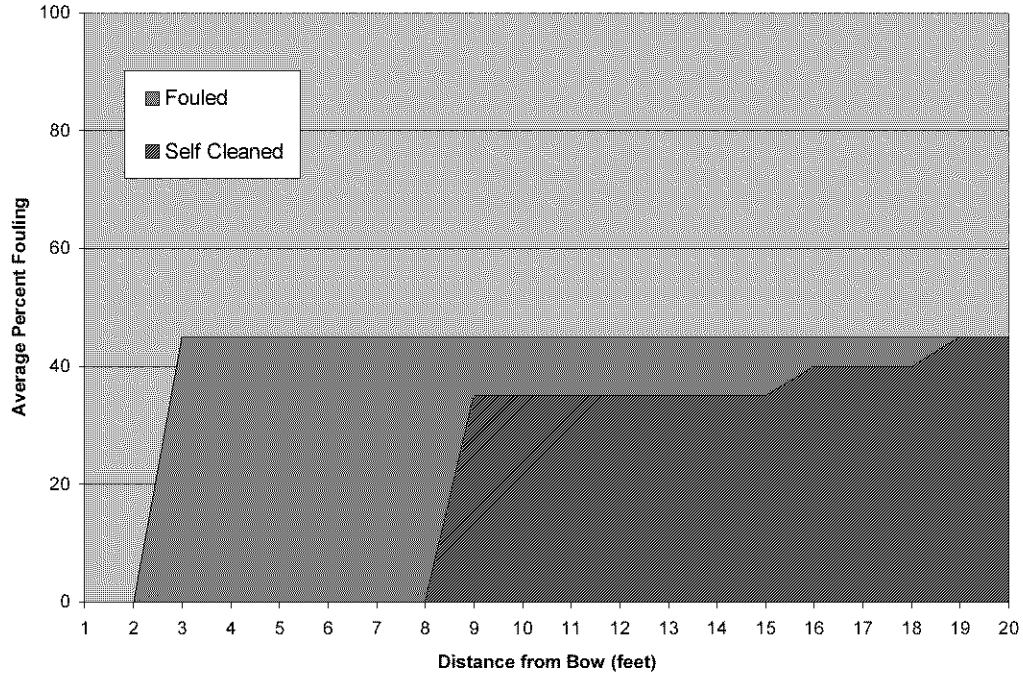

Figure 2.F.2.5.5 Heavy slime film fouling, waterline (20 July 1999).

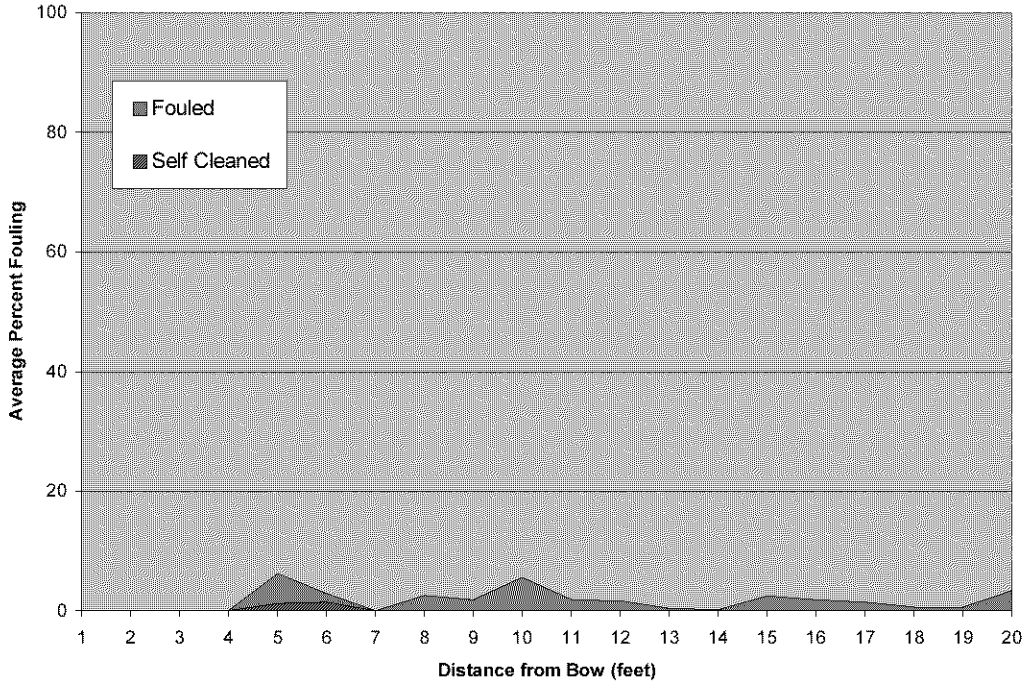

Figure 2.F.2.5.6 Heavy slime film fouling, underwater areas (20 July 1999).

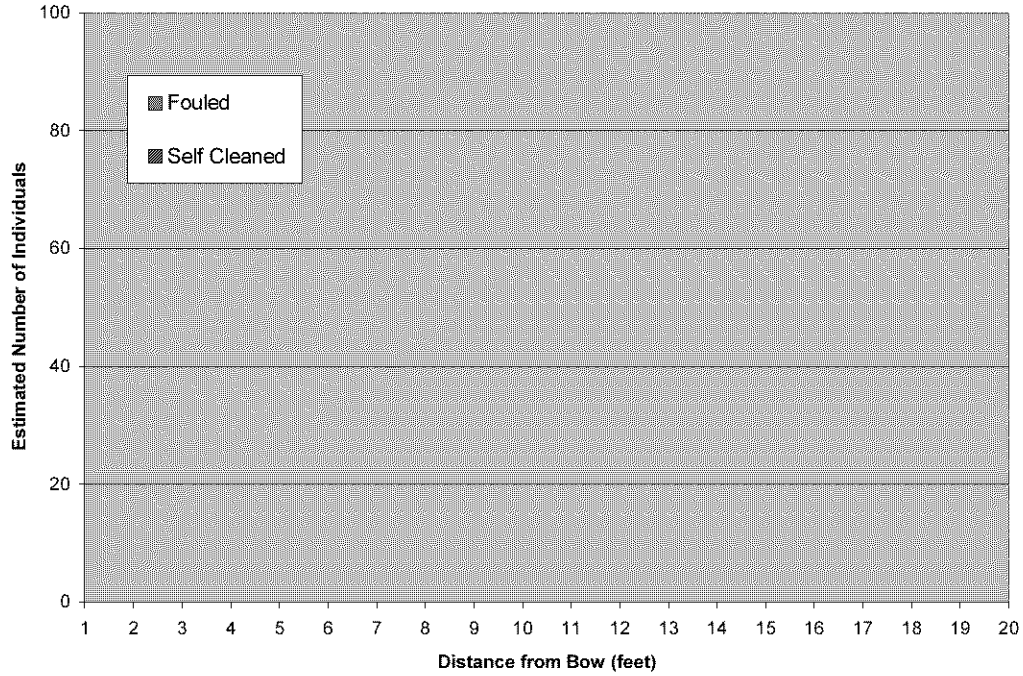

Figure 2.F.2.5.7 Tubeworm fouling, waterline (20 July 1999).

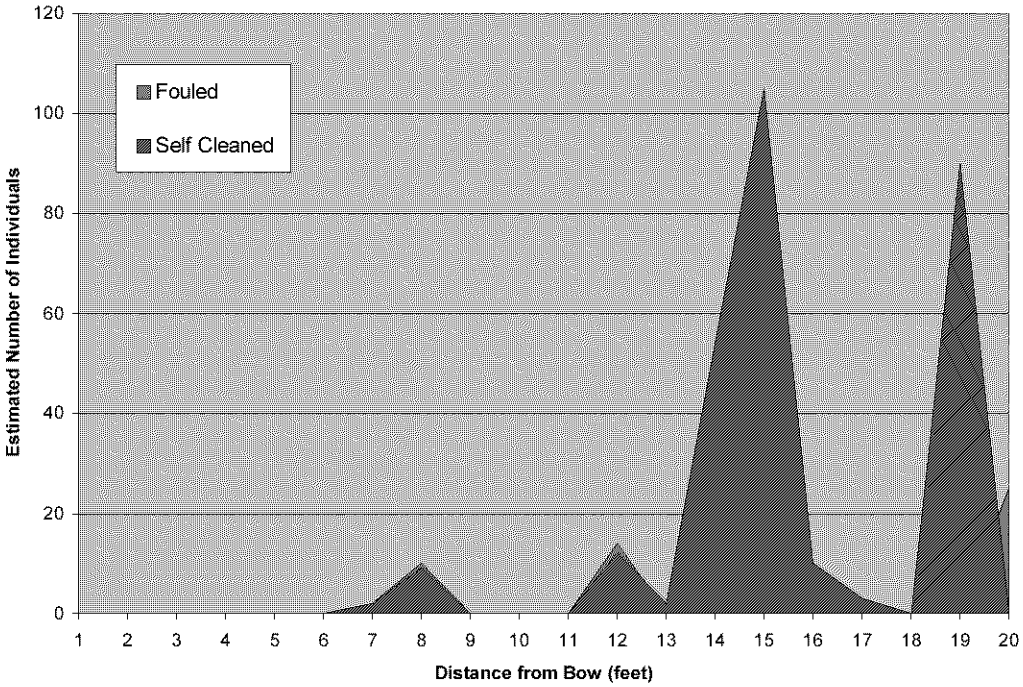

Figure2.F.2. 5.8 Tubeworm fouling, underwater areas (20 July 1999).

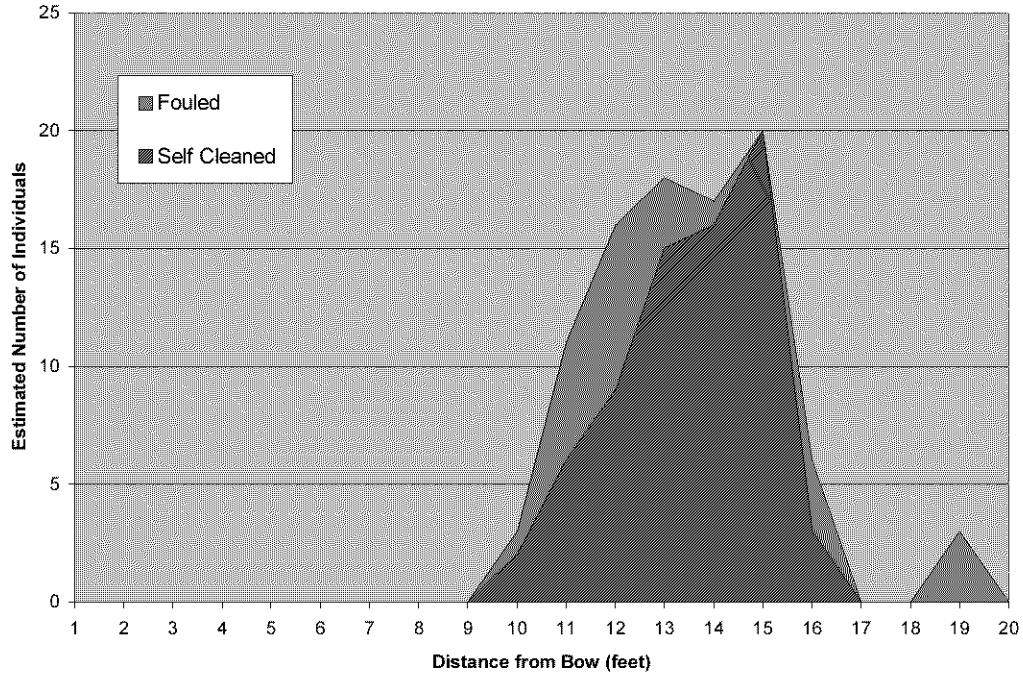

Figure 2.F.2.5.9 Barnacle fouling, waterline (20 July 1999).

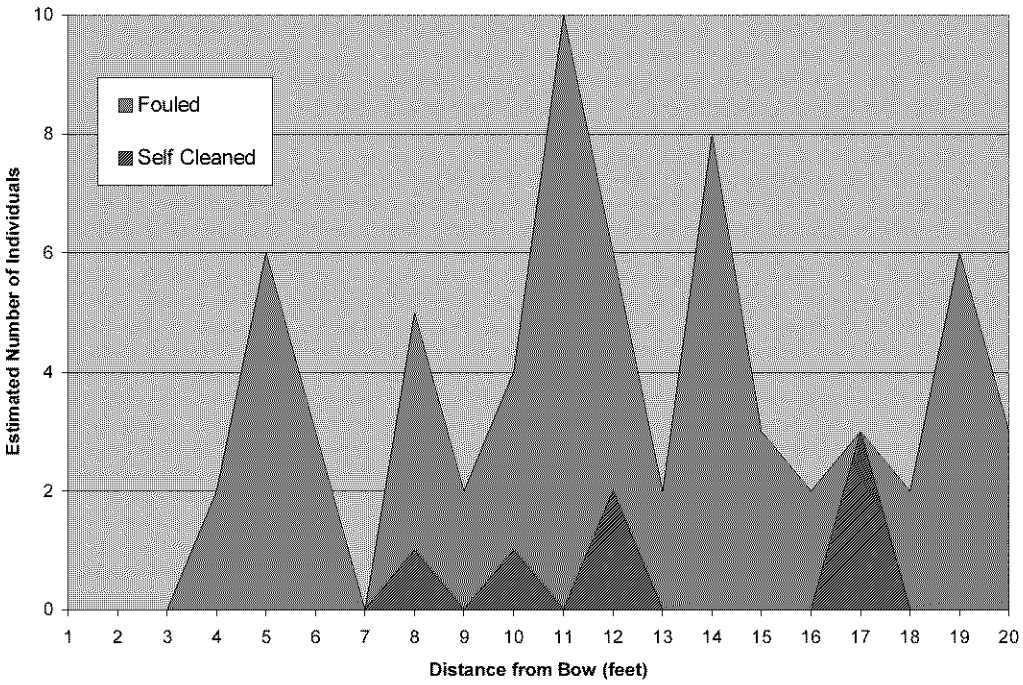

Figure 2.F.2.5.10 Barnacle fouling, underwater areas (20 July 1999).

The fouling-release performance of the T-Craft coating was analyzed and the hard fouling adhesion properties are shown in Table 2.F.2.5.2. *Balanus eburneus*

values are slightly higher than those found on panels immersed at the FIT static immersion site, while values for *Hydroides sp*. and oysters are slightly lower. (Table 2.F.2.5.2).

Table 2.F.2.5.2 Hard fouling adhesion data obtained from T-Craft.

Organism	Average (psi)	SD (psi)	n
Balanus eburneus	8.24	5.4	66
Hydroides sp.	12.24	6.96	47
Oyster	10.94	8.38	2

6.0 Physical Condition

The overall physical condition of the coating is excellent, with no signs of blistering or delamination. There was some mechanical damage to the bow area of the coating due to launching and retrieval of the boat onto the boat trailer. This occurs when the boat moves on and off the bow rollers and hits the metal supports on the trailer. The damage is in the form of long cuts that were successfully repaired in April, 1999 using a repair kit provided by GE. All the repairs have remained intact and are performing well.

7.0 Summary

The RTV11® + 10% DMSC15 oil fouling release coating has shown good performance characteristics. The fouling communities, which developed on this coating, were much reduced when compared to normal non-toxic surfaces. This may be due to fish grazing the surface and due to loss of fouling when the boat was underway. Slime fouling was fairly heavy around the waterline and would require regular cleaning with a brush to keep clean.

Performance penalties due to fouling were measured during the powering trials. The maximum percent increase in propeller rpm (compared to the clean hull condition) measured due to fouling was about 22%. This was reduced to less than 10% after the boat had run for a short period at high speed and self cleaned. Most of the marine growth became detached when the boat reached high speeds (28 knots), however, slime films and some of the hard fouling remained. This would suggest that the coating would require some supplementary in water cleaning. Cleaning and maintenance of the boat hull were extremely easy, with all forms of fouling being easily removed by a light brush.

The overall physical condition of the coating was excellent. The coating had received cuts in the bow area during launch and retrieval with the boat trailer.

Appendices

1 Power Data

2. Biofouling Data

3. Adhesion Data

Appendix 1 Power Data

Date	Hull Condition	Speed	Fuel	
		(knots)	(gph)	RPM
6/23/98	Clean	4.8	2.1	1165
6/23/98	Clean	5.0	2.3	1350
6/23/98	Clean	6.1	3.1	1535
6/23/98	Clean	6.8	3.7	1720
6/23/98	Clean	10.1	4.5	2190
6/23/98	Clean	12.8	5.3	2390
6/23/98	Clean	15.6	6.1	2595
6/23/98	Clean	16.5	6.6	2690
6/23/98	Clean	20	8.2	3190
6/23/98	Clean	21	9	3220
6/23/98	Clean	24	10.9	3625
6/23/98	Clean	24	11.4	3685
7/20/99	Fouled	3	4.2	1060
7/20/99	Fouled	4	4.8	1020
7/20/99	Fouled	4.2	5.5	1450
7/20/99	Fouled	5.4	6.8	1790
7/20/99	Fouled	5.5	6.2	1460
7/20/99	Fouled	7	7.8	1890
7/20/99	Fouled	10.5	12.4	2590
7/20/99	Fouled	12.3	12.3	2540
7/20/99	Fouled	17.5	18.2	3010
7/20/99	Fouled	17.6	17.4	2920
7/20/99	Fouled	19.2	19.6	3180
7/20/99	Fouled	19.4	19.7	3080
7/20/99	Fouled	21	22.1	3550
7/20/99	Fouled	21	20.4	3290
7/20/99	Fouled	22	22.6	3600
7/20/99	Fouled	23	23.9	3740
7/20/99	Fouled	24	24.6	3910
7/20/99	Fouled	25	25.4	4140
7/20/99	Fouled	26	27	4340
7/20/99	Fouled	26	26.3	4310
7/20/99	Self Cleaned	23	10	3615
7/20/99	Self Cleaned	2.8	1.3	900
7/20/99	Self Cleaned	3.8		950
7/20/99	Self Cleaned	4.8	2.1	1240
7/20/99	Self Cleaned	5	3.5	1180
7/20/99	Self Cleaned	5		1480
7/20/99	Self Cleaned	5.3	3.6	1340
7/20/99	Self Cleaned	5.9	5	1500

7/20/99	Self Cleaned	8.5		2150
7/20/99	Self Cleaned	8.6	7.8	2190
7/20/99	Self Cleaned	11.4		2440
7/20/99	Self Cleaned	18.1		2890
7/20/99	Self Cleaned	18.2	9.6	2900
7/20/99	Self Cleaned	21	9.7	3210
7/20/99	Self Cleaned	22		3340
7/20/99	Self Cleaned	24	11.9	3770
7/20/99	Self Cleaned	24		3860
7/20/99	Self Cleaned	26	17.4	4310
7/20/99	Self Cleaned	27		4250

Appendix 2 Biofouling Data

20 July 1999

Organism	Side	Inspection	Location	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Lt Slime	Port	Fouled	1 Chine	0	0	0	0	0	0	30	30	30	40	40	40	40	40	40	40	40	40	40	40
Lt Slime	Stbd	Fouled	1 Chine	0	0	0	0	0	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Lt Slime	Port	Fouled	2 Chine	0	0	0	0	0	40	40	20	40	40	40	40	40	40	40	40	40	40	50	50
Lt Slime	Stbd	Fouled	2 Chine	0	0	0	0	0	50	60	60	60	80	80	80	80	80	80	80	80	80	80	80
Lt Slime	Port	Fouled	3 Chine	0	0	0	0	30	30	30	30	30	30	30	30	30	30	30	40	40	40	40	50
Lt Slime	Stbd	Fouled	3 Chine	0	0	0	30	30	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
Lt Slime	Port	Fouled	4 Chine	0	0	30	40	40	40	30	30	40	40	40	30	30	30	30	30	30	30	30	40
Lt Slime	Stbd	Fouled	4 Chine	0	0	0	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70	70
Lt Slime	Ave	Fouled	Chine	0	0	3.75	23.3	28.3	45.7	43.8	41.3	45	48.8	48.8	47.5	47.5	47.5	47.5	48.8	48.8	48.8	50	52.5
Lt Slime	SD	Fouled	Chine	0	0	10.6	28.8	26.4	15.1	16.9	18.9	16	18.9	18.9	19.8	19.8	19.8	19.8	18.9	18.9	18.9	18.5	16.7
Lt Slime	Port	Fouled	Water Line	0	0	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
Lt Slime	Stbd	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Lt Slime	Ave	Fouled	Water Line	0	0	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Lt Slime	Port	S Cleaned	1 Chine	0	0	0	0	0	8	8	5	5	5	5	5	5	5	5	5	5	5	5	5
Lt Slime	Stbd	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	2	2	2	2	2
Lt Slime	Port	S Cleaned	2 Chine	0	0	0	0	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Lt Slime	Stbd	S Cleaned	2 Chine	0	0	0	0	5	5	5	5	5	5	5	30	10	5	5	5	5	5	5	10
Lt Slime	Port	S Cleaned	3 Chine	0	0	0	0	60	30	20	20	20	20	20	20	20	20	20	20	30	40	40	40
Lt Slime	Stbd	S Cleaned	3 Chine	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Lt Slime	Port	S Cleaned	4 Chine	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Lt Slime	Stbd	S Cleaned	4 Chine	0	0	0	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Lt Slime	Ave	S Cleaned	Chine	0	0	2.5	3.75	18.3	11	9.75	9.38	9.38	9.38	9.38	12.5	10	9.38	9.63	9.63	10.9	12.1	12.1	12.8
Lt Slime	SD	S Cleaned	Chine	0	0	3.54	2.5	22.7	11.9	10	10.2	10.2	10.2	10.2	12.2	10	10.2	9.91	9.91	11.8	14.4	14.4	14.2
Lt Slime	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	40	50	40	40	40	40	40	40	40	40	40
Lt Slime	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Lt Slime	Ave	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	20	25	20	20	20	20	20	20	20	20	20
Hvy Slime	Port	Fouled	1 Chine	0	0	0	0	0	0	0	0	10	40	10	10	0	0	20	10	0	0	0	0
Hvy Slime	Stbd	Fouled	1 Chine	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	Fouled	2 Chine	0	0	0	0	0	3	0	20	5	5	5	3	3	0	0	5	10	3	5	5
Hvy Slime	Stbd	Fouled	2 Chine	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	Fouled	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	2	0	2
Hvy Slime	Stbd	Fouled	3 Chine	0	0	0	0	20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Hvy Slime	Port	Fouled	4 Chine	0	0	0	0	5	0	0	1	0	0	0	0	0	2	0	0	0	0	0	20
Hvy Slime	Stbd	Fouled	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Ave	Fouled	Chine	0	0	0	0	6.25	2.88	0	2.63	1.88	5.63	1.88	1.63	0.38	0.25	2.5	1.88	1.5	0.63	0.63	3.38
Hvy Slime	SD	Fouled	Chine	0	0	0	0	9.46	4.52	0	7.03	3.72	14	3.72	3.54	1.06	0.71	7.07	3.72	3.51	1.19	1.77	6.95
Hvy Slime	Port	Fouled	Water Line	0	0	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Hvy Slime	Stbd	Fouled	Water Line	0	0	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80	80
Hvy Slime	Ave	Fouled	Water Line	0	0	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45
Hvy Slime	Port	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	S Cleaned	1 Chine	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	S Cleaned	3 Chine	0	0	0	0	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Stbd	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Ave	S Cleaned	Chine	0	0	0	0	1.25	1.43	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	SD	S Cleaned	Chine	0	0	0	0	2.5	3.78	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hvy Slime	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	10	10	10	10	10
Hvy Slime	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	70	70	70	70	70	70	70	70	70	70	80	80
Hvy Slime	Ave	S Cleaned	Water Line	0	0	0	0	0	0	0	0	35	35	35	35	35	35	35	40	40	40	45	45
Tubeworms	Port	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	Fouled	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	Fouled	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	9	6	0	0	0	0
Tubeworms	Port	Fouled	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	Fouled	3 Chine	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	Fouled	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	50	0	0	0	0	25
Tubeworms	Stbd	Fouled	4 Chine	0	0	0	0	0	0	0	10	0	0	0	14	0	0	0	0	0	0	0	0
Tubeworms	Totl	Fouled	Chine	0	0	0	0	0	0	2	10	0	0	0	14	0	0	59	6	0	0	0	25
Tubeworms	Ave	Fouled	Chine	0	0	0	0	0	0	0.25	1.25	0	0	0	1.75	0	0	7.38	0.75	0	0	0	3.13
Tubeworms	SD	Fouled	Chine	0	0	0	0	0	0	0.71	3.54	0	0	0	4.95	0	0	17.5	2.12	0	0	0	8.84
Tubeworms	Port	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Tot	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	4	5	6	0	0	0	0

Tubeworms	Stbd	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	2	50	100	4	0	0	0
Tubeworms	Stbd	S Cleaned	3 Chine	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Port	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	90	0
Tubeworms	Stbd	S Cleaned	4 Chine	0	0	0	0	0	0	0	9	0	0	0	12	0	0	0	0	0	0	0	0
Tubeworms	Tot	S Cleaned	Chine	0	0	0	0	0	0	2	9	0	0	0	12	2	54	105	10	3	0	90	0
Tubeworms	Ave	S Cleaned	Chine	0	0	0	0	0	0	0.25	1.13	0	0	0	1.5	0.25	6.75	13.1	1.25	0.38	0	11.3	0
Tubeworms	SD	S Cleaned	Chine	0	0	0	0	0	0	0.71	3.18	0	0	0	4.24	0.71	17.5	35.1	2.38	1.06	0	31.8	0
Tubeworms	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tubeworms	Tot	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	1	5	0	0	0	0	1	2	0	4	1
Barnacles	Stbd	Fouled	1 Chine	0	0	0	0	0	0	0	0	0	0	0	3	0	2	0	0	0	0	0	0
Barnacles	Port	Fouled	2 Chine	0	0	0	0	0	2	0	0	0	1	4	3	2	1	3	1	1	2	2	1
Barnacles	Stbd	Fouled	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	5	0	0	0	0	0	0
Barnacles	Port	Fouled	3 Chine	0	0	0	0	1	1	0	0	1	0	0	0	0	0	0	0	0	0	0	1
Barnacles	Stbd	Fouled	3 Chine	0	0	0	0	0	0	0	3	0	1	1	0	0	0	0	0	0	0	0	0
Barnacles	Port	Fouled	4 Chine	0	0	0	1	2	0	0	2	1	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	Fouled	4 Chine	0	0	0	1	3	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
Barnacles	Totl	Fouled	Chine	0	0	0	2	6	3	0	5	2	4	10	6	2	8	3	2	3	2	6	3
Barnacles	Ave	Fouled	Chine	0	0	0	0.25	0.75	0.38	0	0.63	0.25	0.5	1.25	0.75	0.25	1	0.38	0.25	0.38	0.25	0.75	0.38
Barnacles	SD	Fouled	Chine	0	0	0	0.46	1.16	0.74	0	1.19	0.46	0.53	2.05	1.39	0.71	1.77	1.06	0.46	0.74	0.71	1.49	0.52
Barnacles	Port	Fouled	Water Line	0	0	0	0	0	0	0	0	0	3	11	16	18	17	20	6	0	0	3	0
Barnacles	Stbd	Fouled	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Tot	Fouled	Water Line	0	0	0	0	0	0	0	0	0	3	11	16	18	17	20	6	0	0	3	0
Barnacles	Port	S Cleaned	1 Chine	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	S Cleaned	1 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	S Cleaned	2 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Stbd	S Cleaned	3 Chine	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Port	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0	3	0	0	0
Barnacles	Stbd	S Cleaned	4 Chine	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
Barnacles	Tot	S Cleaned	Chine	0	0	0	0	0	0	0	1	0	1	0	2	0	0	0	0	3	0	0	0
Barnacles	Ave	S Cleaned	Chine	0	0	0	0	0	0	0	0.13	0	0.13	0	0.25	0	0	0	0	0.38	0	0	0
Barnacles	SD	S Cleaned	Chine	0	0	0	0	0	0	0	0.35	0	0.35	0	0.71	0	0	0	0	1.06	0	0	0
Barnacles	Port	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	2	6	9	15	16	20	3	0	0	0	0

Barnacles	Stbd	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Barnacles	Tot	S Cleaned	Water Line	0	0	0	0	0	0	0	0	0	2	6	9	15	16	20	3	0	0	0

Appendix 3 Adhesion Data

20 July 1999

Panel	*AcroBarnacle Type*	*Date*	*Size*	*Area*	*Force(lb)*	*Adh*	*MPa Adh psi*
Port	T-Craft	BALANUS EBURNEUS					
			5/24/99	18			
				37.04	0.12	0.014	2.10 *
				85.84	0.48	0.025	3.62 *
				60.24	0.45	0.033	4.84 *
				30.27	0.24	0.035	5.13 *
				57.80	0.49	0.038	5.49 *
				45.94	0.41	0.040	5.78 *
				43.24	0.40	0.041	5.99 *
				72.28	0.69	0.042	6.18 *
				37.28	0.42	0.050	7.29 *
				69.04	0.82	0.053	7.69 *
				44.96	0.57	0.056	8.21 *
				44.41	0.57	0.057	8.31 *
				46.21	0.61	0.059	8.54 *
				61.13	0.82	0.060	8.68 *
				79.39	1.10	0.062	8.97 *
				57.92	0.87	0.067	9.72 *
				73.99	1.24	0.075	10.85 *
				74.62	1.48	0.088	12.84 *
				46.54	1.10	0.105	15.30 *
			7/22/99	12			
				36.03	0.29	0.036	5.21 *
				44.41	0.38	0.038	5.54 *
				30.53	0.41	0.060	8.69 *
				29.49	0.42	0.063	9.22 *
				39.62	0.66	0.074	10.78 *
				48.48	0.83	0.076	11.08 *
				26.39	0.58	0.098	14.23 *
				30.74	0.71	0.103	14.95 *
				20.66	0.52	0.112	16.29 *
				35.79	1.08	0.134	19.53 *
				31.26	0.99	0.141	20.50 *
				28.84	1.50	0.231	33.66 *
Starboard	T-Craft	BALANUS EBURNEUS					
			5/24/99	22			
				46.75	0.08	0.008	1.11 *

		55.72	0.11	0.009	1.28 *
		40.35	0.14	0.015	2.25 *
		52.19	0.26	0.022	3.23 *
		50.55	0.29	0.026	3.71 *
		42.53	0.28	0.029	4.26 *
		55.03	0.42	0.034	4.94 *
		76.52	0.60	0.035	5.08 *
		62.49	0.51	0.036	5.28 *
		59.21	0.52	0.039	5.68 *
		55.89	0.57	0.045	6.60 *
		58.03	0.62	0.048	6.92 *
		57.04	0.69	0.054	7.83 *
		54.62	0.90	0.073	10.67 *
		62.23	1.13	0.081	11.75 *
		55.63	1.02	0.082	11.87 *
		63.48	1.22	0.085	12.44 *
		61.11	1.23	0.090	13.03 *
	7/22/99	22			
		46.86	0.08	0.008	1.11 *
		33.29	0.38	0.051	7.39 *
		46.78	0.61	0.058	8.44 *
		48.27	0.87	0.080	11.67 *

Center for Corrosion and Biofouling Control
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CCBC-99-GE-TCRAFT February 23, 2000

The performance of the 21 foot T-Craft coated with GE RTV11 + DMSC15 and DBTDL fouling-release bottom coat.

Exposure Period: June 1998 to February 2000

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Executive Summary
In May 1998 the 22' T-Craft power boat (operated by the Center for Corrosion and Biofouling Control, Florida Institute of Technology) was coated by personnel from General Electric (GE) with the General Electric RTV11® + 10% DMSC15 oil Duplex fouling release coating. The boat was placed in the water on 15 June of 1998, and has since been monitored for biofouling barnacle adhesion strength and powering efficiency. Data from previous power trials are presented in reports submitted to GE, "The performance of the 21 foot T-Craft coated with GE RTV11® + DMSC15 and DBTDL fouling-release bottom coat". CCBC-99-GE-TCRAFT-1 March 1999 and, "The performance of the 21 foot T-Craft coated with GE RTV11® + DMSC15 and DBTDL fouling-release bottom coat". CCBC-99-GE-TCRAFT-1 August 1999.

The coating is performing very well, however, the most recent power trials suggest that the fouling-release characteristics have become reduced with time. This has reduced the self-cleaning properties and increased drag penalties due to fouling.

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Figure 5.2 % Increase in propeller rpm vs boat velocity for the fouled compared to clean hull condition (16 Feb 2000) 69

1.0 Background

The Center for Corrosion and Biofouling Control at the Florida Institute of Technology (FIT) uses a 22' T-Craft power boat for its operations in the Indian River Lagoon, Florida (Figure 2.F.3.1.1). In March 1998 it was decided to use this vessel as a test platform for the RTV11 + 10% DMSC15 oil fouling-release coating developed by General Electric (GE). The boat was removed from the water in May 1998 and the hull sand blasted to remove the existing copper based antifouling system. The boat was washed and moved under cover where a team from GE applied the fouling release coating according to the specification shown in Table 2.F.3.1.1. The coating was applied between 26 to 28 May 1998. The coating was allowed to cure and the boat launched 15 June 1998.

Figure 2.F.3.1.1 22 T-Craft with GE fouling-release bottom coat.

The fouling release performance of this coating is being evaluated at the Florida Institute of Technology Static Immersion Site. The barnacle fouling adhesion properties are shown in Table 2.F.3.1.2.

Table 2.F.3.1.1 Coating specifications for the T-Craft.

Application Layer	Date	Temp. (°F)	RH (%)	WFT (mil)
Barrier Coats				
5 gal Amerlock 400 ivory + 1 pt naphtha	5/26	88	56	22-24

2 gal Amerlock 400 pearl gray + 1 pt naphtha	5/27	77	72	14-16
Mist Coats (port and starboard side were different)				
4 gal Amerlock 400 pearl gray + 1 gal GE SCM501C (port side)	5/28	85	67	12-14 (port)
½ gal Shell Versamid + ½ gal Shell Epon 828 + 1 gal butanol (starboard side)	5/28	85	67	2-3 (stbd)
Tie Coat				
5 gal Wacker J-501 + 1 gal GE SF69	5/28	85	67	18-20
Fouling – Release Coat				
5 gal GE RTV11 + ½ gal DMSC15 + ½ gal naphtha + 30 ml DBTDL	5/28	85	67	16-20
Patch Coats				
500 g GE SEA210A + 6 ml GE SCM501C	5/29	85	65	2-3
450 ml Wacker J-501 + 50 ml GE SF69	5/29	85	65	16-20
3500 ml GE RTV11® + 350 ml DMSC15 + 10 ml DBTDL	5/29	85	65	18-20

Table 2.F.3.1.2 Barnacle adhesion strength obtained from panels coated with RTV11® + 10% DMSC 15 immersed at the FIT static immersion site on 17 July 1997

Panel Number	Days Exposure	Barnacle Type	Sample Size	Ave.Adh psi	SDAdh psi
97129A	64	BALANUS EBURNEUS	10	3.17	1.86
97129A	121	BALANUS EBURNEUS	11	2.88	2.85
97129A	823	BALANUS VARIAGATUS	1	6.38	
97129B	64	BALANUS EBURNEUS	3	1.26	1.33
97129B	378	BALANUS EBURNEUS	5	6.21	3.52
97129B	425	BALANUS EBURNEUS	18	4.07	1.97
97129B	606	BALANUS VARIAGATUS	1	2.91	
97129B	606	BALANUS EBURNEUS	4	2.84	2.95
97129B	606	BALANUS IMPROVISUS	7	3.46	2.21
97129B	823	BALANUS EBURNEUS	1	5.64	
97129B	939	BALANUS IMPROVISUS	17	3.89	2.63
97129B	939	BALANUS EBURNEUS	1	3.59	
97131A	64	BALANUS EBURNEUS	5	2.21	1.69
97131A	121	BALANUS EBURNEUS	6	1.92	1.46
97131A	823	BALANUS VARIAGATUS	2	7.79	0.74
97131B	64	BALANUS EBURNEUS	2	0.52	0.03
97131B	188	BALANUS EBURNEUS	4	1.72	0.72
97131B	243	BALANUS EBURNEUS	11	4.95	2.31

97131B	320	BALANUS IMPROVISUS	1	14.59	
97131B	442	BALANUS EBURNEUS	8	4.34	2.48
97131B	823	BALANUS VARIAGATUS	4	7.04	4.86
97131B	823	BALANUS EBURNEUS	2	4.92	1.98
97131B	939	BALANUS EBURNEUS	3	1.90	1.04
97131B	939	BALANUS IMPROVISUS	15	3.44	1.73

2.0 Instrumentation

The boat was instrumented to measure speed over the ground, speed through the water, engine revolutions per minute (rpm) and engine fuel consumption in gallons per minute (gpm) using the instrumentation shown in Table 2.F.3.2.1.

Table 2.F.3.2.1 Instrumentation for power trials.

Data	Item	Model #
Speed over the ground	Garmin GPS III	403850
Speed through the water	West Marine Speed 100 Speed/Log/Temp	266827
Engine rpm and fuel consumption	FloScan Series 8000 Fuel Computer	8000-264-1P

3.0 Method

The following procedure was used to assess the skin friction and fouling release properties of the coating during the February 2000 power trial. Underwater video of the hull could not be taken due to failure of the video camera.

- Fill fuel tanks to capacity.
- Run power trials, starting at about 2 knots. Maintain speed for 2 minutes. Monitor speed, rpm and gpm. Increase speed and repeat data collection up to speeds of about 22 knots.
- Run the boat at top speed (about 22 knots) for 20 minutes (self cleaning).
- Run power trials, starting at about 2 knots. Maintain speed for 2 minutes. Monitor speed, rpm and gpm. Increase speed and repeat data collection up to speeds of about 22 knots.
- Perform underwater visual inspection of hull.
- Take underwater hard fouling adhesion measurements.
- In-water cleaning of hull using a soft cloth.
- Run power trials, starting at about 2 knots. Maintain speed for 2 minutes. Monitor speed, rpm and gpm. Increase speed and repeat data collection up to speeds of about 26 knots.
- Analyze the boat power data to estimate performance.

4.0 Boat Operating History

The boat is used for regular research activities in the Indian River Lagoon. Table 2.F.3.4.1 summarizes the operating schedule since the coating was applied in June 1998.

Table 2.F.3.4.1 Boat operating schedule since GE coating application

Date	Activity
6/15/98	Boat launched.
6/23/98	Hull cleaned and first power trial.
6/25/98	Foil testing, run for 4 hours (0 to 25 knots).
7/1/98	Foil testing, run for 4 hours (0 to 25 knots).
7/2/98	Panel inspection and cage maintenance. 1 hour (20 knots).
7/9/98	Out of water inspection of boat.
7/17/98	Power trials.
8/4/98	Foil testing, run for 4 hours (0 to 25 knots).
8/7/98	Foil testing, run for 4 hours (0 to 25 knots).
8/22/98	Attempted power trials, postponed due to weather.
9/1/98	Attempted power trials, camera flooded.
9/10/98	Attempted power trials, postponed due to weather.
10/9/98	Inspection and cage maintenance. 1 hour (20 knots).
10/30/98	Power trials and platform maintenance.
11/20/98	Panel inspection and cage maintenance. 1 hour (20 knots).
11/23/98	Boat maintenance. 20 minutes (25 knots).
12/22/98	Panel, boat and cage inspection. 1 hour (20 knots).
12/23/98	Take boat out of water for outboard service.
1/13/99	Return boat to water.
1/29/99	Inspection and cage maintenance. 1 hour (20 knots).
2/18/99	Remove boat from water for hull modifications to improve foil data collection.
4/13/99	Launch boat with wet well and try out "new foil"
4/15/99	Tested boat/foil system in harbor
4/19/99	Panel inspection and cage maintenance. Foil run
5/5/99	Panel inspection and cage maintenance. Foil run.
5/24/99	Pulled boat.
6/3/99	Launched boat after patch repair. Panel inspection and cage maintenance. 1 hour (20 knots).
6/4/99	Power boat trial- baseline with through hull.
6/15/99	Panel inspection and cage maintenance. 1 hour (20 knots).
6/21/99	Panel inspection and cage maintenance. 1 hour (20 knots).
6/29/99	Panel inspection and cage maintenance. Hydro Panel testing.
7/1/99	Thru Hull Foil Testing failed, platform to drop off panels
7/20/99	Power Trials.
7/21/99	Panel inspection and cage maintenance. 1 hour (20 knots).
7/27/99	Ran panel S1 to completion + three calibration curves.
7/30/99	Panel inspection and cage maintenance. 1 hour (20 knots).
8/4/99	Thru Hull Testing
8/13/99	Panel inspection and cage maintenance. Foil Test.
8/18/99	Panel inspection and cage maintenance. 1 hour (20 knots).
8/23/99	Gear in starter replaced
8/24/99	Panel inspection and cage maintenance. 1 hour (20 knots).
8/25/99	Panel inspection 1 hour (20 knots).,
8/27/99	Platform preparation for Hurricane Dennis 1 hour (20 knots)..
8/30/99	Boat removed from water for mechanical maintenance.

9/8/99	Boat returned to water.
9/10/99	Foil testing and panel inspection 1 hour (20 knots)..
9/16/99	Inspected damage to platform Hurricane Floyd. Status okay 1 hour (20 knots).
9/23/99	Platform repair 1 hour (20 knots)..
9/28/99	Panel inspection, Adhesion testing 1 hour (20 knots)..
9/30/99	Thru hull testing, panel inspection 2 hour (20 knots).
10/4/99	Drag testing 2 hour (20 knots).
10/14/99	Platform secured due to Hurricane Irene 1 hour (20 knots)..
10/18/99	Hurricane Irene impact on platform checked, Boat maintenance 1 hour (20 knots)..
10/19/99	Platform repaired 1 hour (20 knots).
10/28/99	Panel inspection and cage maintenance 1 hour (20 knots)..
11/1/99	Cage repaired 1 hour (20 knots)..
11/18/99	Panel inspection 1 hour (20 knots)..
11/29/99	Panel inspection and cage maintenance 1 hour (20 knots)..
12/9/99	Drag testing, panel inspection 2 hour (20 knots)..
1/12/00	Panel inspection and cage maintenance 1 hour (20 knots)..
1/13/00	Platform and panel inspection 1 hour (20 knots)..
1/19/00	Platform and panel inspection 1 hour (20 knots)..
1/26/00	Panel inspection and cage maintenance 1 hour (20 knots)..
2/4/00	Panel inspection 1 hour (20 knots)..
2/11/00	Panel inspection and cage removed 1 hour (20 knots)..
2/16/00	Power trials. Boat maintenance and panel inspection 1 hour (20 knots)..

5.0 Boat Biofouling and Powering Data

5.1 Biofouling

The hull was covered by a heavy slime/microalgal film that showed no signs of being removed by hydrodynamic forces, which were generated when the boat was underway. The film was tenacious and took a large effort to remove using a soft cloth. There was only scattered hard fouling on the major underwater portion of the hull. This included less than 50 individual barnacles and tubeworms. Large numbers of barnacles were, however, present on the transom which is in a hydrodynamically quiet zone

5.2 Barnacle Adhesion Data

Barnacle adhesion data were obtained for the port and starboard side and the transom of the boat. No significant differences were seen between the adhesion strength of barnacles to the different areas of the boat. However, there does appear to have been an increase in barnacle adhesion strength with time. This would suggest that there has been a change in the fouling release properties of the coating since it was applied in June 1998.

Table 2.F.3.5.1 Barnacle Adhesion Data for the T-Craft RTV11+ 10% DMSC15 Coating

Position	Days Exposed	Barnacle Type	Sample Size	Ave.Adh psi	SD Adh psi
Port	343	BALANUS EBURNEUS	18	7.61	3.24
Port	402	BALANUS EBURNEUS	12	14.14	7.89
Port	441	BALANUS EBURNEUS	18	13.73	5.40
Port	611	BALANUS IMPROVISUS	17	13.74	6.11
Starboard	343	BALANUS EBURNEUS	17	6.24	3.78
Starboard	402	BALANUS EBURNEUS	4	7.15	4.42
Starboard	441	BALANUS EBURNEUS	18	12.25	4.19
Starboard	611	BALANUS IMPROVISUS	10	13.20	6.16
Transom	402	BALANUS EBURNEUS	14	6.48	3.91
Transom	611	BALANUS IMPROVISUS	8	13.24	5.48

5.3 Powering Data

The most recent power trials were run on 16 February 2000. Powering data are presented as propeller revolutions per minute (rpm) versus boat speed (knots). Third order polynomials were run on the rpm vs. boat speed curves. From the curve fit equations the performance data are presented as percentage change in rpm from the clean hull condition. Because the boat is a planing hull, there will rarely be an exact match of rpm and boat speed, however, the data clearly show differences in performance due to biofouling.

Table 2.F.3.5.2 3rd OrderPolynomial Equations for Power Trials

Run	Condition	Equation
1	Fouled	y = 1.0309x3 - 42.193x2 + 669.16x - 893.19
2	Self Cleaned	y = 0.7902x3 - 34.74x2 + 608.4x - 870.98
3	Clean	y = 0.5121x3 - 24.532x2 + 481.29x - 574.49

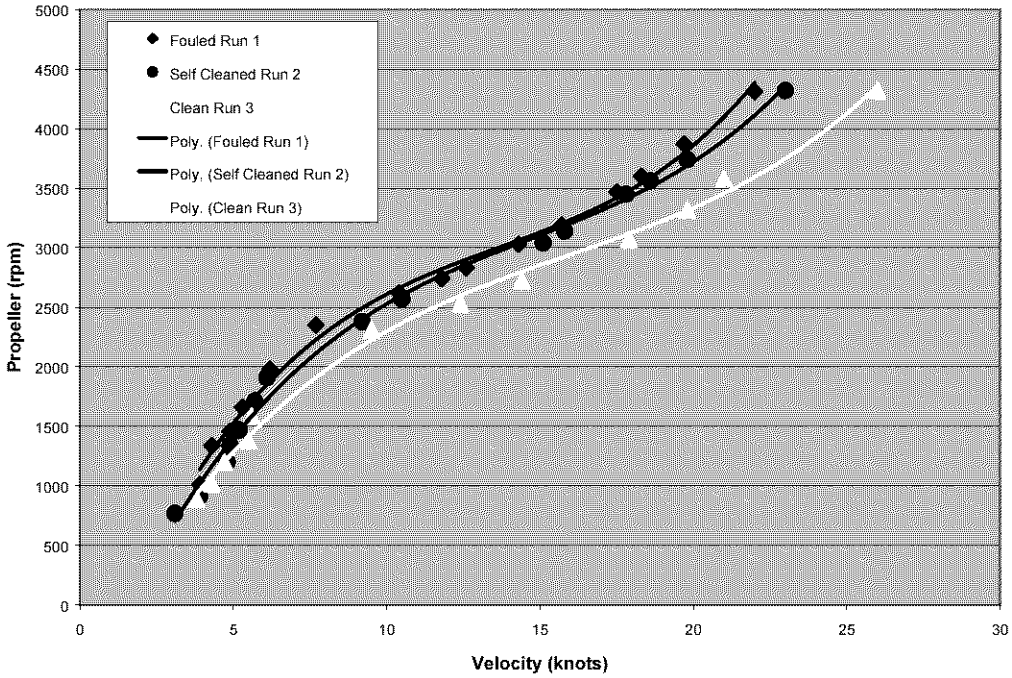

Figure 2.F.3.5.1 Propeller rpm vs. boat velocity for the three power trials (16 Feb 2000).

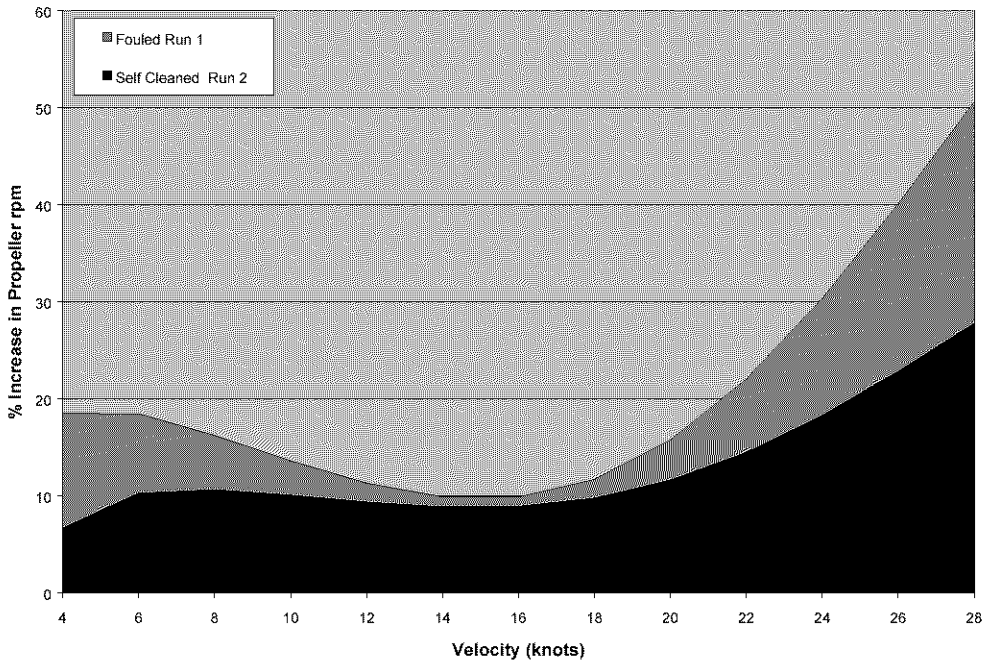

Figure 2.F.3.5.2 Percentage increase in propeller rpm vs. boat velocity for the fouled compared to clean hull condition (16 Feb 2000).

The data demonstrated that the heavy slime and microalgae films that had developed on the hull significantly reduced performance. The initial power trial (run 1) had slightly higher powering penalties than the second power trial (run 2) which was run after approximately 20 minutes of self cleaning at 20 knots. However, no significant self-cleaning occurred. The power trial data obtained after the hull had undergone an in-water clean showed between a 10 to 20% improvement in performance over the non-cleaned condition.

6.0 Physical Condition

The overall physical condition of the coating is excellent, with no signs of blistering or delamination.

7.0 Summary

The RTV11® + 10% DMSC15 oil coating has shown good overall characteristics, however, it appears that the fouling-release performance has declined from the original condition. This is demonstrated by observing the increase in barnacle adhesion strength with time (between 6 to 8 psi at day 343 and between 13 to 14 psi day 611). Furthermore, the most recent power trials showed that the coating was no longer able to self clean from the slime and microalgae fouling.

It is worth noting that the static immersion panels have retained their fouling release properties for at least 900 days. This would suggest that either there is a difference in the properties of the panel and boat coatings, or that the dynamic conditions created by an operational boat enhances the removal of the oil from the coating, hence reducing the fouling-release properties. It is well known that static immersion testing may not provide sufficient hydrodynamic energy to challenge the release properties of coatings.

Appendices

Power Data

Hull Condition	Speed (knots)	Propeller (rpm)	Fuel (gph)
Run 1			
Fouled	3.9	1010	1.6
Fouled	4.3	1340	2.3
Fouled	4.9	1460	2.7
Fouled	5.3	1660	3.9
Fouled	5.7	1720	4.2
Fouled	6.2	1980	5.6
Fouled	7.7	2350	6.6
Fouled	10.4	2620	7.3
Fouled	11.8	2740	7.5
Fouled	12.6	2830	8.1
Fouled	14.3	3030	9.7
Fouled	15.7	3190	10.1
Fouled	17.5	3470	10.6

Fouled	18.3	3600	11.3
Fouled	19.7	3870	13.3
Fouled	22	4310	16.3
Run 2			
Self Cleaned	3.1	770	1.5
Self Cleaned	3.9	910	1.6
Self Cleaned	4.8	1200	2
Self Cleaned	4.9	1340	2.2
Self Cleaned	5.2	1470	2.6
Self Cleaned	5.7	1710	4.3
Self Cleaned	6.1	1910	5.1
Self Cleaned	9.2	2380	6.4
Self Cleaned	10.5	2570	7.1
Self Cleaned	15.1	3040	8.6
Self Cleaned	15.8	3140	9.2
Self Cleaned	17.8	3450	11.2
Self Cleaned	18.6	3560	11.6
Self Cleaned	19.8	3740	12
Self Cleaned	23	4320	16.5
Run 3			
Clean	3.8	890	1.9
Clean	4.3	1020	2.2
Clean	4.7	1200	2.3
Clean	5.5	1380	2.6
Clean	5.6	1590	3.6
Clean	9.5	2310	6.1
Clean	12.4	2530	6.7
Clean	14.4	2720	7.7
Clean	17.9	3070	8.8
Clean	19.8	3320	9.7
Clean	21	3580	11.2
Clean	26	4320	16.5

APPENDIX 3. TOXICITY DATA

Appendix 3.A. Summary of coating toxicity measured using EPA test methods.

Table 3.A.1 . Summary of coating toxicity measured using EPA test methods. Numbers in parentheses designate the number of the downselect coating DBTDL refers to dibutyltindilaurate.

Coating	Mysid LC_{50}	Silverside Fish LC_{50}	Diatom IC_{50}	DBTDL (µg/L) 100% exudate (1st 24 soak)	DBTDL (µg/L) 100% exudate (4th 24 soak)
RTV11® (1)	135%	>300%	9%	966	1823
Silica filled base	143%	>300%	33%	69	78
RTV11® + 10% SF1154 (2)	212%	>300%	63%	60	72
RTV11® + 10% DBE224 (3)	142%	>300%	102%	42	271
RTV11® + 10% DMSC15 (5)	246%	>300%	105%	57	95
RTV11® + 10% SF1147 (8)	221%	>300%	205%	36	111
RTV11® + 10% ablative carbinol (10)	25%	9%	9%	1	1
RTV11® + 10% ablative phenyl (11)	131%	>300%	23%	91	93
RTV11® + 10%CMS222 (12)	193%	>300%	55%	100	174
RTV11® + DMSC25 (16)	185%	>300%	14%	497	1996
RTV511 + DMSC15 (17)	185%	>300%	22%	322/	1097
Commercially available silicone coating	>300%	>300%	10%	267	73
Ablative copper coating	10%	5%	8%	820 ug/L Cu++	820 ug/L Cu++

Appendix 3.B. Final report from SPAWAR

Marine Acute and Chronic Toxicity Test Results of Silicone Foul-Release Coatings to the Mysid Shrimp (*Mysidopsis bahia*), the Inland Silverside (*Menidia beryllina*), and the Chain Diatom (*Skeletonema costatum*).

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EXECUTIVE SUMMARY

The U.S. Navy requires hull coatings that are environmentally acceptable, have an effective fouling resistance, and are durable enough to perform for a minimum of five to seven years. An effective and durable silicone foul-release coating system, over a five-year cycle, will result in increased hull speeds, reduced fuel consumption, decreased underwater hull cleaning, reduced scheduled docking requirements, and minimized hazardous waste generation during coating removal.

A series of acute static-renewal (96-hour) EPA approved bioassays were conducted to estimate the potential toxicity of 13 silicone foul-release coatings manufactured by General Electric. One coating was also tested for chronic effects (growth and survival) with a 7-day test. Bioassays were conducted on the mysid shrimp (*Mysidopsis bahia*), the inland silverside (*Menidia beryllina*), and the marine chain diatom (*Skeletonema costatum*). Two additional coatings (GE-0 and International Paints' copper-based BRA 640), previously tested with the shrimp and silverside, were tested only with the chain diatom.

LC_{50}'s (the concentration of a toxicant lethal to 50% of the tested population) or IC_{50}'s (the concentration of a toxicant that inhibits 50% of the parameter of interest; i.e. chlorophyll fluorescence) were observed in all diatom tests and all but one mysid test, but only three coatings produced LC_{50}'s in the fish tests. DBT was measurable in all coating leachates. However, a general correlation between toxicity and DBT concentration was not apparent. For most coatings, the leach rate of DBT was higher at Day 4 of the bioassays than at Day 1.

Of the 13 silicone coatings tested, RTV11® + 10% ablative carbinol was the most toxic for all three species, generating LC_{50}'s at 9% and 25% for the fish and mysid respectively, and an IC_{50} at 9% solution for the diatom. DBT measurements for this coating were extremely low, suggesting that other compounds were responsible for its lethality. The second most toxic coating, 2001-4-6 Treco also contained relatively low DBT levels. At 31 and 92 ug/L DBT for Day 1 and Day 4 leachates, respectively, it is feasible that DBT may have contributed to its toxicity.

As a group, C180-140-1, C180-140-2 and C180-140-3 demonstrated relatively moderate toxicity, with C180-140-2 apparently the most lethal of the three. This group leached the most DBT (322 – 1996 μg/L in 100% leachates) of all coatings tested, and it is suspected that these high concentrations played a role in the fate of organisms exposed to these coatings. For these three coatings, there did appear to be a correlation between DBT and toxicity to the mysids and diatoms, with C180-140-2 leaching the most DBT, followed by C180-140-1 and then C180-140-3.

Although IC_{50}'s were observed in all chain diatom tests, RTV11® + 10%, ALT251, RTV11® + 10% CMS222, RTV11® + 10% DBE224, RTV11® + 10% DMSC15, and RTV11® + 10% SF1154 demonstrated relatively low toxicity. The only discrepancy was

RTV11® + 10% DBE224, which produced relatively high toxicity in both the fish and mysids.

C507-64-1 was the only coating that did not produce an LC_{50} in the mysids. No toxicity was observed in either the acute or the chronic fish tests, but the diatom was very sensitive to this coating, where an IC_{50} of 10% was observed.

GE-0 and BRA 640 were both highly toxic to the chain diatom (the only species tested for these two coatings), resulting in IC_{50}s with11 and 8% solutions, respectively. High copper concentration (820 μg/L) in the 100% leachates probably contributed to toxicity observed in BRA 640.

INTRODUCTION

The U.S. Navy requires hull coatings that are environmentally acceptable, with effective fouling release and endurance to perform for a minimum of five to seven years. An effective and durable coating should increase hull speeds, reduce fuel consumption, decrease the need for underwater hull cleaning, reduce the need for scheduled docking, and minimize the generation of hazardous waste during coating removal.

A series of static-renewal (96-hour) EPA (Environmental Protection Agency) approved bioassays were conducted to estimate the potential toxicity of 13 silicone foul-release coatings on the mysid shrimp (*Mysidopsis bahia*), the inland silverside (*Menidia beryllina*), and the marine chain diatom (*Skeletonema costatum*). A chronic 7-day bioassay was performed on one coating. In addition, a copper sulfate reference solution was tested (positive control) on all species. Bioassay organisms representing different phyla were chosen and tested to represent a potential "risk" to the marine environment. Mysid shrimp were selected to represent a benthic, or bottom-dwelling, response, while inland silversides (fish) were selected to represent a pelagic, or swimming, animal response. The phytoplankton marine chain diatom was used to observe any potential effects on the primary producers in marine waters. The end-points measured were survival in the mysids and fish (LC_{50}: = the concentration of a toxicant that results in mortality of 50% of the tested population), growth in the fish (mean weight, mg), and biomass, or chlorophyll fluorescence, in the diatoms (IC_{50}: = the concentration of a toxicant that inhibits 50% of a physiological process).

Coating extracts were analyzed for the leachable catalyst dibutyltin dilaurate (DBT) or total copper. Coatings were leached in seawater and 100% leachates were analyzed by hydride derivitization followed by atomic absorption for DBT measurements. Copper was measured from 100% leachates with a HACH DR/2000 Spectrophotometer.

MATERIALS AND METHODS

Test Equipment Preparation for Mysids and Fish

All test chambers were constructed from borosilicate glass beakers with lids. The copper reference assays were conducted in polypropylene tri-pour beakers. All beakers were washed with a critical cleaner (Citranox) and rinsed with 10% nitric acid. A minimum of three deionized water rinses followed each cleaning procedure. All acute toxicity tests with the mysids were conducted in 300 ml beakers with 200 ml dilution water. The fish were maintained in 400 ml beakers containing 250 ml of dilution water for acute tests and 600 ml beakers containing 500 ml of dilution water for chronic tests.

Source and Acclimation of Test Species

One-day old mysids and seven-day old fish were shipped overnight from Aquatic Indicators, St. Augustine, Florida, to our laboratory. Both species were slowly

acclimated in a 25°C waterbath and transferred by pipette to holding tanks containing filtered (0.45 μm) seawater. The dilution water used for testing was obtained from the SPAWAR Biological Effects Program (BEP) bioassay facility located near the mouth of San Diego Bay, California. Water was filtered through a coarse sand filter prior to filtration through a 5 μm filter cartridge and finally a 0.45 μm filter cartridge. The test animals were slowly acclimated to the test water salinity of $33^{0}/_{00}$ (parts per thousand) over a period of 3 to 4 days from an initial salinity of approximately $20^{0}/_{00}$. All test organisms were fed daily with freshly hatched *Artemia* brine shrimp.

The marine diatom *Skeletonema costatum* was obtained from Monterey, California. The cultures were maintained on an enriched seawater medium (ESM) (ASTM, 1995) using filtered (0.22 μm) seawater collected at our test facility. Sub-samples (approximately 1 ml) of stock cultures were routinely aliquoted into fresh media to maintain high cell densities. The diatom was cultured in an incubator at 20°C under cool white fluorescent bulbs at a light intensity of approximately 4000 lux for 12 hours per day.

Preparation of Seawater Extracts for All Coatings

All test coupons (~ 3.8 cm X 3.8 cm in size) were soaked in filtered (0.45 μm) seawater for 24 hours at 25 °C prior to use. New solutions were made daily using the same test coupons for the following day's water renewal. An initial dose of one coupon soaked for 24 hours in 250 ml of filtered seawater was tested for some coatings (1 coupon/250 ml seawater soaked for 24 hours = 100% extract or leachate). An increase in dosage was accomplished by soaking 3 coupons in 250 ml of filtered seawater (300% extract or leachate = 12 coupons or equivalent surface area of the coating soaked in 1 liter of seawater for 24 hours). Extracts ran as high as 300% for all bioassays while lower concentrations were made by diluting the 300% solution with makeup water. Leachates (100% concentration) were analyzed for DBT by purge and trap hydride derivitization followed by atomic absorption (Stallard et al., 1989). Identification of DBT was accomplished by gas chromatography (Testa and Dooley, 1989; Meyers-Schulte and Dooley, 1990). Detection of tin is at less than 1 part per trillion (nanograms per liter). One leachate (BRA 640) was analyzed for copper with a HACH DR/2000 Spectrophotometer.

Experimental Test Design and Protocols for Mysidopsis bahia and Menidia beryllina (Acute)

Toxicity testing of all coatings consisted of 4-day static-renewal acute tests. These assays were conducted to assay for potential toxicity arising from exposure to silicone-based coatings in both species. Reference tests with the toxicant copper sulfate were conducted alongside the coating tests to ensure good health and normal sensitivity of the test organisms.

Environmental Protection Agency (EPA) test protocols were followed for the mysid and fish bioassays (EPA/600/4-90/027F, August 1993). For acute bioassays, test chamber sizes for the mysids and fish were 300 and 400 ml beakers filled with 200 and 250 ml of

leachate solution, respectively. The average age of the animals was 5 days and 13 days at the start of the bioassays for the mysids and fish, respectively. Ten animals were administered to each beaker. Each test concentration was replicated twice. Assays began by pouring approximately 50 ml of the appropriate test dilution into beakers, gently pipetting organisms from holding tanks into the beakers, and topping off with test solution to a final volume of either 200 or 250 ml. Test beakers were covered with glass lids and held in a recirculating waterbath at 25°C. All animals were fed daily with newly hatched *Artemia* brine shrimp. Solutions were renewed every 24 hours at which time beakers were cleaned and seawater chemistry measurements (temperature, pH, dissolved oxygen) were recorded. Minimum requirements for test acceptability for dissolved oxygen are 40% saturations for acute tests and the seawater temperature must not fluctuate more than ± 2°C.

Test concentrations ranged from 18.75% to 300% extract. In addition, seawater controls were used for each test. Percent survival was calculated and graphed for all tests. LC_{50} and IC_{50} values were estimated by linear interpolation between the two concentrations whose responses bracketed the response of interest (EPA/600/R-95/136, August 1995). The EPA requires that at least 90% of larvae in the controls survive for the test to be acceptable.

Experimental Test Design and Protocols for Menidia beryllina (Chronic)

A 7-day bioassay was conducted to measure potential chronic effects of one coating for the fish. As with the acute bioassays, EPA methods were followed in the chronic tests (EPA/600/4-91/003, July 1994). Test chambers for chronic bioassays were 600 ml beakers filled with 500 ml of leachate solution. The age of animals at the start of the test was 10 days. Ten fish were administered to each beaker. Each test concentration was replicated three times. Chronic tests were conducted under the same conditions as acute tests. As with the acute tests, a copper reference test was run alongside the coating test to ensure good health and normal sensitivity of the test organisms.

At the end of the chronic tests, surviving fish were sacrificed by exposure to a cold water bath. After a freshwater rinse to remove *Artemia* and salts, fish were placed on tarred weighing pans and dried for 24 hours at 60 °C. Mean individual weight was calculated for each test concentration and plotted against the control weights to determine if there was any effect on growth. Chronic test results are acceptable if a) the average survival of control larvae is at least 80% and b) average dry weight of surviving control larvae is at least 0.5 mg.

Experimental Test Design and Protocols for Chain Diatom Biomass (Fluorescence) in Skeletonema costatum

Prior to testing, subcultures of *Skeletonema* were maintained in enriched seawater medium (ESM) in 500 ml borosilicate Erlenmeyer flasks under a light regime of 12:12 hours (light:dark) at a light intensity of approximately 4000 lux from cool white fluorescent bulbs. Culture temperature was maintained at 20°C. Test protocols used

were from the American Society for Testing and Materials Standard Guide for Conducting Static 96-hr Toxicity Test with Microalgae E1218 (ASTM, 1995). At the beginning of each assay, test flasks containing 150 ml of test solution were inoculated with approximately 2 X 10^4 cells/ml *Skeletonema*. Test solution was made by combining leachate and filtered (0.22 μm) seawater in appropriate volumes to achieve the desired dilution (i.e. 18.75% extract). For most tests, dilutions ranged from 18.75% to 300%. Test concentrations for BRA 640 and GE-0 assays ranged from 0.5% to 100%. Seawater controls were used in each test. As with the fish and mysids, seawater was collected from the SPAWAR test facility in Point Loma, San Diego, California. No leachates exhibited a background fluorescence that could confound test results. A Turner Model 112 fluorometer was used to measure *in vivo* fluorescence from the growing cultures. The fluorometer was equipped with a combination T-5 lamp, a red sensitive photomultiplier tube (R-136), a blue excitation filter (5-60), and a red filter (2-64) to detect fluorescence at wavelengths > 640 nanometers (nm). Chlorophyll *a* fluorescence has maximum emission at 663 nm. The fluorometer was zeroed between readings with filtered (0.22 μm) seawater. All flasks were read within one hour after introduction of the diatoms into the flasks and at 24-hour intervals for a period of 96 hours. The measured fluorescence is directly related to cell number and to the presence of viable diatom cells relative to the leachate concentration. Mean relative fluorescence, standard deviation, and coefficient of variation were calculated for the controls and each leachate concentration. Relative fluorescence, expressed as percent of control was plotted over time for the entire test. An IC_{50} was calculated from 96-hour data. The test acceptability criteria for this test require that the controls contain at least 10^5 cells/ml at 96 hours.

RESULTS

All bioassays were completed successfully and deemed valid according to EPA acceptability criteria (i.e. control survival greater than or equal to 90% in the mysid and fish tests and control densities greater than 10^5 cells/ml in the diatom test). Water quality parameters were within acceptable ranges and copper sulfate reference tests resulted in acceptable LC_{50}'s. A summary of results for all coatings tested is presented in Table 3.B.1.

Toxicity of RTV + 10% Ablative Carbinol and RTV + 10% Ablative Phenyl to Mysidopsis bahia (mysid shrimp), Menidia beryllina (inland silverside), and Skeletonema costatum (chain diatom)

Leachate concentrations ranged from 18.75% to 300% for all tests. RTV11® + 10% ablative carbinol was the most toxic among the 13 coatings tested with all three species (Table 3.B.1). LC_{50}s were observed at 25% and 9% leachate for the mysid (Figure 3.B.3) and fish (Figure 3.B.4) tests, respectively. An IC_{50} was estimated at 9% leachate for the chain diatom (Figures 3.B.5, 3.B.6). Nearly complete inhibition of chlorophyll fluorescence was observed at the lowest concentration (18.75%) after only one day of exposure (Figure 3.B.5). Very low levels of DBT (0.8 and 0.5 μg/L on day 1 and day 4, respectively) were measured in the 100% leachate (Table 3.B.1, Figure 3.B.2).

RTV11® + 10% ablative phenyl was relatively toxic to both the mysid shrimp (Figure 3.B.7) and chain diatom (Figures 3.B.9, 3.B.10; LC_{50} of 131% and IC_{50} of 23% leachate, respectively), but no LC_{50} occurred in the fish bioassay (Figure 3.B.8, Table 3.B.1). Some mortality was observed in the fish, beginning with the 150% leachate (85% survival, Figure 3.B.8). DBT concentrations in the 100% leachate were 91 μg/L on extracts prepared for day 1 and 93 μg/L for day 4 of the acute bioassays (Table 3.B.1, Figure 3.B.2).

Toxicity of 2001-1-1 Treco and 2001-4-6 Treco to Mysidopsis bahia (mysid shrimp), Menidia beryllina (inland silverside), and Skeletonema costatum (chain diatom)

Leachate concentrations ranged from 18.75% to 300% for all tests. For 1-1 Treco, an LC_{50} was observed at 143% leachate for the mysids (Figure 3.B.11), but no LC_{50} was obtained for the fish. Survival of the fish, however, was only 60% in the 300% leachate (Figure 3.B.12). An IC_{50} was observed in the chain diatom at 33% leachate (Figures 3.B.13, 3.B.14). DBT measurements were 69 μg/L in Day 1 100% leachates and 78 μg/L in Day 4 100% leachates (Table 3.B.1, Figure 3.B.2).

The 4-6 Treco was more toxic than 1-1 Treco for all three species tested (Table 3.B.1). LC_{50}s were observed at 113% leachate for the mysid shrimp (Figure 3.B.15) and 286% leachate for the fish (Figure 3.B.16). An IC_{50} was generated at 10% leachate for the

chain diatom (Figures 3.B.17, 3.B.18). The DBT concentration in the 100% leachate was 31 µg/L (Day 1) and 93 µg/L (Day 4) (Table 3.B.1, Figure 3.B.2).

Toxicity of C180-140-1, C180-140-2, and C180-140-3 to Mysidopsis bahia (mysid shrimp), Menidia beryllina (inland silverside), and Skeletonema costatum (chain diatom)

Toxicity of this group of coatings was mixed, with relatively high toxicity observed in the diatom, moderate toxicity in the mysid shrimp, and essentially no toxicity in the fish. Mysid LC_{50}'s were the same (185% leachate) for both C180-140-1 and C180-140-3 (Figures 3.B.19, 3.B.27). IC50's for the chain diatom were 14% leachate and 22% leachate for C180-140-1 and C180-140-3, respectively (Figures 3.B.21, 3.B.22, 3.B.29, 3.B.30). No LC50's were noted in the fish for either coating (Figures 3.B.20, 3.B.28). C180-140-1 and C180-140-3 DBT values were 497 and 322 µg/L in Day 1 100% leachates and 1996 µg/L and 1097 µg/L in Day 4 leachates, respectively (Table 3.B.1, Figure 3.B.2).

C180-140-2 exhibited the most toxicity among the three coatings, with a mysid LC_{50} at 135% leachate (Figure 3.B.23) and diatom IC_{50} at 9% leachate (Figures 3.B.25, 3.B>26). Only a slight lethal response was observed in the fish, where 85% survival was recorded in the 300% concentration (Figure 3.B.24). DBT measurements in C180-140-2 were the highest among the coatings tested (966 µg/L at Day 1 and 1823 µg/L at Day 4; Table 3.B.1, Figure 3.B.2).

Toxicity of RTV + 10% ALT251, RTV + 10% CMS222, RTV + 10% DBE224, RTV + 10% DMSC15, and RTV + 10% SF1154 to Mysidopsis bahia (mysid shrimp), Menidia beryllina (inland silverside), and Skeletonema costatum (chain diatom)

In general, this group exhibited relatively low toxicity. Of the five, DBE 224 was the most lethal coating to the mysid shrimp, producing an LC_{50} at 142% leachate (Figure 3.B.39). The remaining four coatings exhibited less toxicity (Table 3.B.1). LC_{50s} were 193% for CMS222 (Figures 3.B.37, 3.B.38), 212% for SF1154 (Figures 3.B.49, 3.B.50), and 221% for ALT251 (Figures 3.B.33, 3.B.34), and 246% leachate for DMSC15 (Figures 3.B.45, 3.B.46).

The fish bioassays also revealed DBE224 to be the most toxic in this group of five coatings, with an LC_{50} observed at 300% (Table 3.B.1, Figure 3.B.40). No other coatings in this group resulted in LC_{50s} with fish, but some mortality was noted in the higher concentrations. In the 300% test solutions, survival was 65% for DMSC15 (Figure 3.B.44), 80% for ALT251 (Figure 3.B.32) and SF1154 (Figure 3.B.48), and 85% for CMS222 (Figure 3.B.36).

Of the three species used, the chain diatom was the most sensitive to this group of coatings. CMS222 (IC_{50} = 55% leachate) (Figures 3.B.37, 3.B.38) and SF1154 (IC_{50} = 63% leachate) (Figures 3.B.49, 3.B.50), however, were more toxic than DBE224, where an IC_{50} of 102% leachate was obtained (Figures 3.B.41, 3.B.42). DMSC15 produced an

IC_{50} at 105% leachate (Figures 3.B.45, 3.B.46), while ALT251 (IC_{50} = 205% leachate) (Figures 3.B.33, 3.B.34) was the least toxic of all 12 coatings for the diatom bioassays.

DBE224 and CMS222 leached the most DBT in this group, with Day 1 measurements of 42 and 100 μg/L and Day 4 measurements of 271 and 174 μg/L, respectively, in the 100% leachates (Table 3.B.1, Figure 3.B.2). DBT values were 36 μg/L (Day 1) and 111 μg/L (Day 4) for ALT251, 57 μg/L (Day 1) and 95 μg/L (Day 4) for DMSC15, and 60 μg/L (Day 1) and 72 μg/L (Day 4) for SF1154 (Table 3.B.1, Figure 3.B.2).

Toxicity of C507-64-1 to Mysidopsis bahia (mysid shrimp), Menidia beryllina (inland silverside), and Skeletonema costatum (chain diatom)

Leachate concentrations ranged from 18.75% to 300% for both acute and chronic toxicity bioassays. This was the only coating of the 13 tested where no LC_{50} was observed in the mysids (Figure 3.B.51). Some toxicity, however, was apparent at 300% leachate, where only 70% of the mysids survived (Figure 3.B.51).

No effect on survival was observed in either the acute or chronic fish tests (Figures 3.B.52, 3.B.53). In addition, there did not appear to be any effect on fish growth (Figure 3.B.54). Mean individual weight of control fish well exceeded the minimum 0.50 mg required for chronic test acceptability (Figure 3.B.54).

C507-64-1 was among the most toxic coatings to the chain diatom, where an IC_{50} of 10% leachate was observed (Figures 3.B.55, 3.B.56).

Acute 100% leachates contained 267 μg/L and 73 μg/L DBT on Day 1 and Day 4, respectively (Table 3.B.1, Figure 3.B.2). The chronic leachates, which were prepared from different paint samples, contained 85 and 81 μg/L DBT on Days 1 and 4, respectively. The Day 7 chronic leachate contained 85 μg/L DBT.

Toxicity of BRA 640 and GE-0 to Skeletonema costatum (chain diatom)

Leachate concentrations ranged from 0.5% to 100%. Both coatings were highly toxic to the diatom, with IC_{50s} observed at 8% and 11% solution for BRA 640 (Figure 3.B.57, 3.B.58) and GE-0 (Figure 3.B.59, 3.B.60), respectively. Copper levels for BRA 640 (820 μg/L in 100% leachate) were much higher than what is normally required to produce an IC_{50} in the chain diatom (Table 3.B.1). DBT was not measured in either of these coatings.

Toxicity of copper sulfate (reference toxicant) to Mysidopsis bahia (mysid shrimp) and Menidia beryllina (Inland silverside)

Exposure to copper sulfate reference solutions ranged between 18.75 and 300 μg/L in addition to a seawater control. LC_{50s} were observed in the mysid (216 μg/L) (Figure 3.B.61) and in the fish (200 μg/L) (Figure 3.B.62). An LC_{50} was observed at 214 μg/L

copper in the chronic fish test (Figure 3.B.63). These results were within the expected toxicity range (137-196 µg/L for mysids and 124-362 µg/L for fish) (Morrison et al., 1989).

CONCLUSIONS

The chain diatom appeared to be the most sensitive species tested, followed by the mysid shrimp and the less sensitive fish. IC_{50s} were observed in all diatom tests, and all but one mysid test (C507-64-1) resulted in an LC_{50}. Only three coatings, however, produced LC_{50s} in the fish tests. DBT was measurable in all coating leachates, but a general correlation between toxicity and DBT concentration was not apparent. In general, the leach rate of DBT was higher at Day 4 of the bioassays than at Day 1.

The most toxic coating of those tested with all three species was RTV11® + 10% ablative carbinol. Although extreme toxicity was observed in all three bioassays, leachates from the coating contained minimal DBT, suggesting that other compounds were responsible for its lethality. The second most toxic coating, 2001-4-6 Treco also contained relatively low DBT levels. Concentrations of 31 and 92 µg/L DBT for Day 1 and Day 4 leachates, respectively, however, suggest that it is feasible that DBT may have contributed to its toxicity.

As a group, C180-140-1, C180-140-2, and C180-140-3 demonstrated relatively moderate toxicity, with C180-140-2 apparently the most lethal of the three. DBT concentrations in this group were at least one order of magnitude higher than most other coatings analyzed (322 – 1996 µg/L in 100% leachates) and likely played a role in the fate of organisms exposed to these leachates. For these three coatings, there did appear to be a positive relationship between DBT and toxicity to the mysids and diatoms, with C180-140-2 leaching the most DBT, followed by C180-140-1 and then C180-140-3 (Table 3.B.1, Figure 2).

Although IC_{50}'s were observed in all chain diatom tests, RTV11® + 10% ALT251, RTV11® + 10% CMS222, RTV11® + 10% DBE224, RTV + 10% DMSC15, and RTV11® + 10% SF1154 resulted in relatively low toxicity. The only discrepancy was RTV11® + 10% DBE224, which caused relatively high mortality in both the fish and mysids.

C507-64-1 was essentially non-toxic to both fish and mysids. This was the only coating that did not produce an LC_{50} for the mysids. The diatom, however, was very sensitive to this coating, which could be due at least in part to relatively high levels of DBT (267 µg/L) measured in the day 1 acute 100% leachate.

GE-0 and BRA 640 were both highly toxic to the chain diatom (the only species tested for these two coatings), resulting in IC_{50s} of 11 and 8% solution, respectively. High copper concentration (820 µg/L) in the 100% leachates probably contributed to toxicity observed in BRA 640.

ACKNOWLEDGEMENTS

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Table 3.B.1 Summary of test results.

Table 1

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Summary of Test Results

Coating	Mysid Test LC50	Fish Test LC50	Diatom Test IC50	DBT (ug/L) 100% leachate (Day 1/ Day 4)
RTV + 10% ablative carbinol	25%	9%	9%	1/1
RTV + 10% ablative phenyl	131%	>300%	23%	91/93
2001-1-1 Treco	143%	>300%	33%	69/78
2001-4-6 Treco	113%	286%	10%	31/92
C180-140-1	185%	>300%	14%	497/1996
C180-140-2	135%	>300%	9%	966/1823
C180-140-3	185%	>300%	22%	322/1097
RTV + 10% ALT251	221%	>300%	205%	36/111
RTV + 10% CMS222	193%	>300%	55%	100/174
RTV + 10% DBE224	142%	300%	102%	42/271
RTV + 10% DMSC15	246%	>300%	105%	57/95
RTV + 10% SF1154	212%	>300%	63%	60/72
GE-0	-	-	11%	-
BRA 640	-	-	8%	820 ug/L Cu++
C507-64-1 (acute)	>300%	>300%	10%	267/73
C507-64-1 (chronic)	-	>300%	-	85/81

Coatings Tested

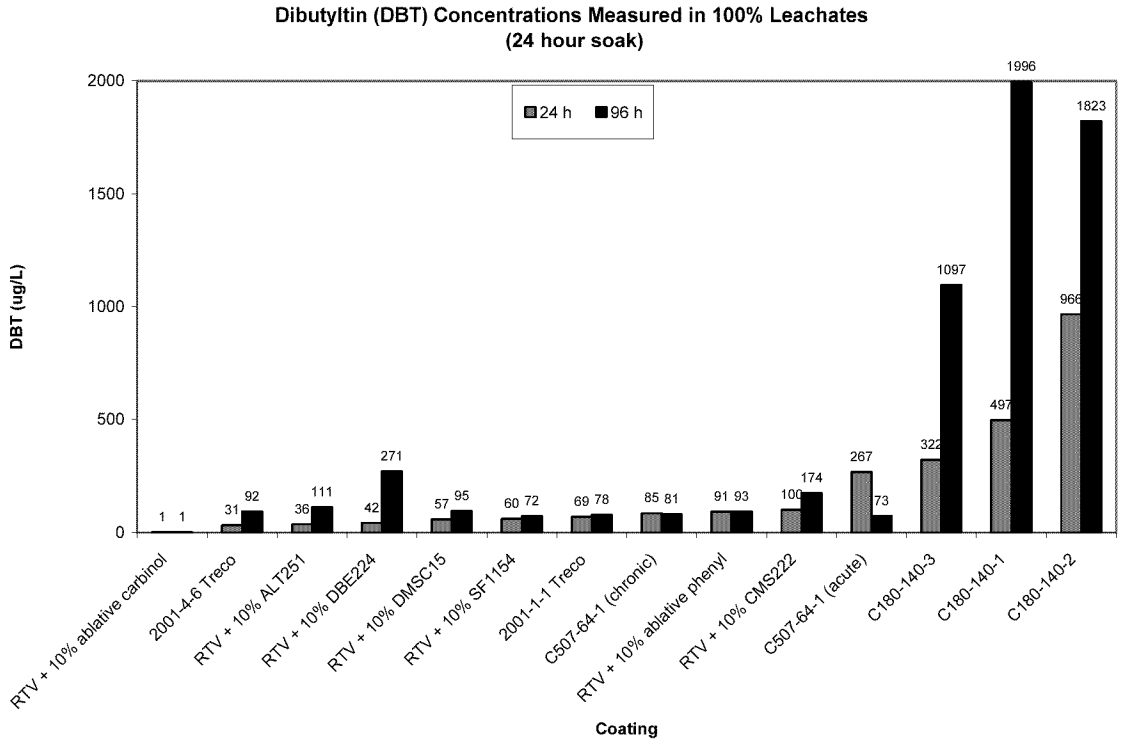
- C-180-140-1
- C-180-140-2
- C-180-140-3
- RTV + 10% ablative carbinol
- RTV + 10% ablative phenyl
- RTV + 10% ALT251
- RTV + 10% CMS222
- RTV + 10% DBE224
- RTV + 10% DMSC 15
- RTV + 10% SF1154
- 2001-1-1 Treco
- 2001-4-6 Treco
- C507-64-1

- BRA 640 (chain diatom only)
- GE-0 (chain diatom only)

SPAWAR
Systems Center
San Diego

Figure 1

Figure 3.B.1 Coatings tested.



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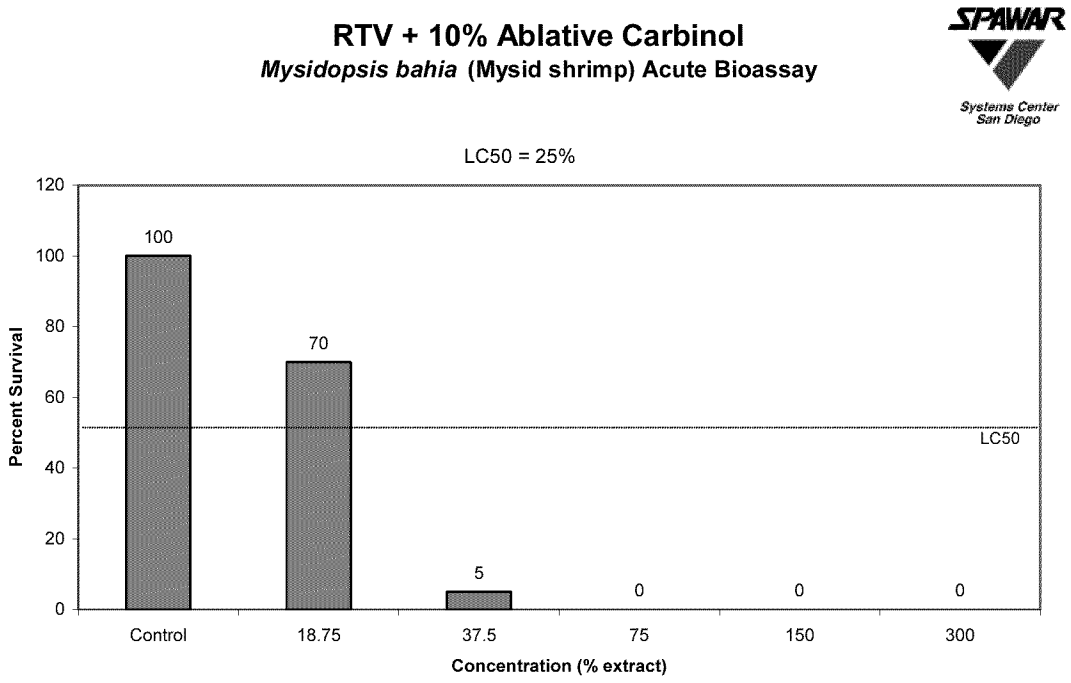

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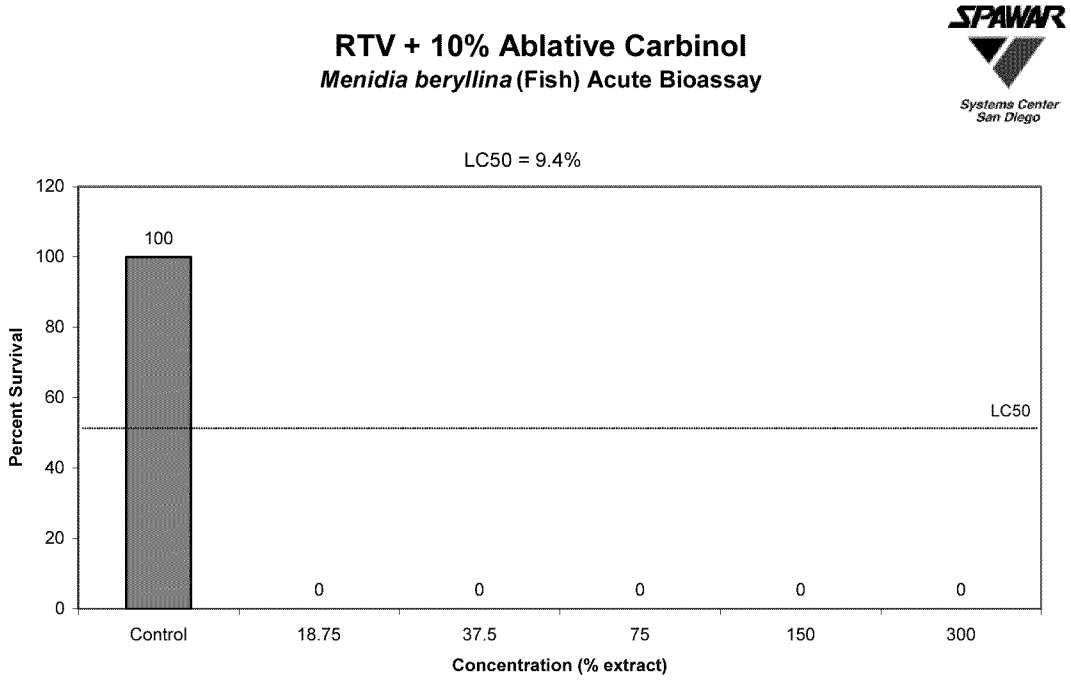

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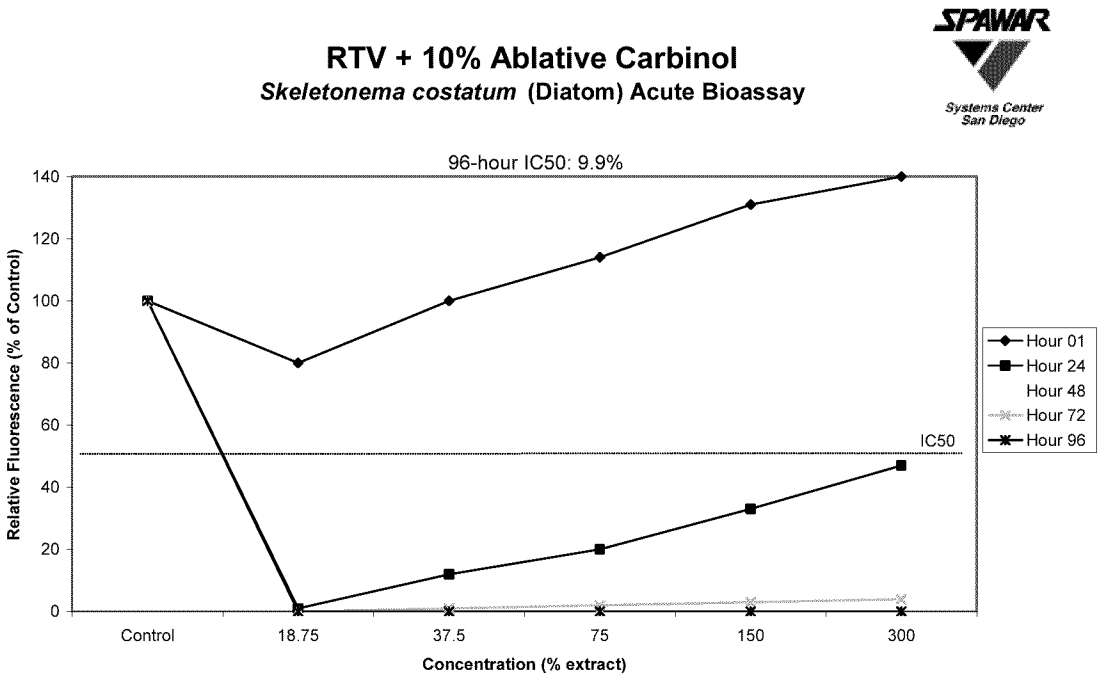

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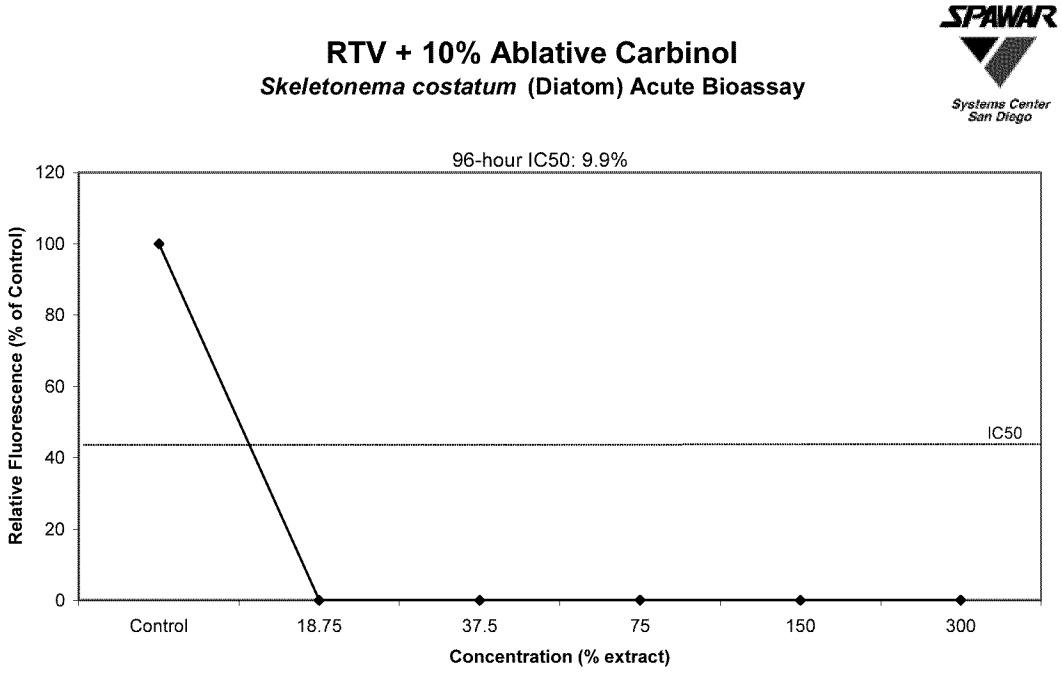

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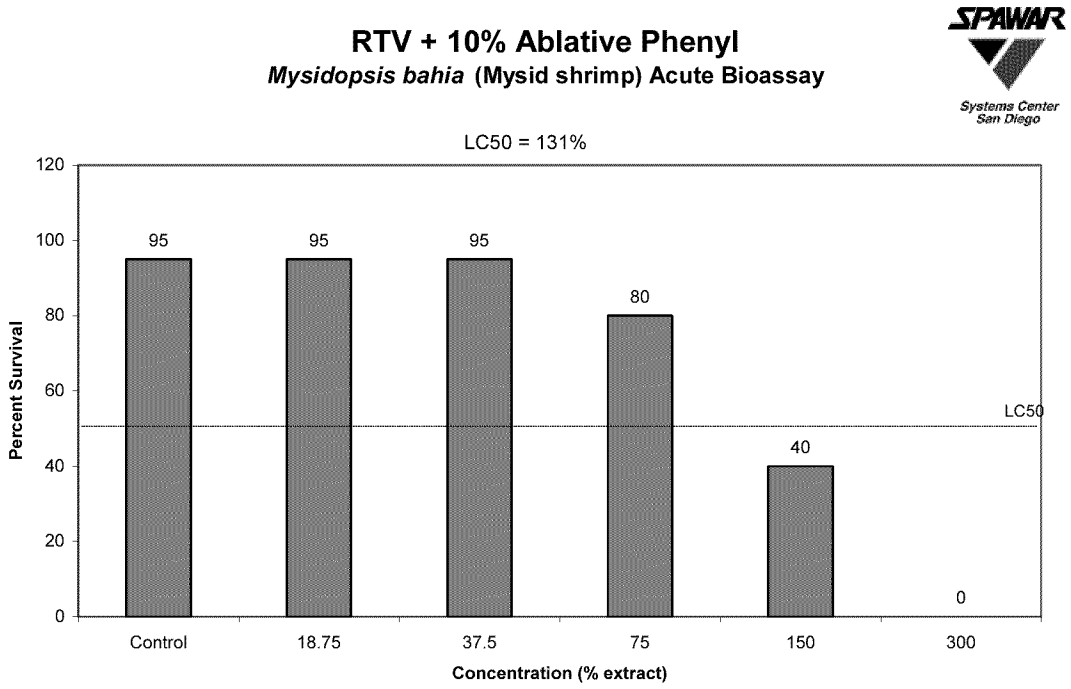

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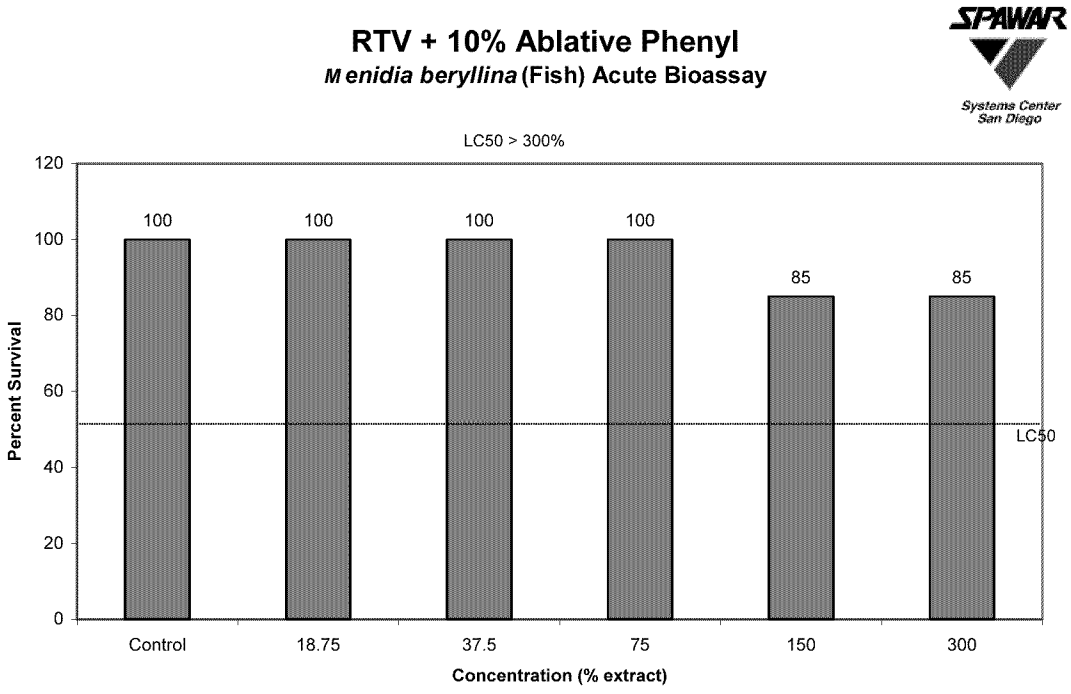

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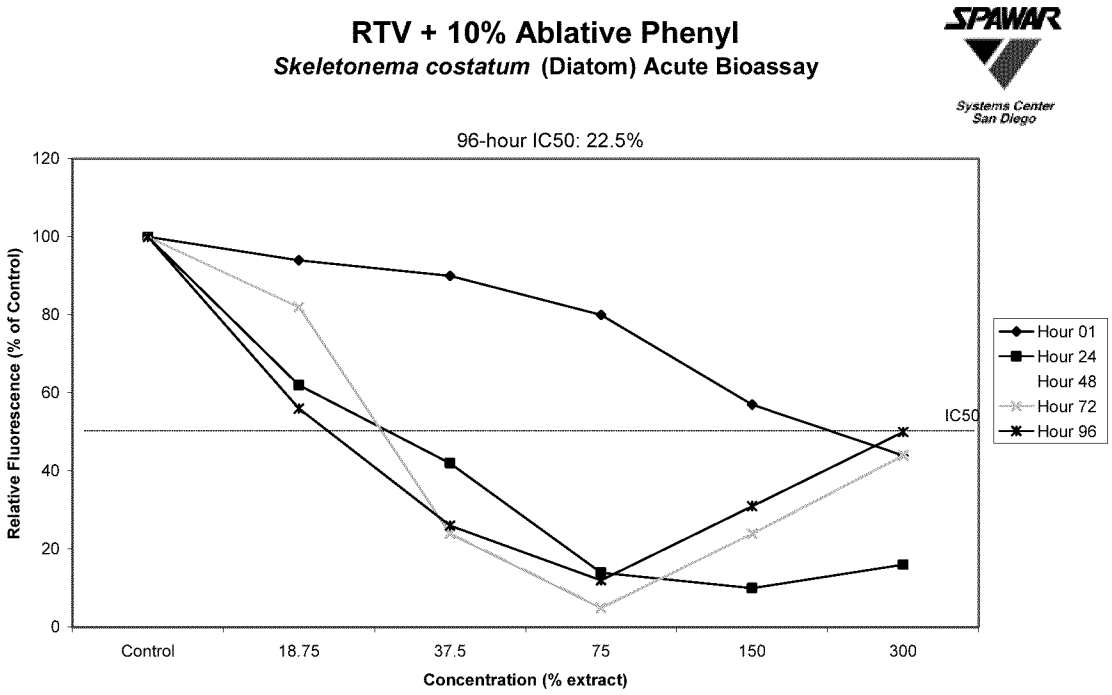

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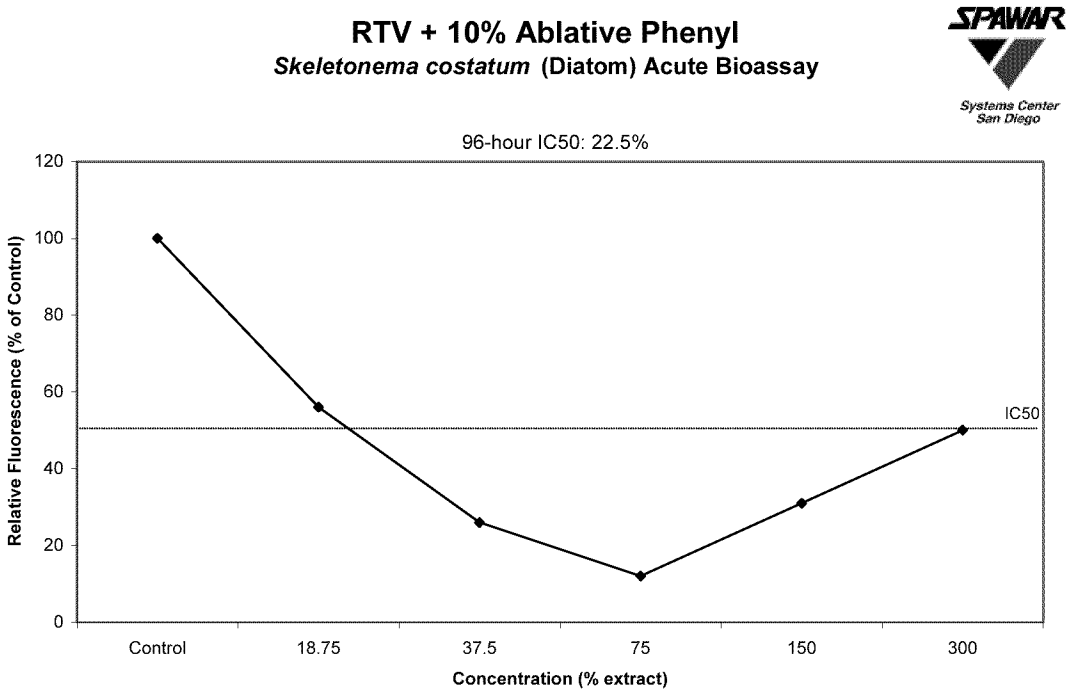

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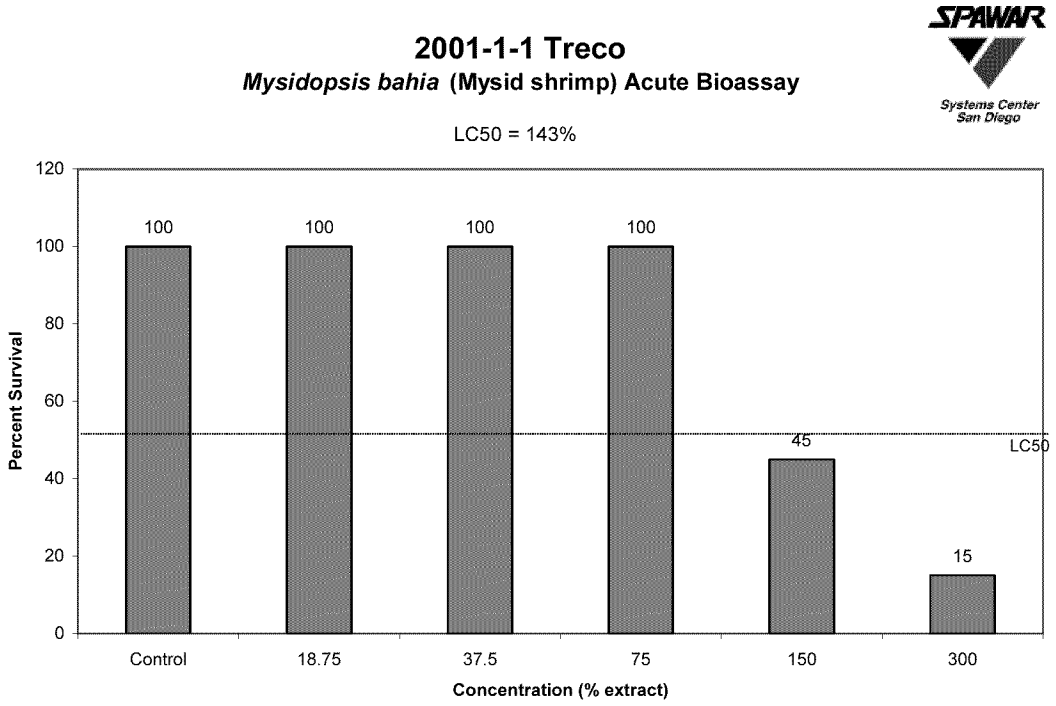

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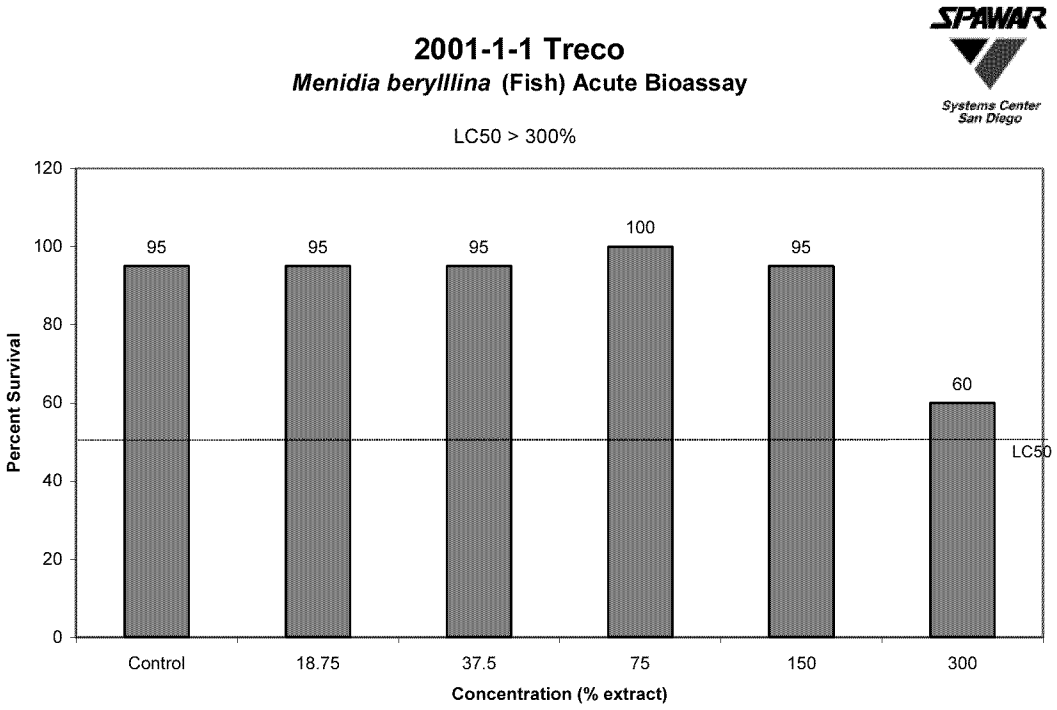

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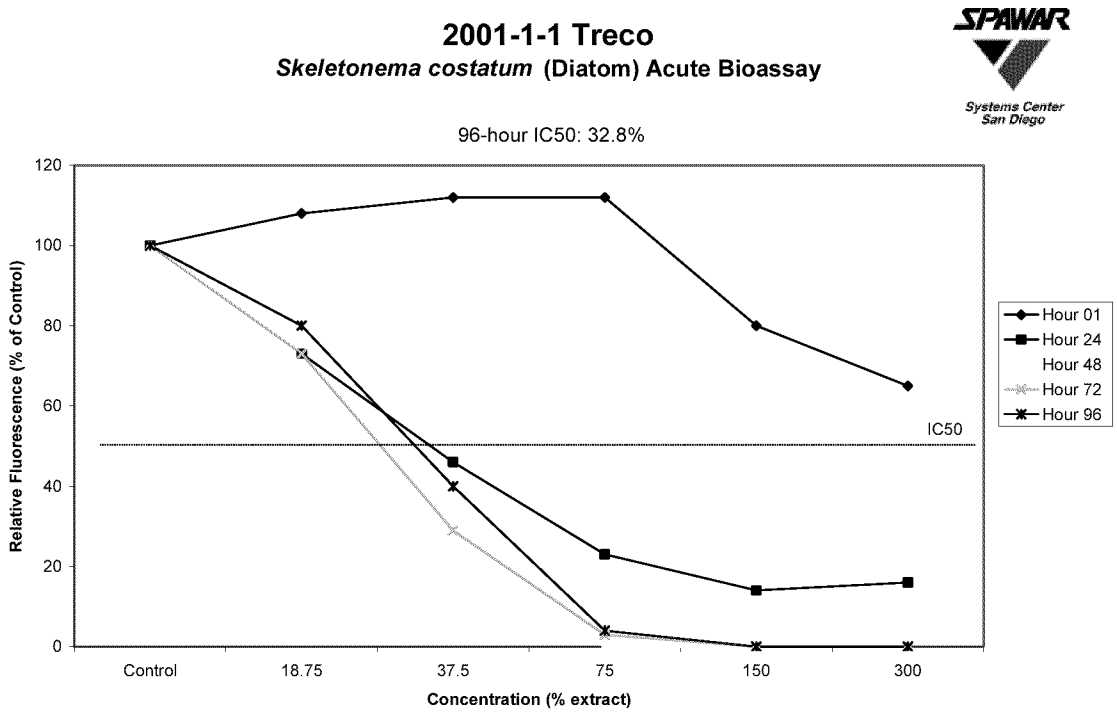

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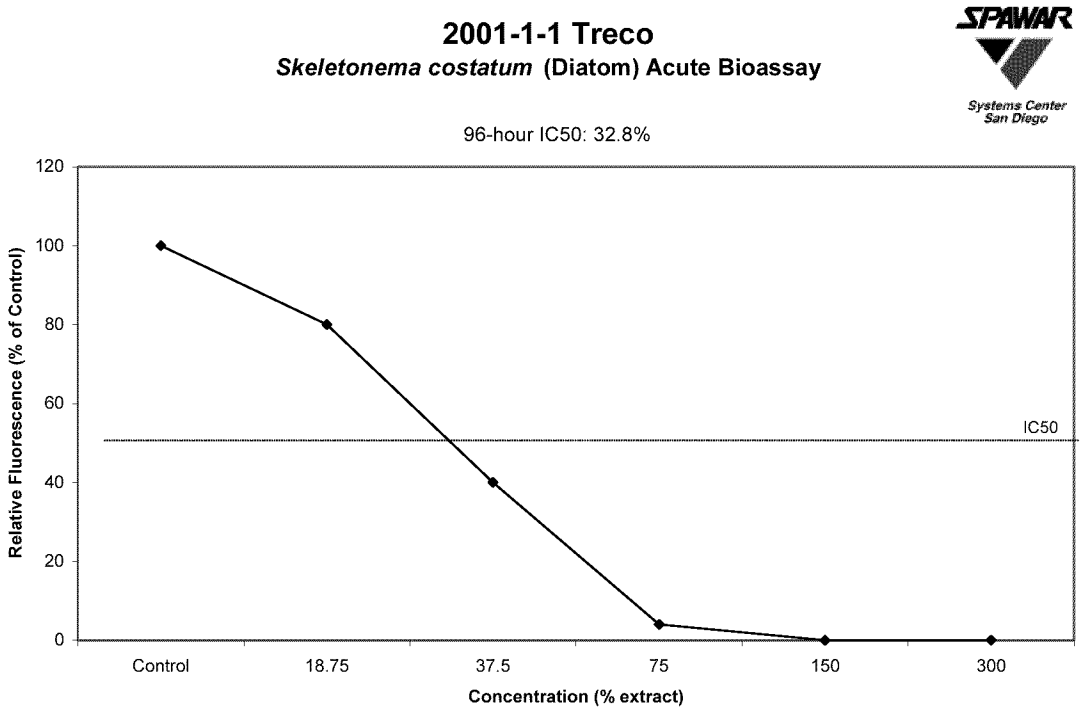

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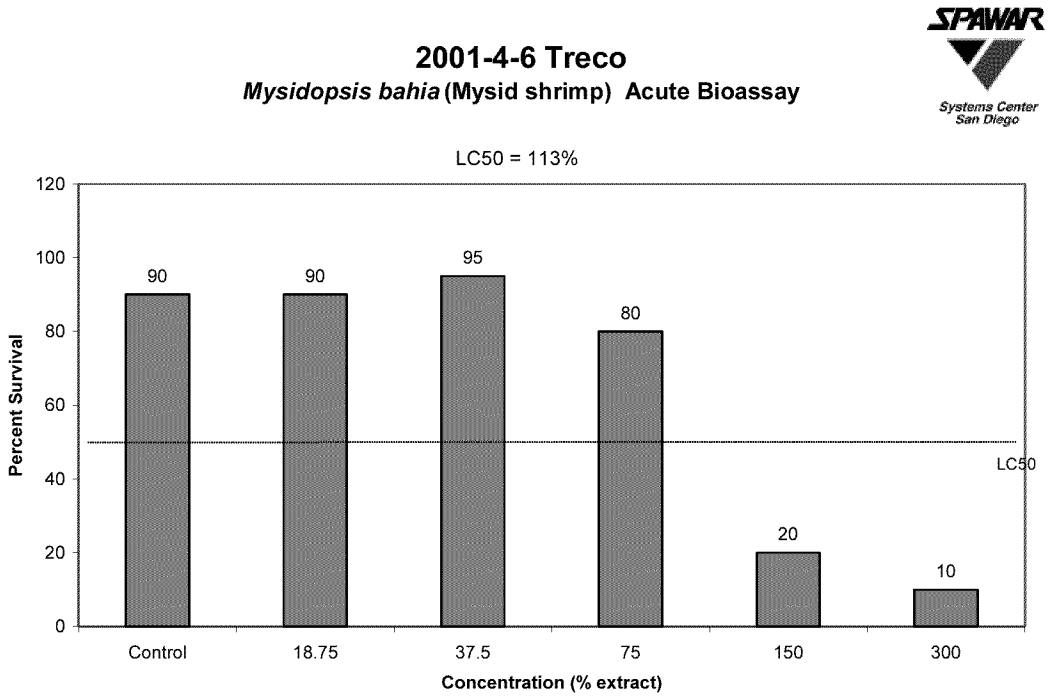

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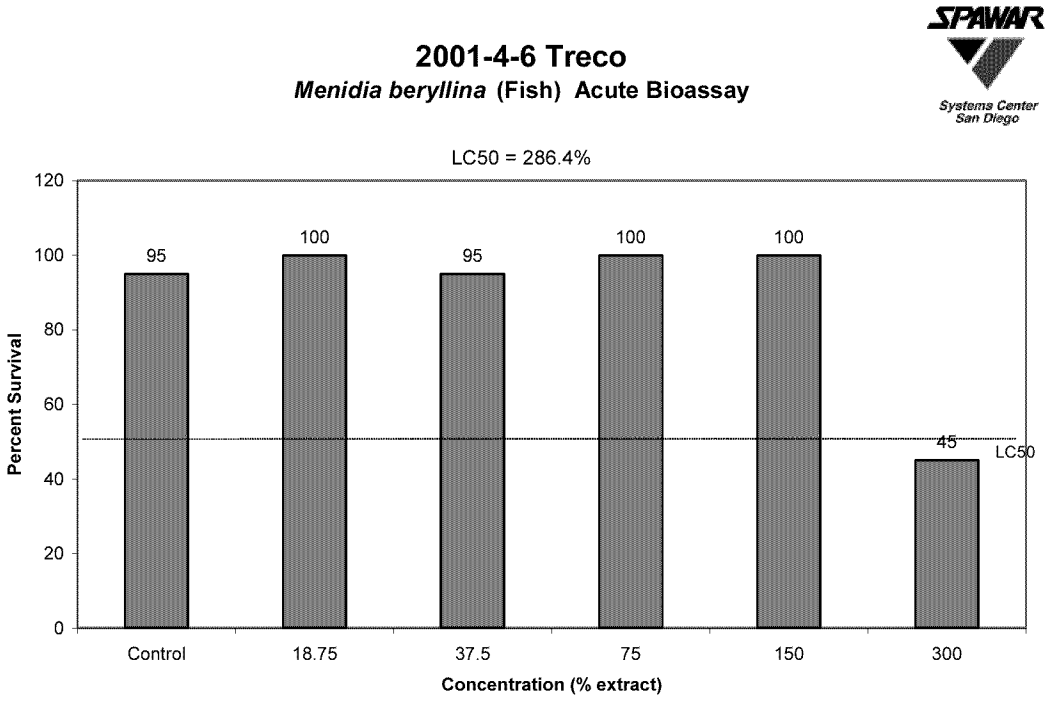

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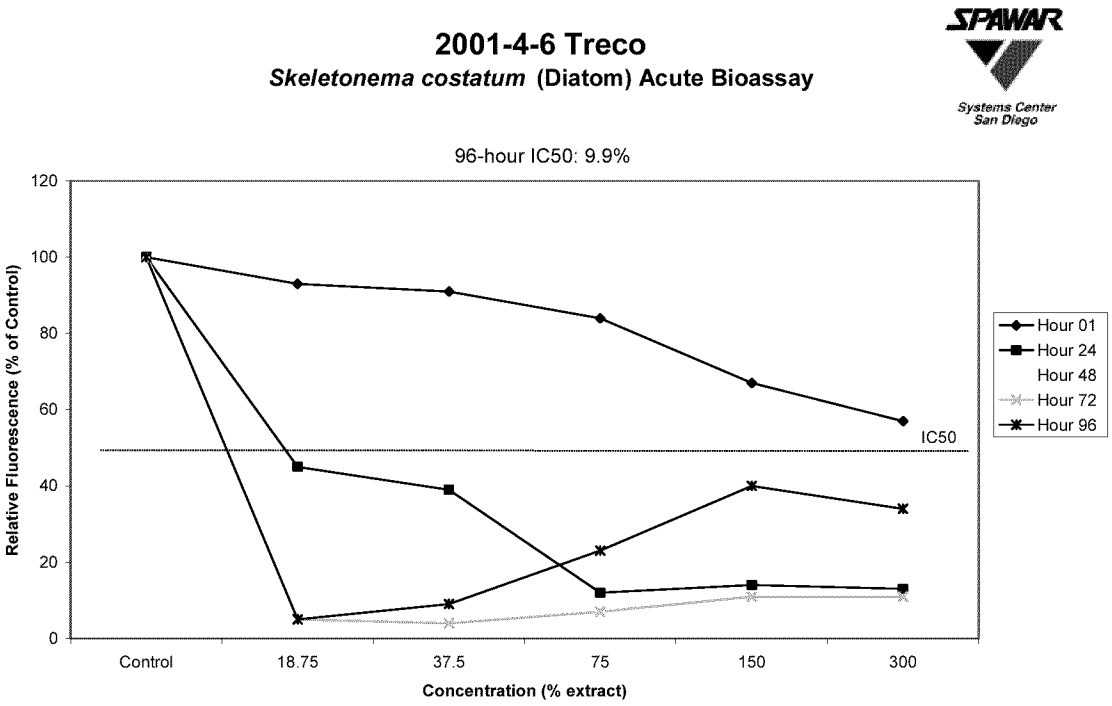

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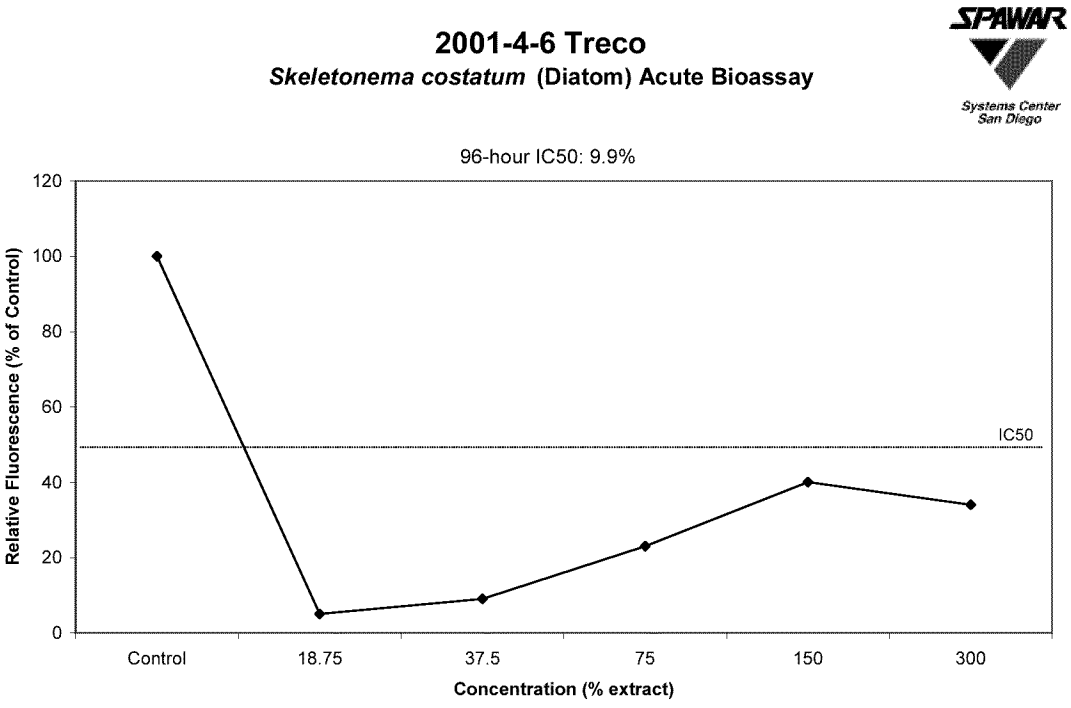

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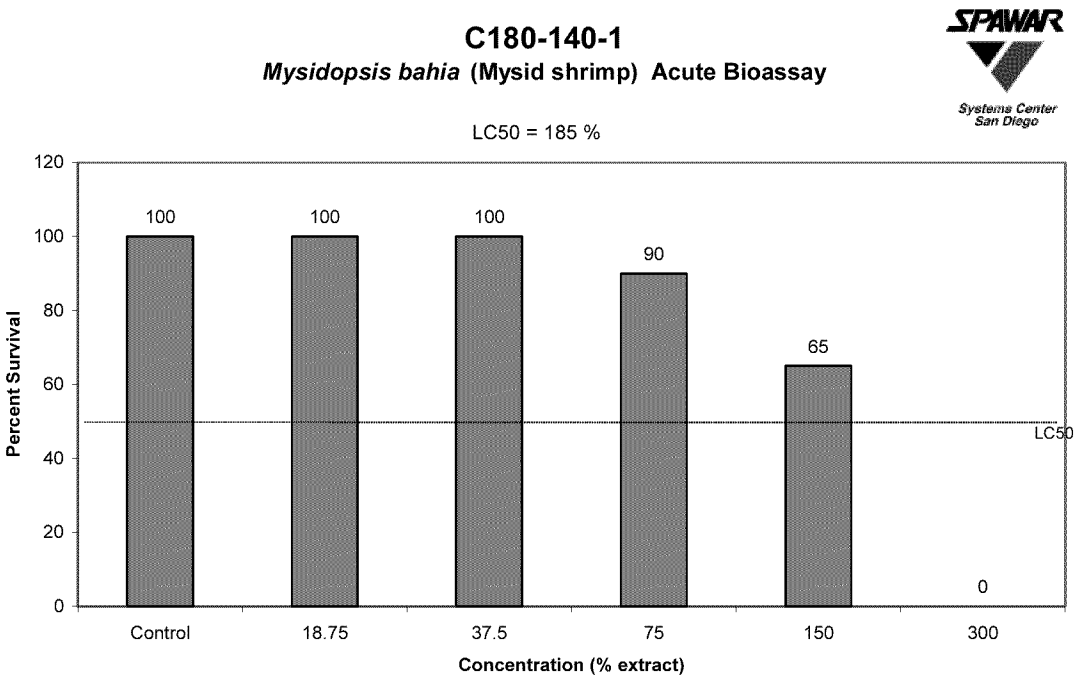
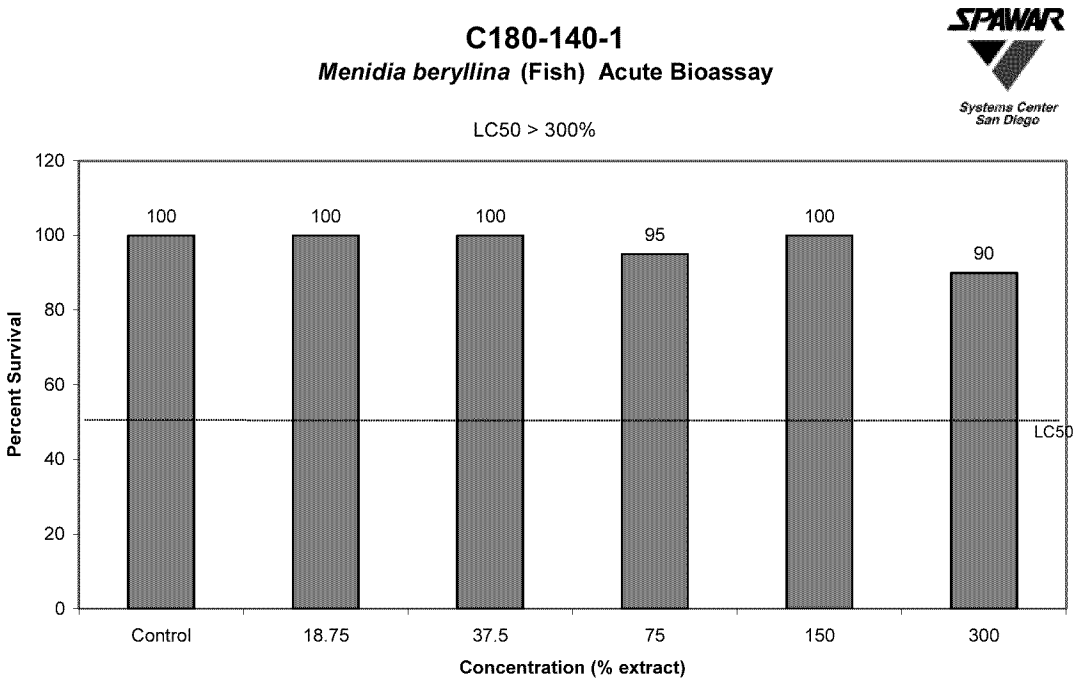

C180-140-1
Mysidopsis bahia (Mysid shrimp) Acute Bioassay
SPAWAR
Systems Center
San Diego
LC50 = 185 %
Percent Survival
120
100
80
60
40
20
0
100
100
100
90
65
0
LC50
Control
18.75
37.5
75
150
300
Concentration (% extract)

Figure 3.B.19



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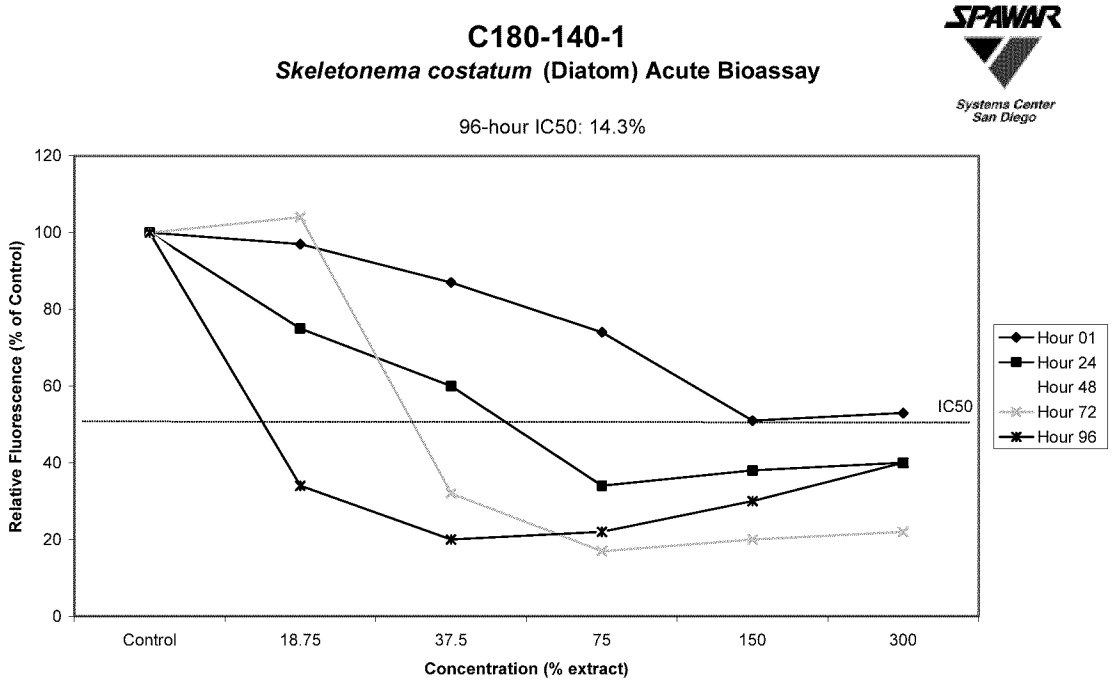

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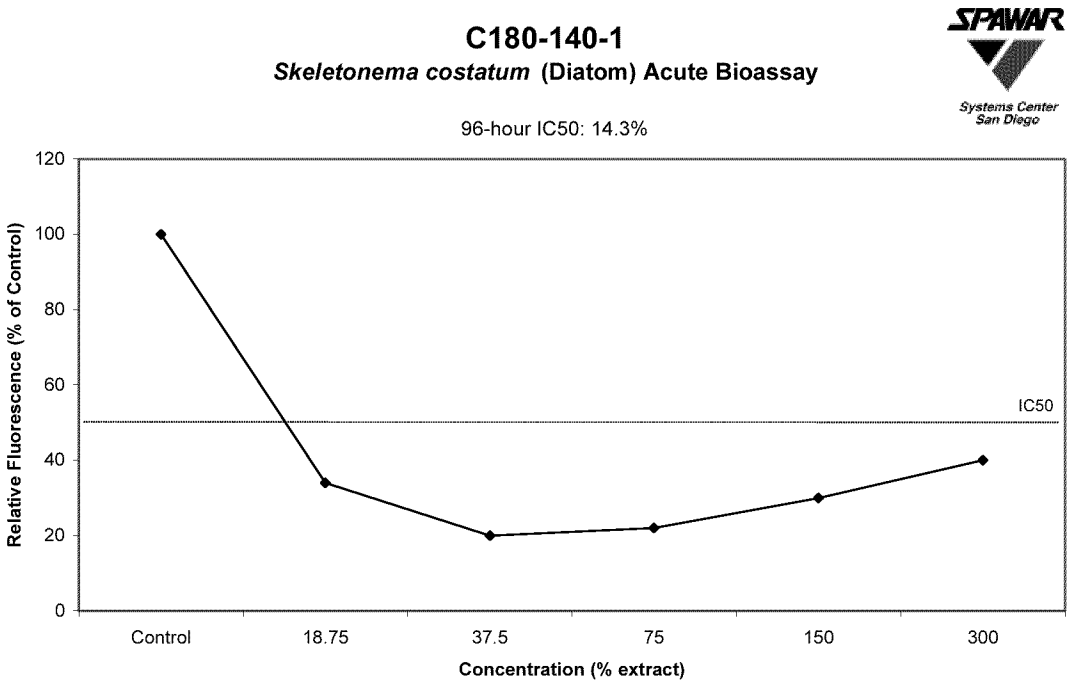

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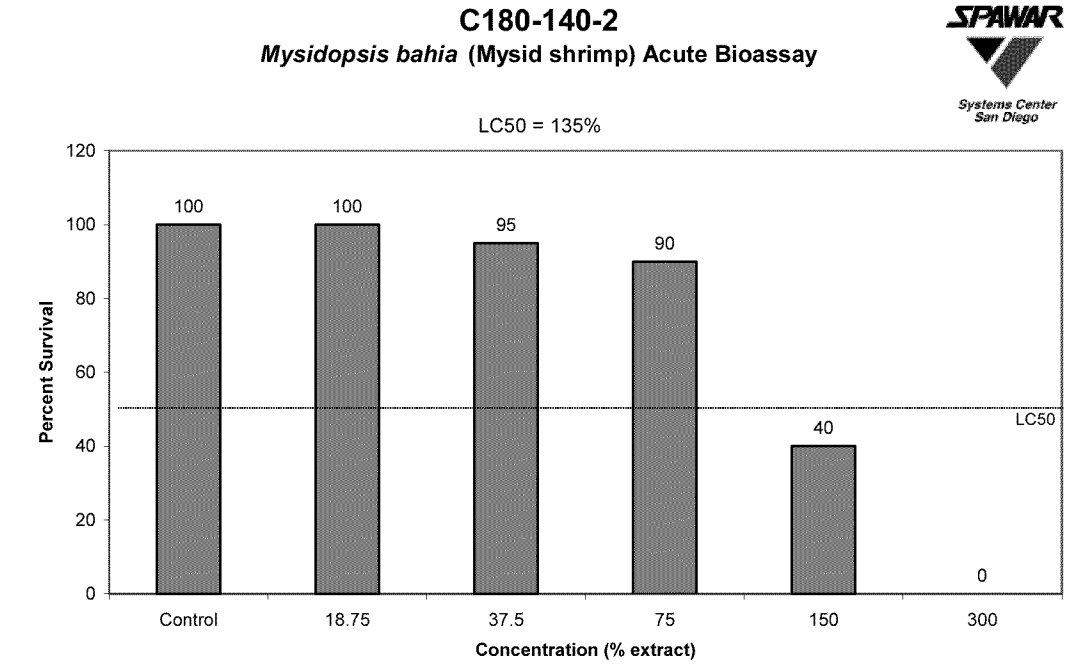

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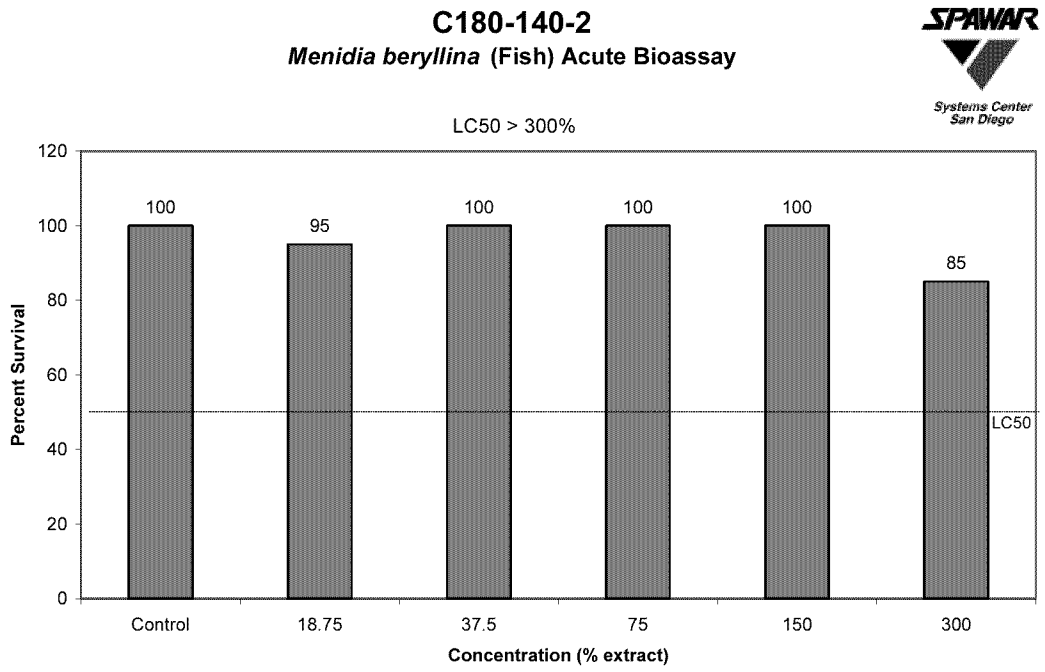

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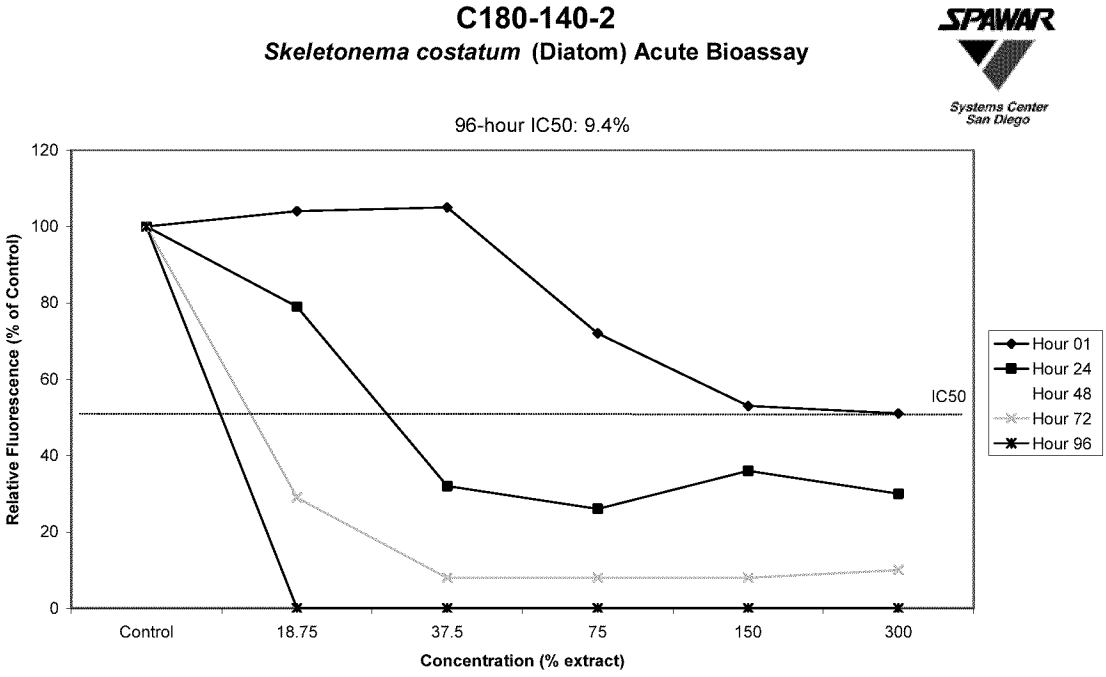

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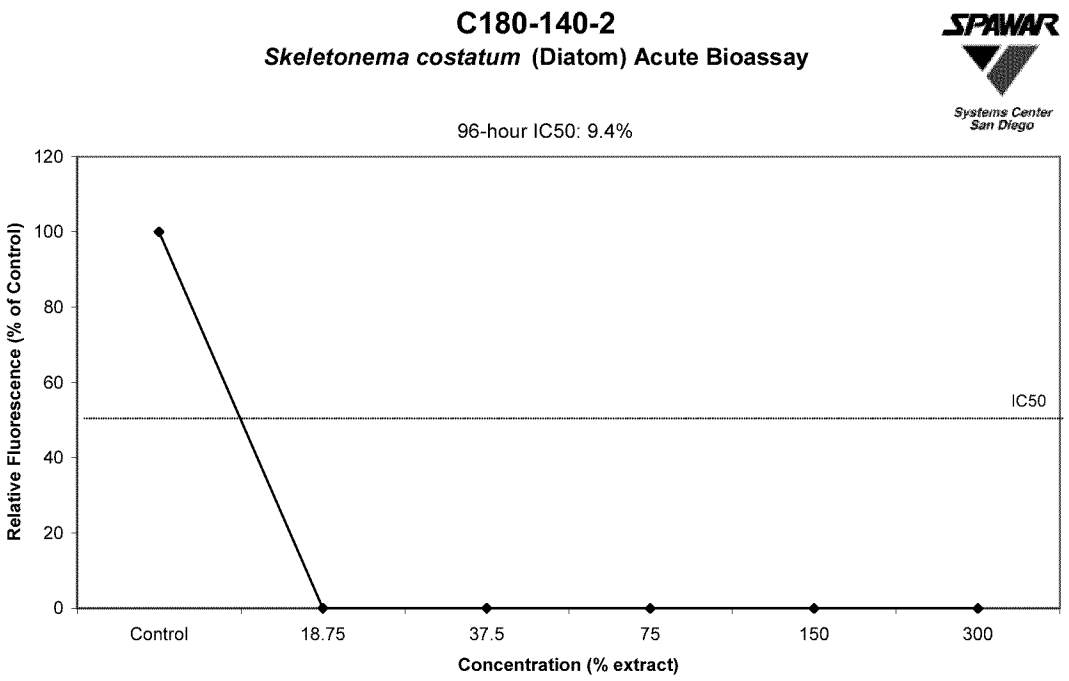

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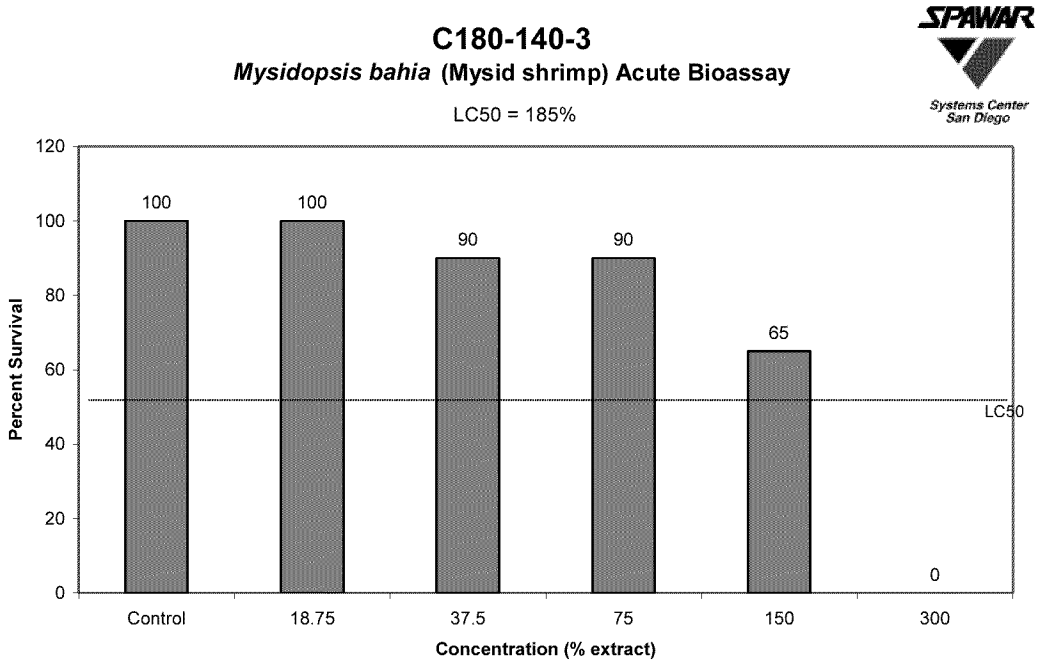

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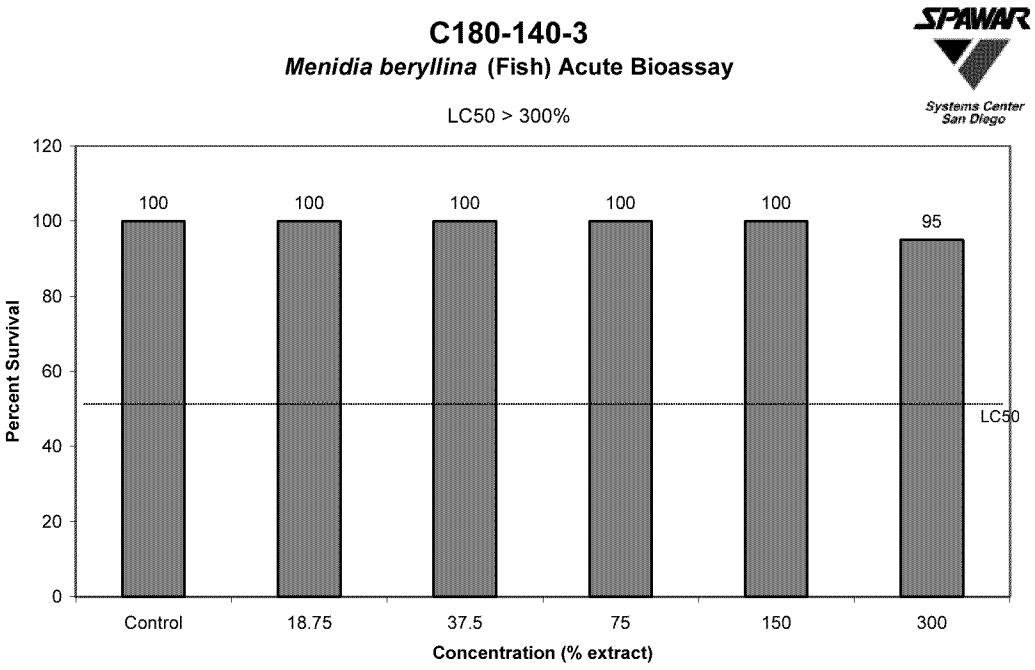

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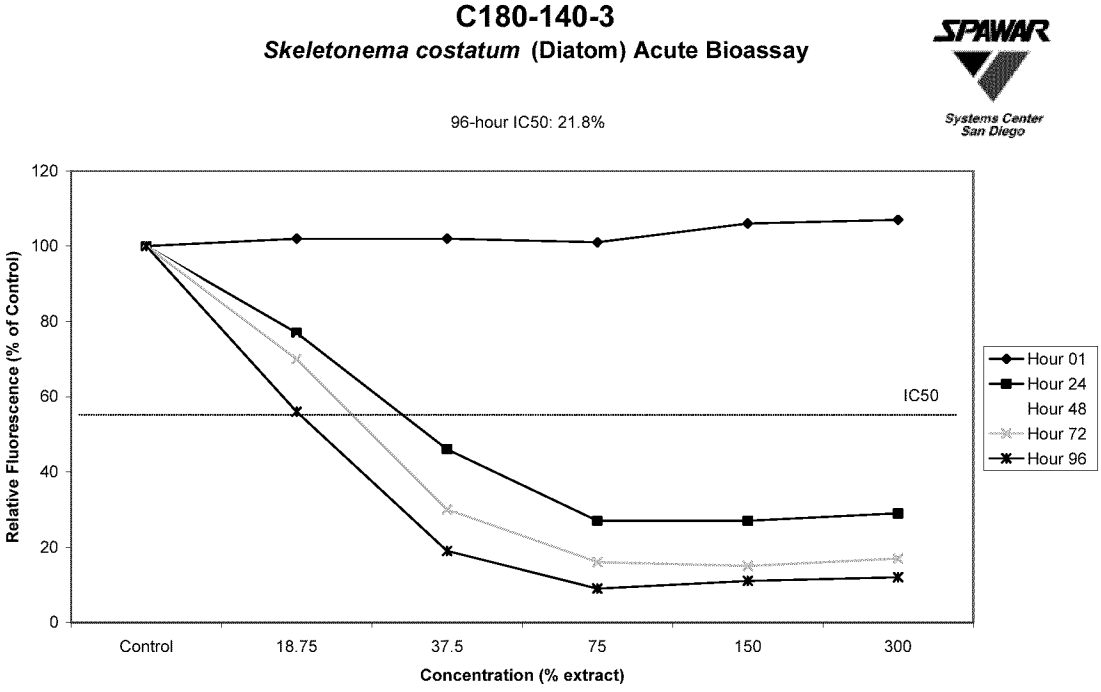

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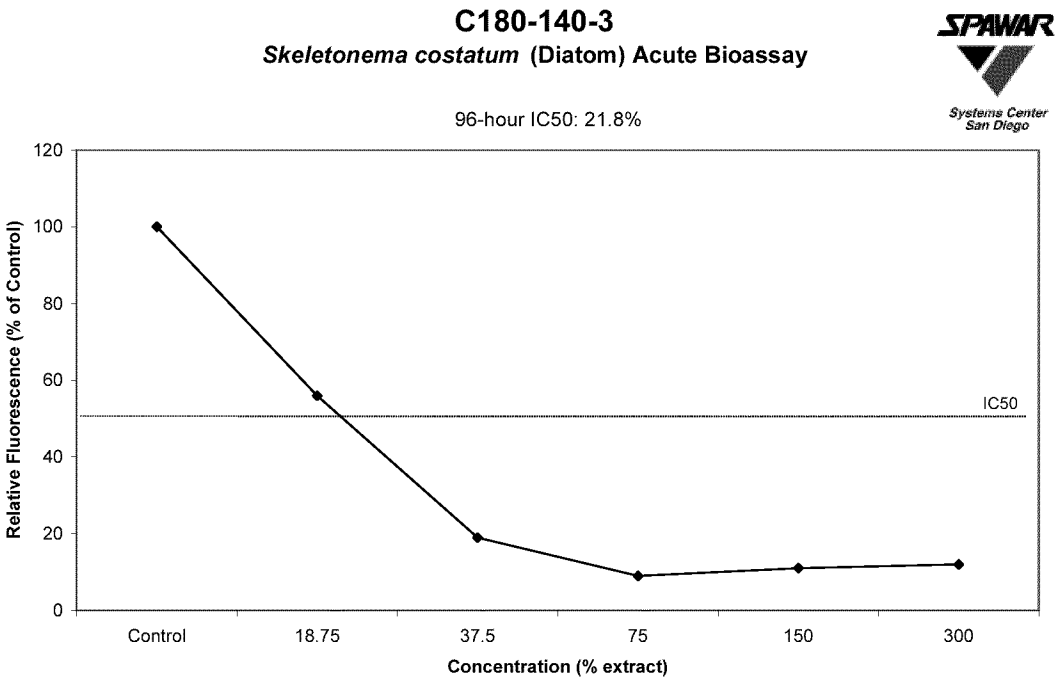

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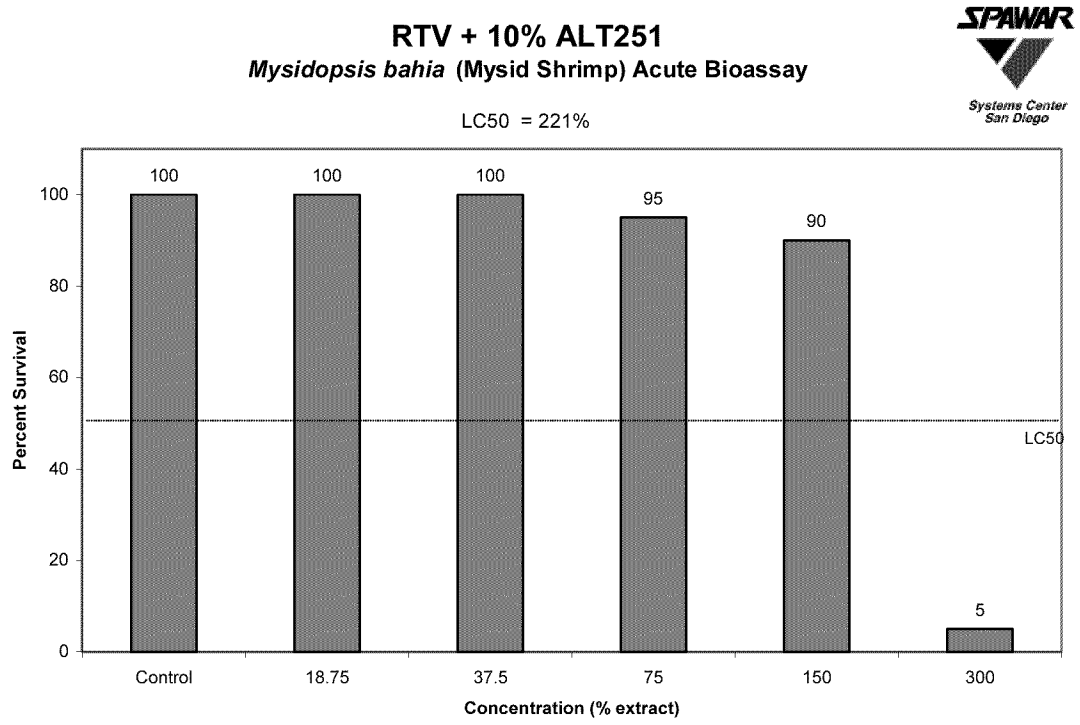

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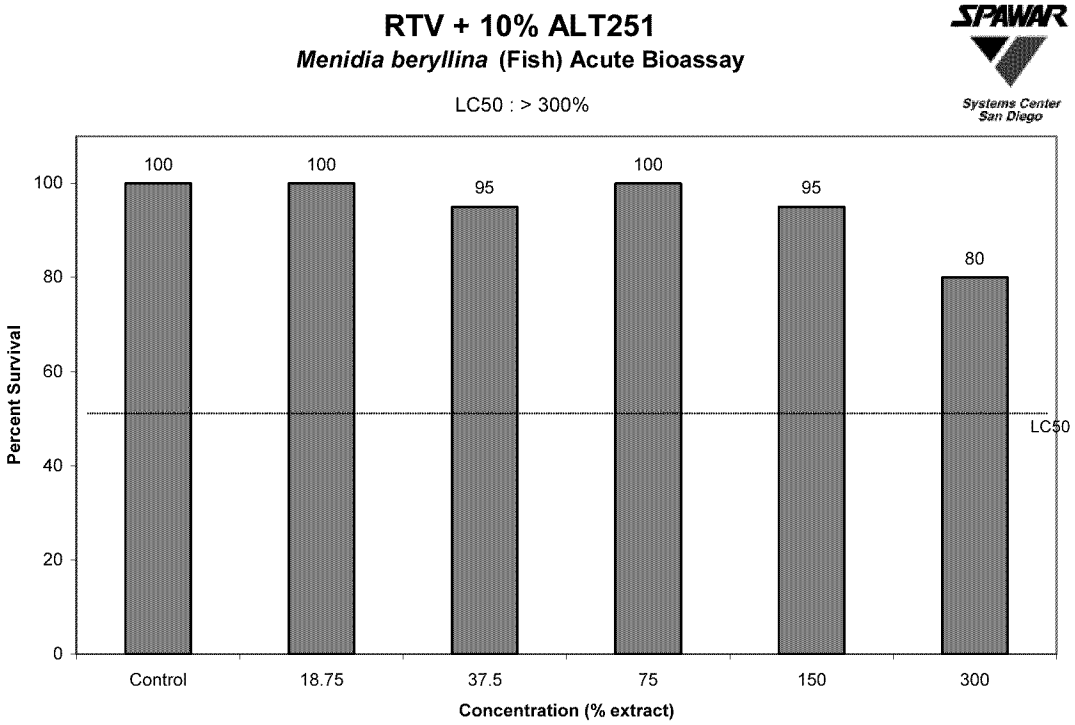

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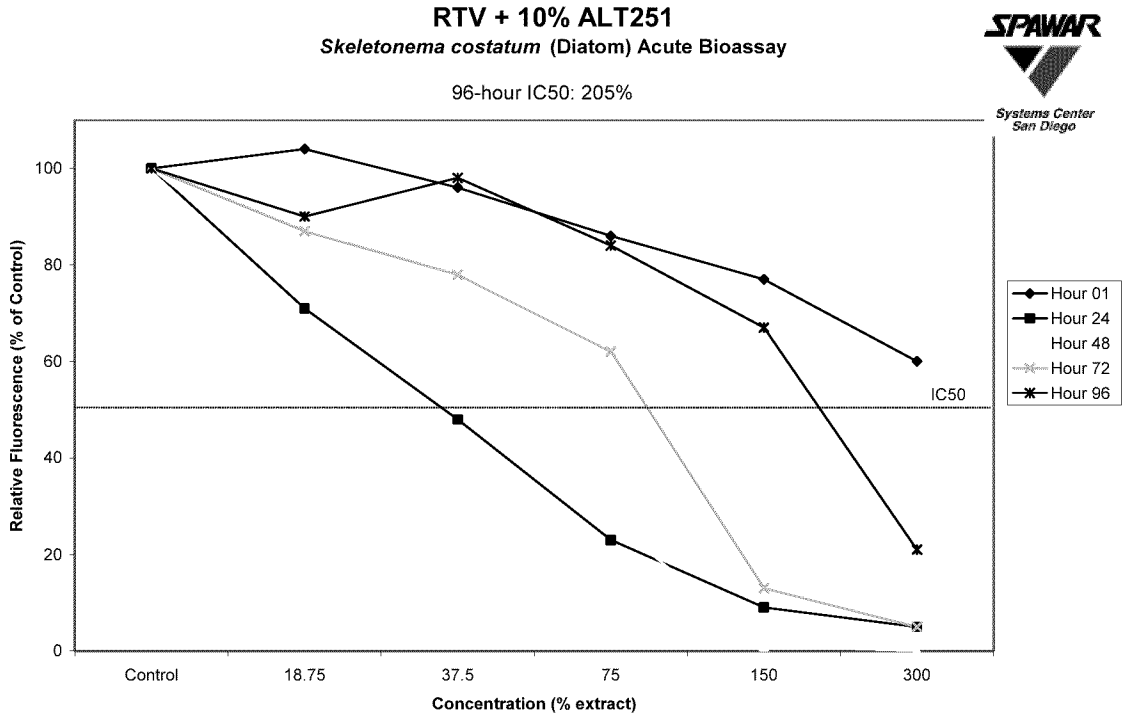

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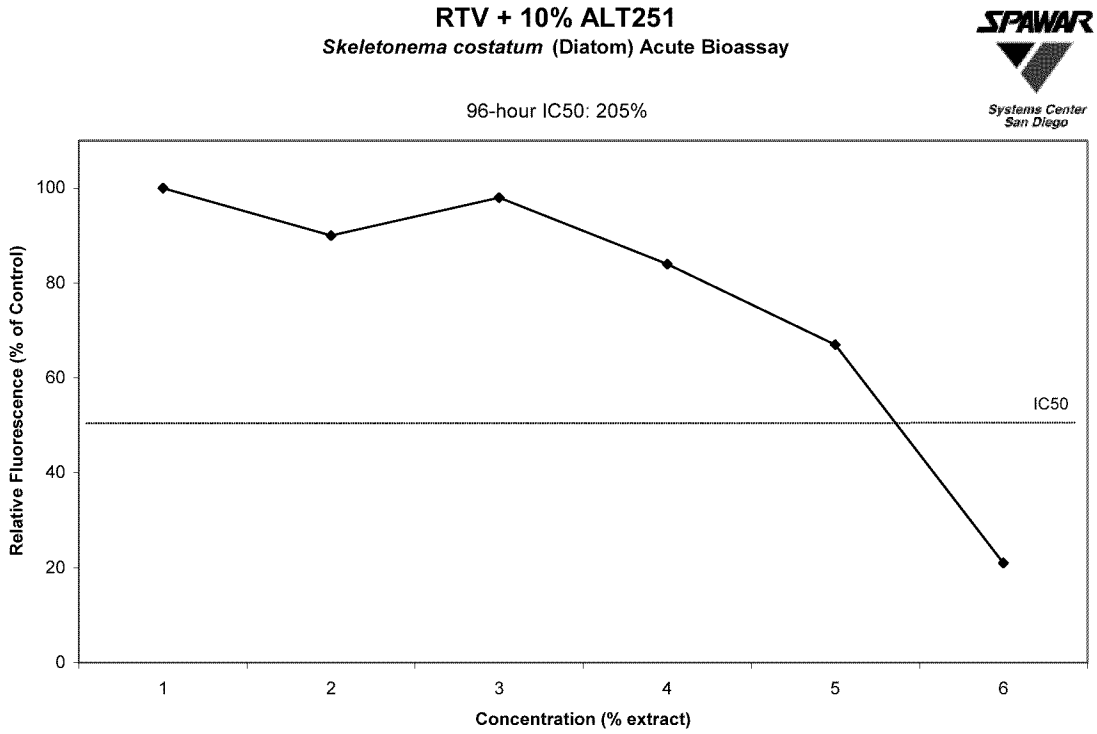

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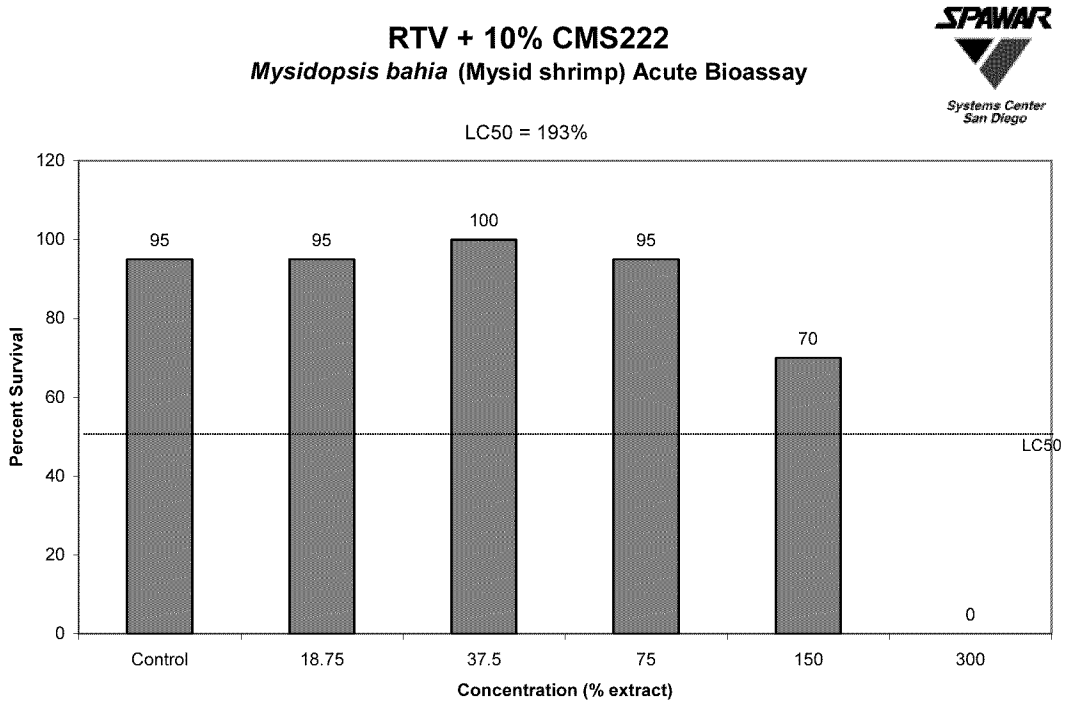

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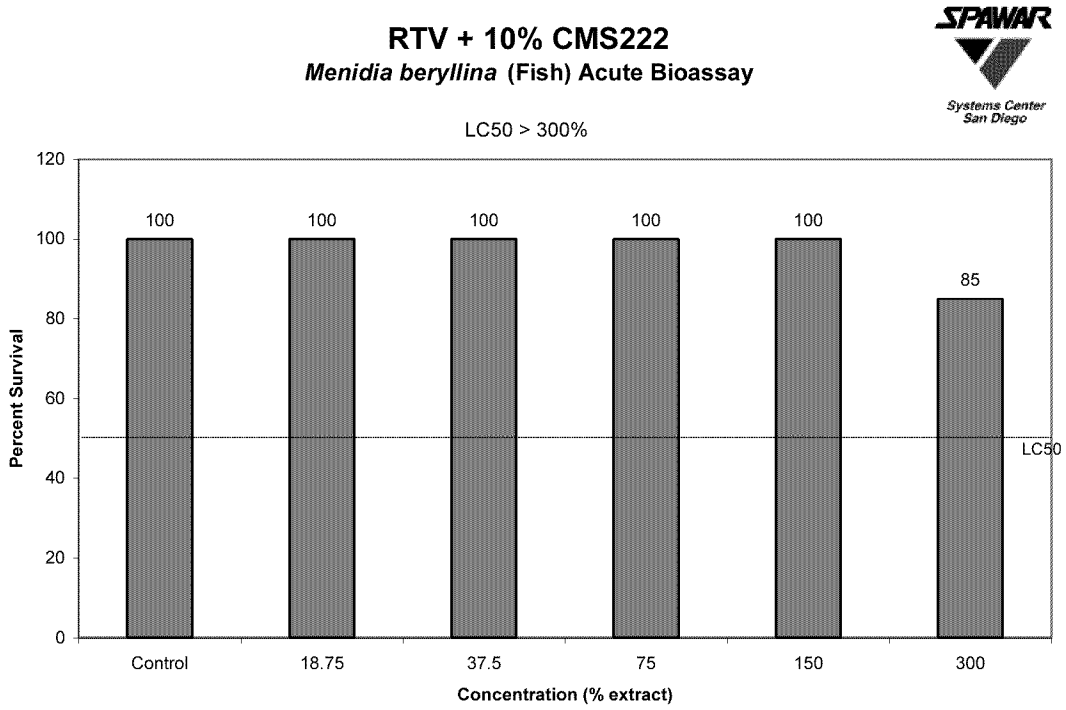

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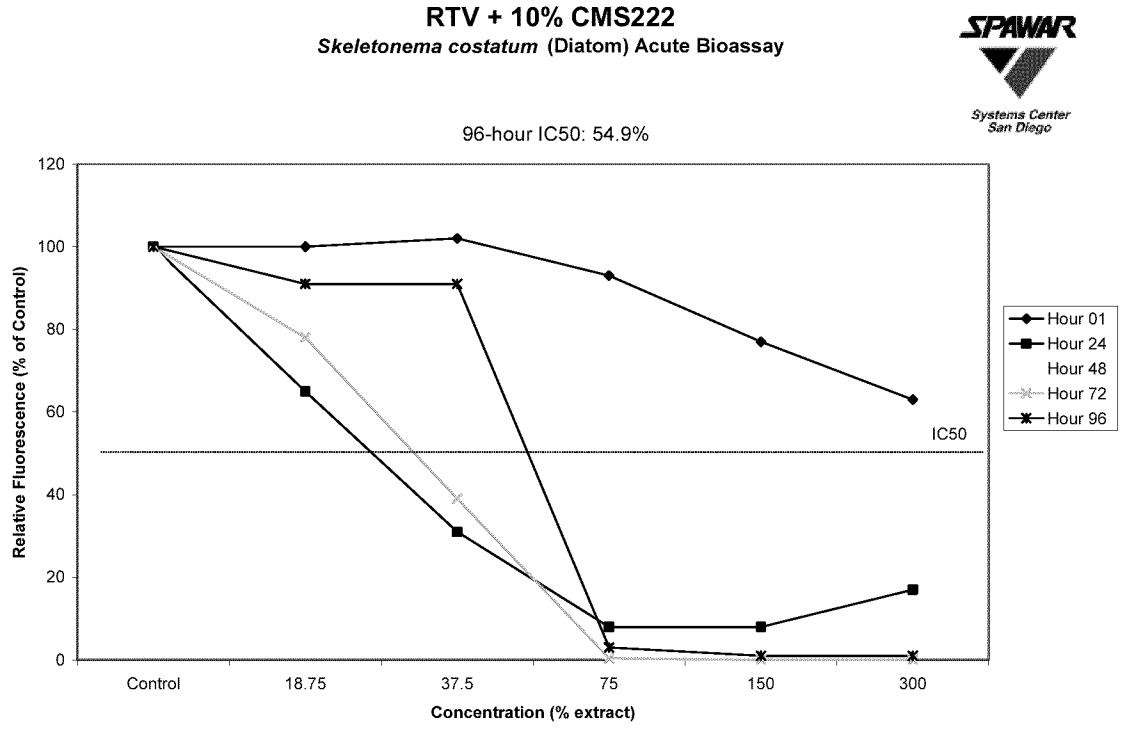

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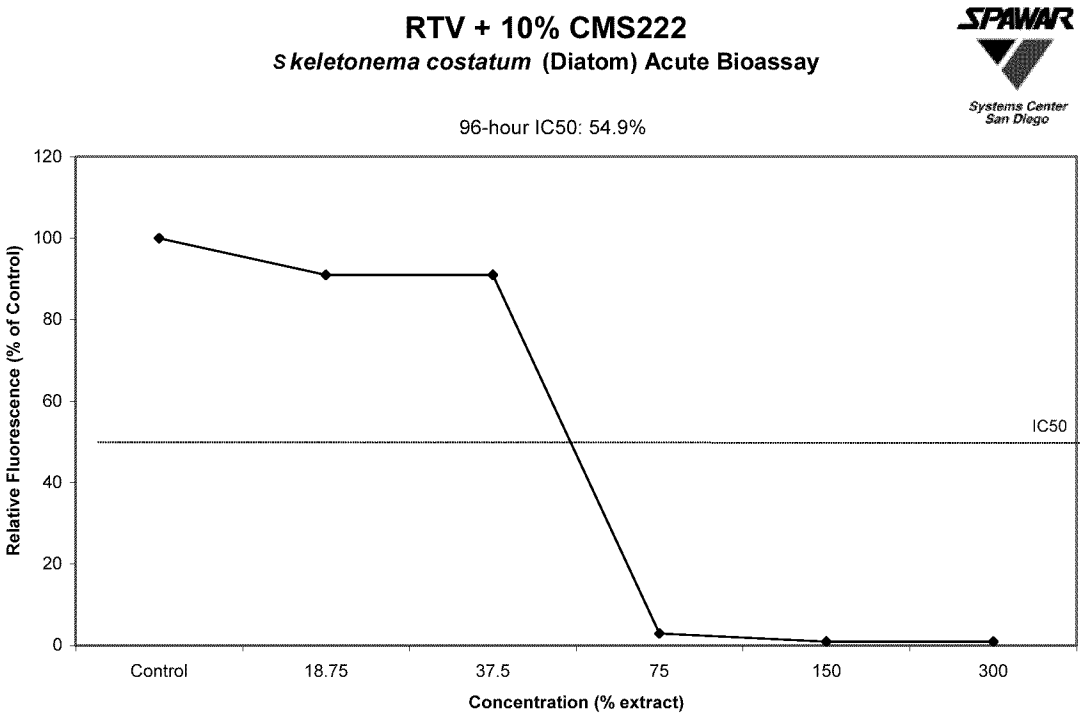

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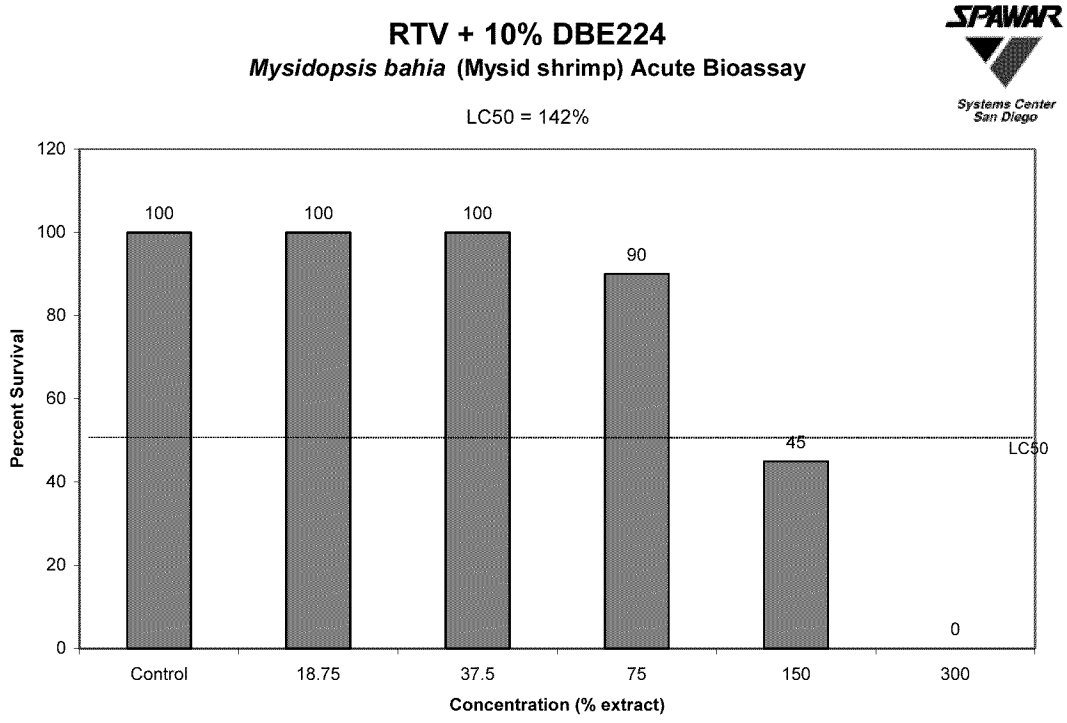

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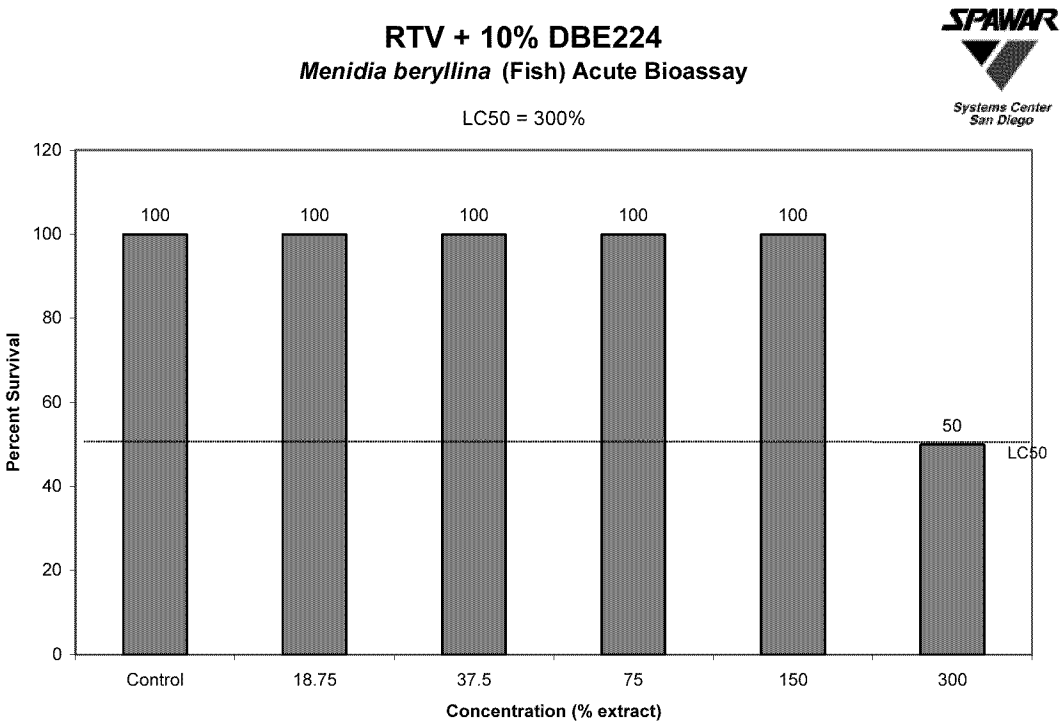

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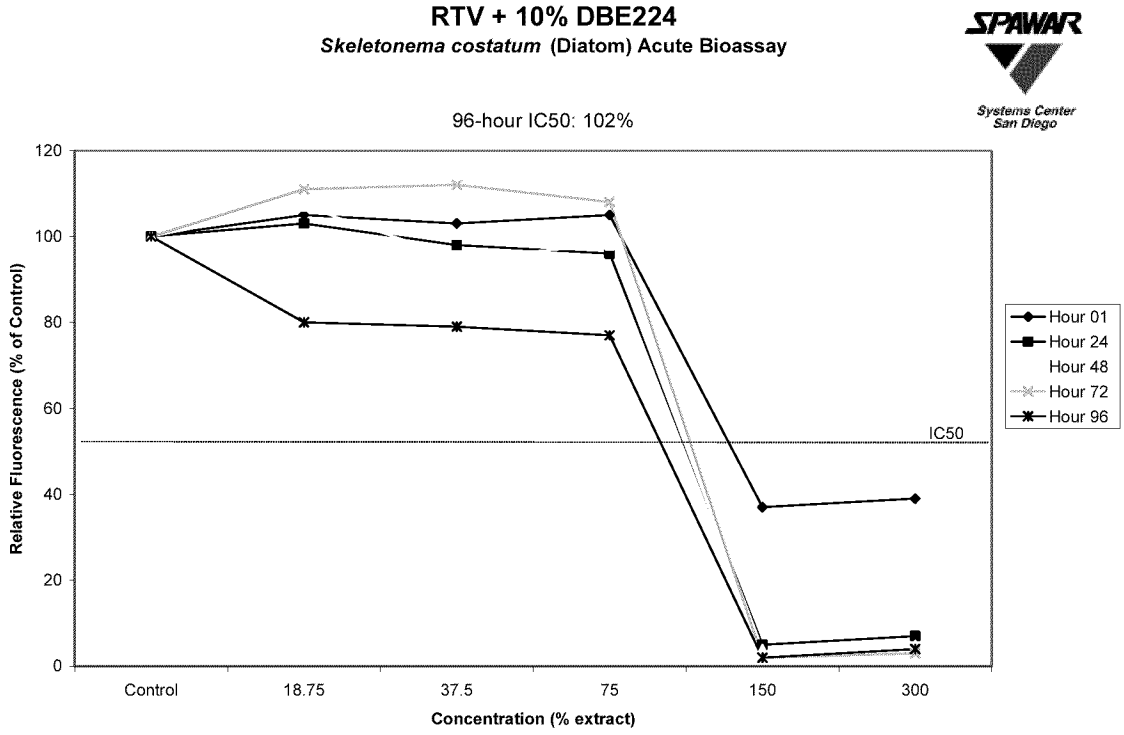

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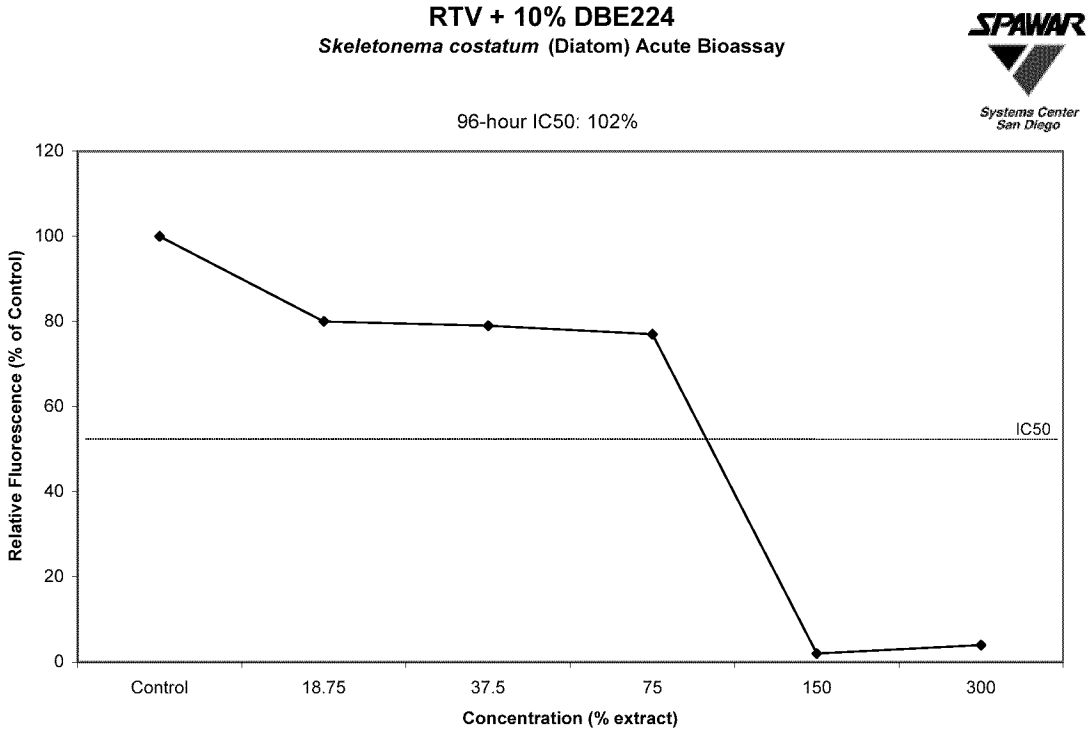

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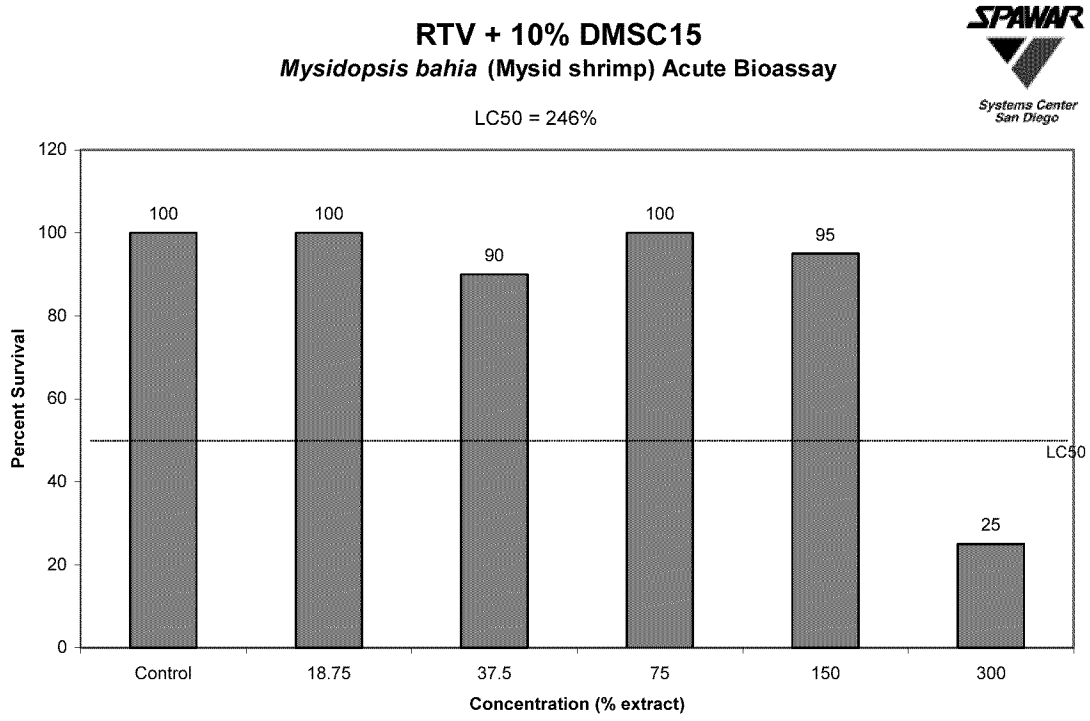

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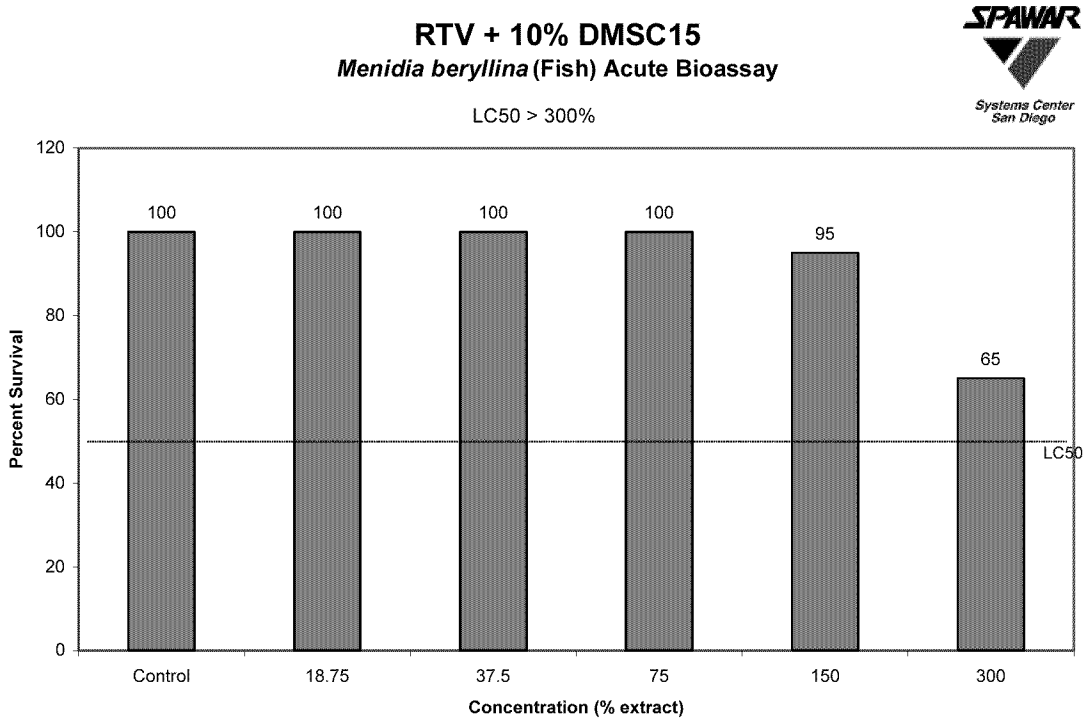

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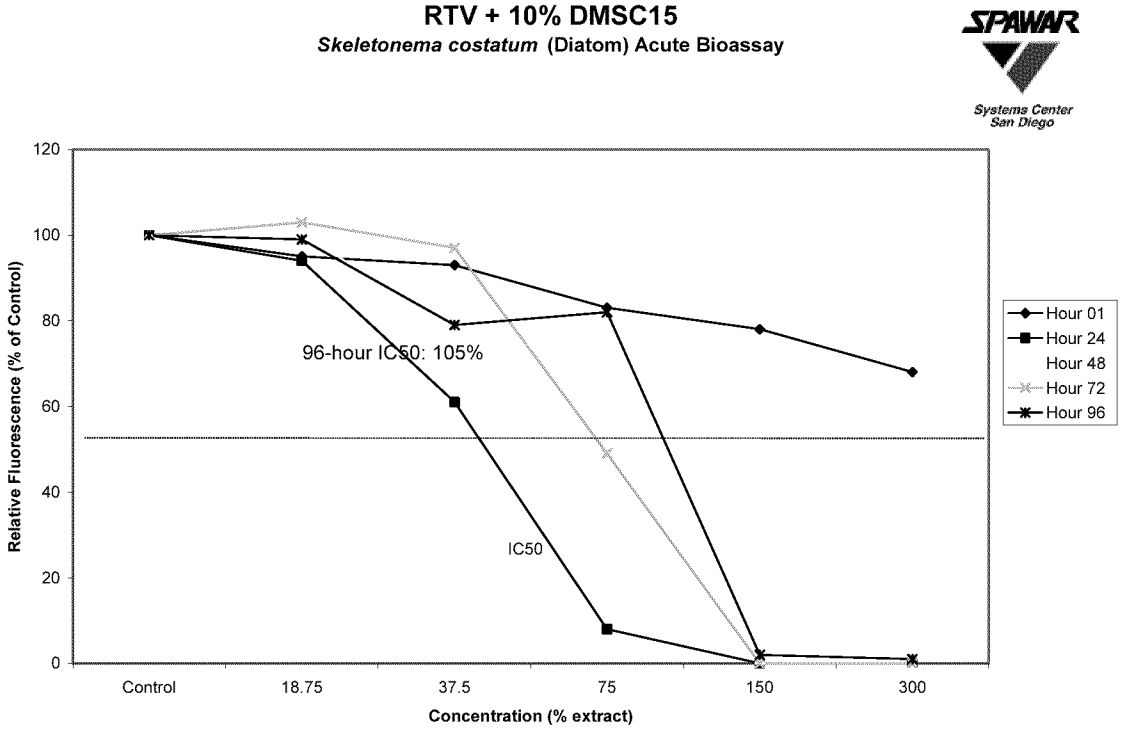

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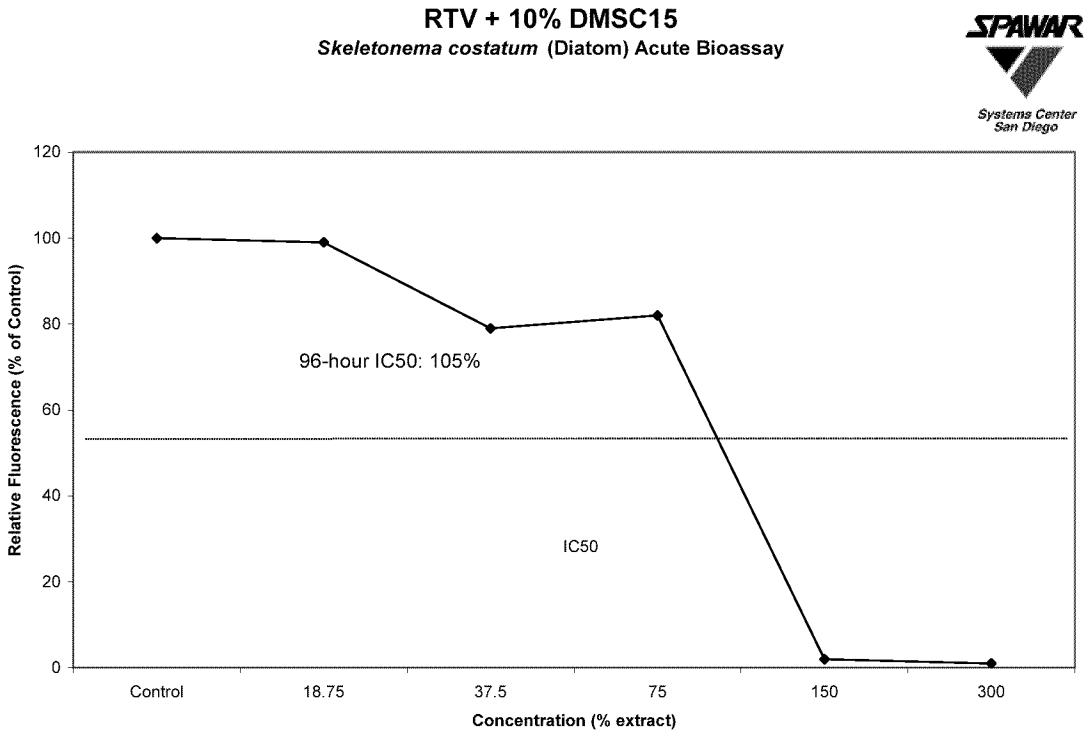

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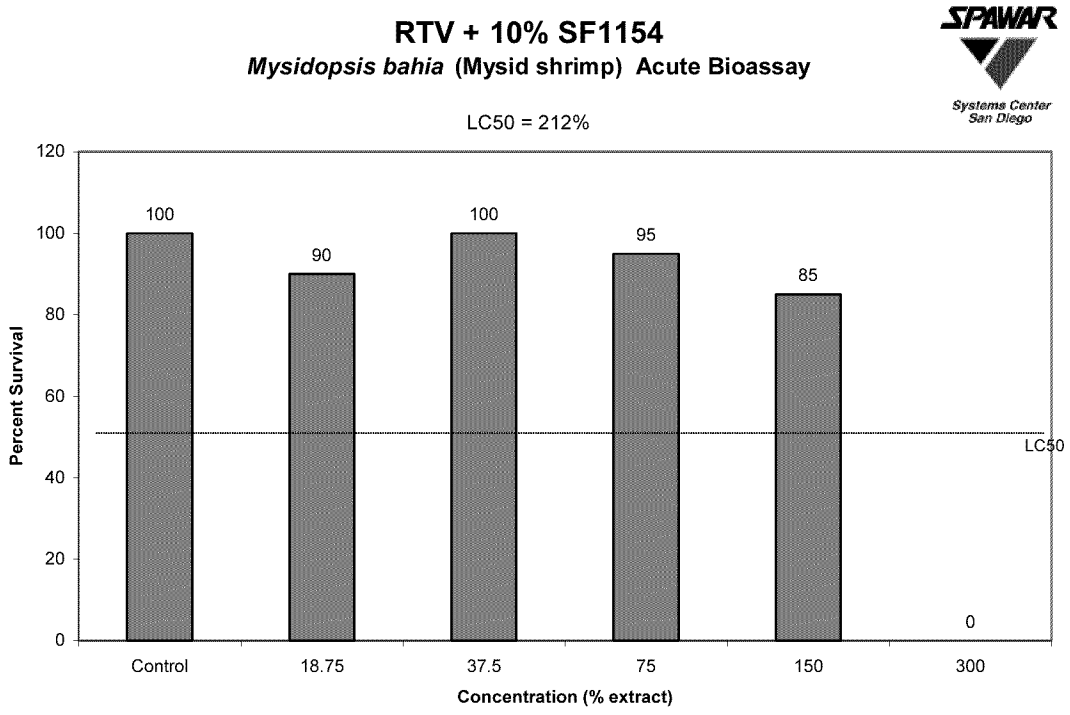

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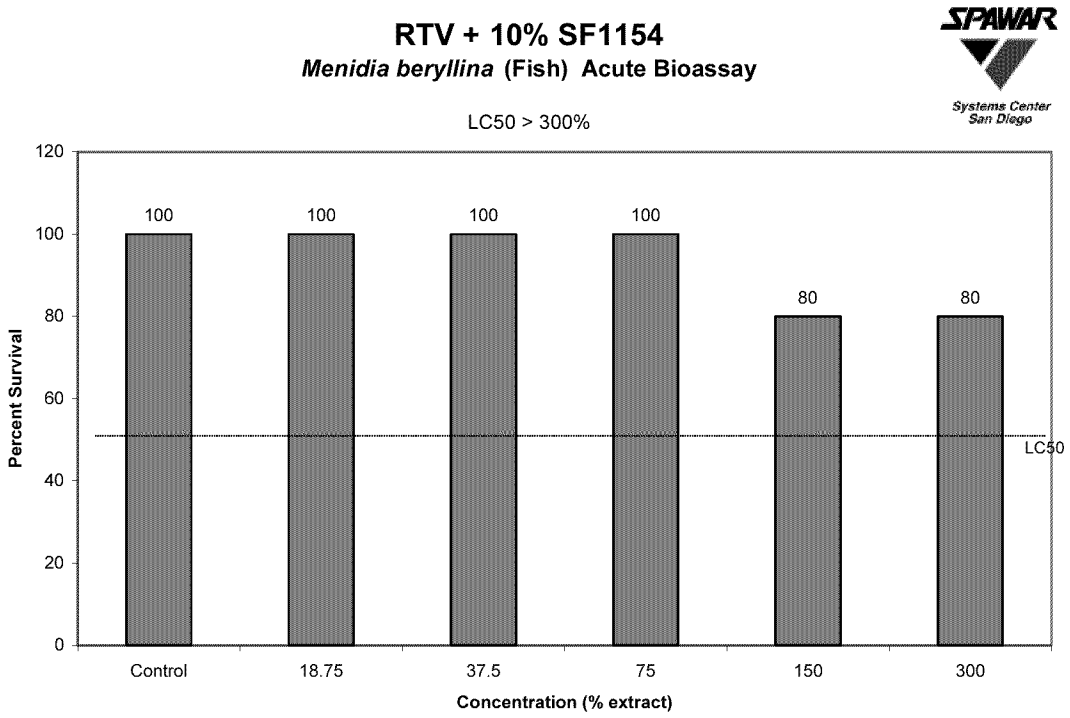

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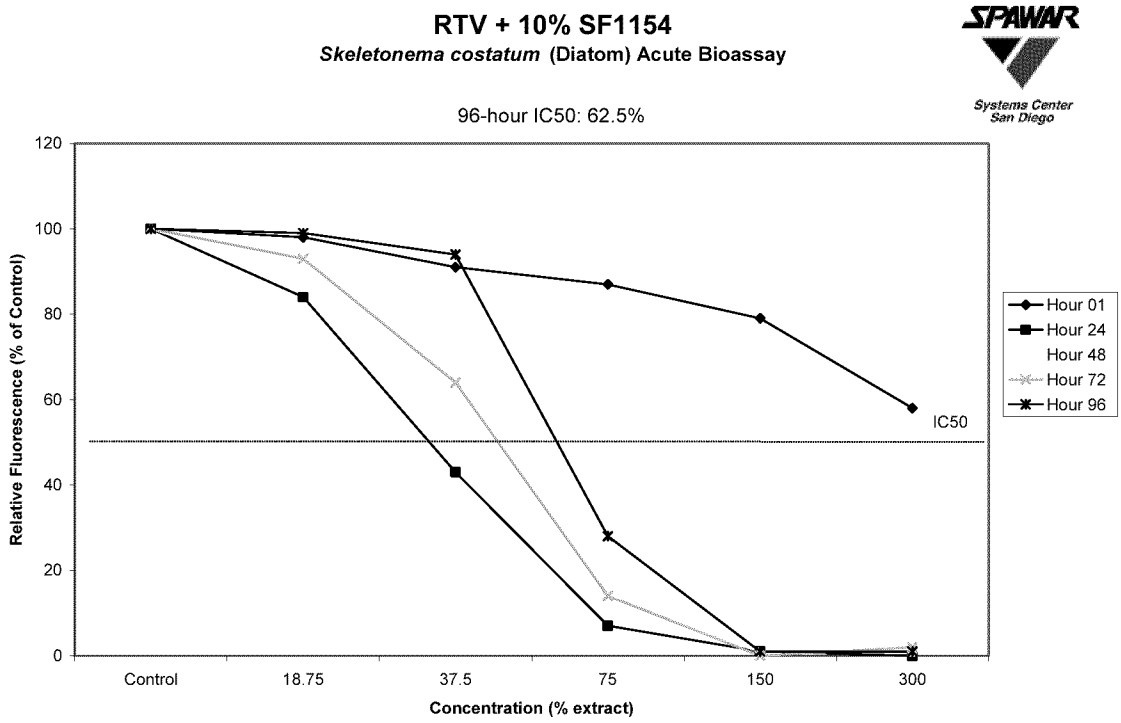

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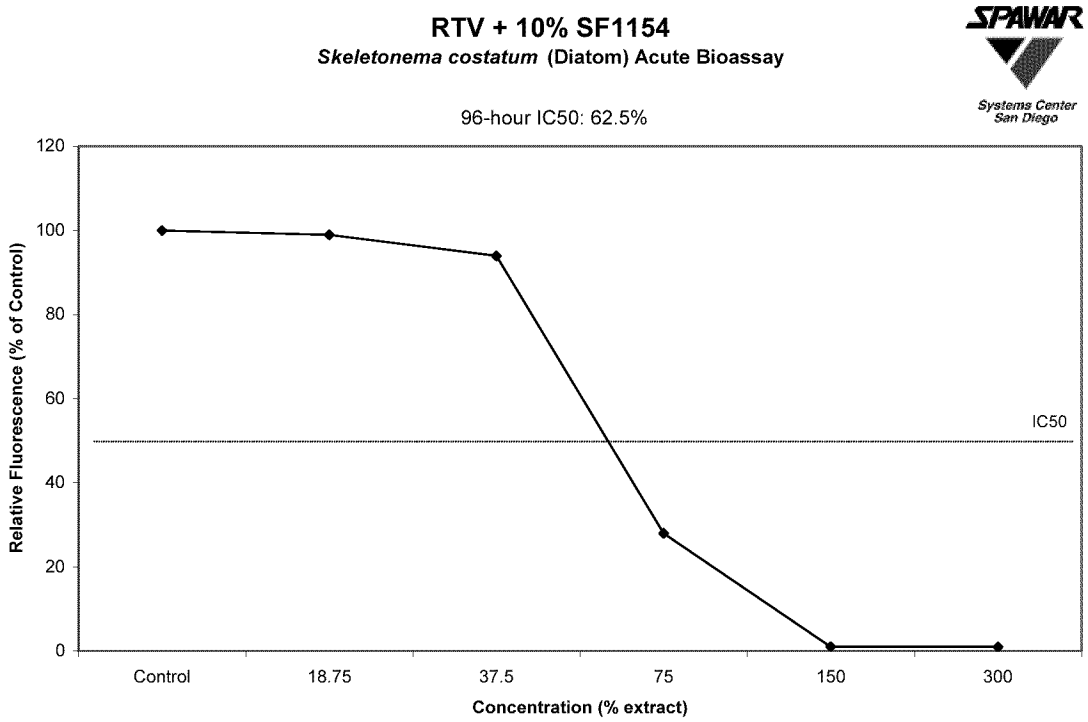

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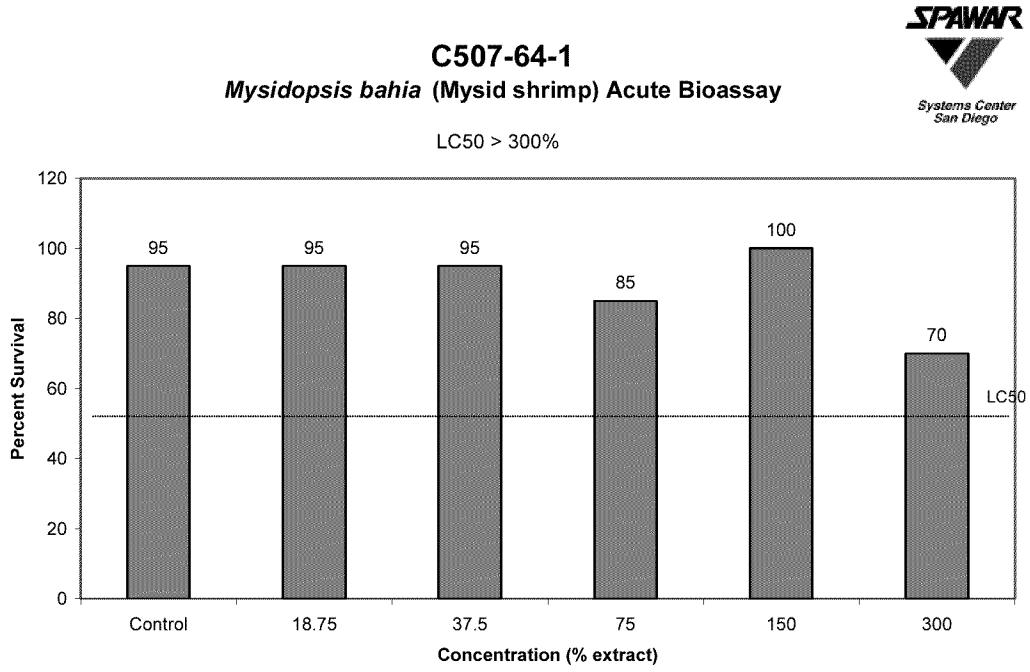

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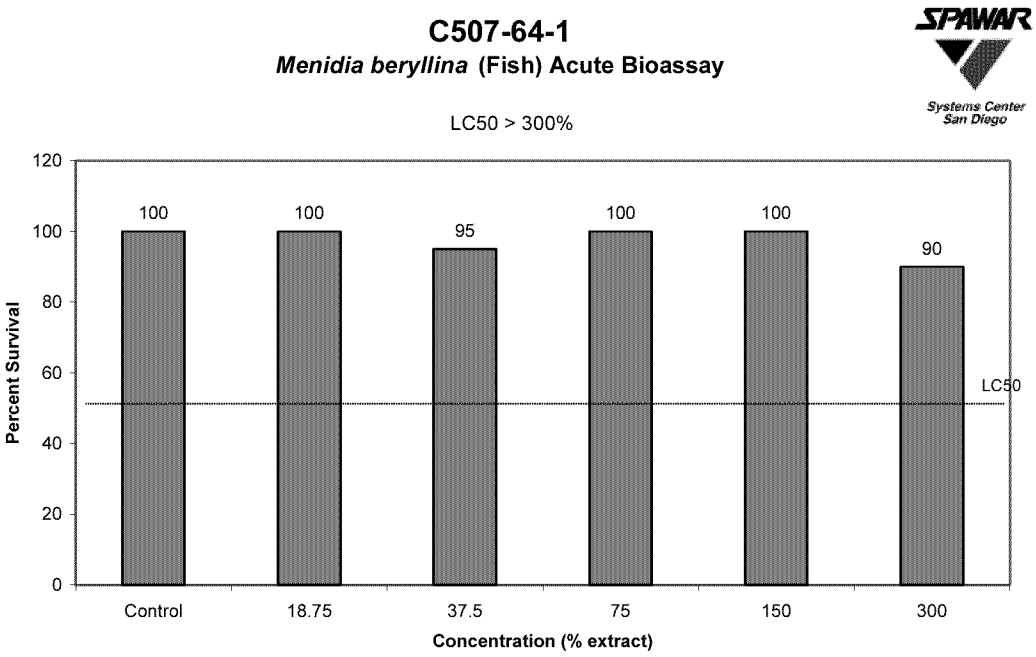

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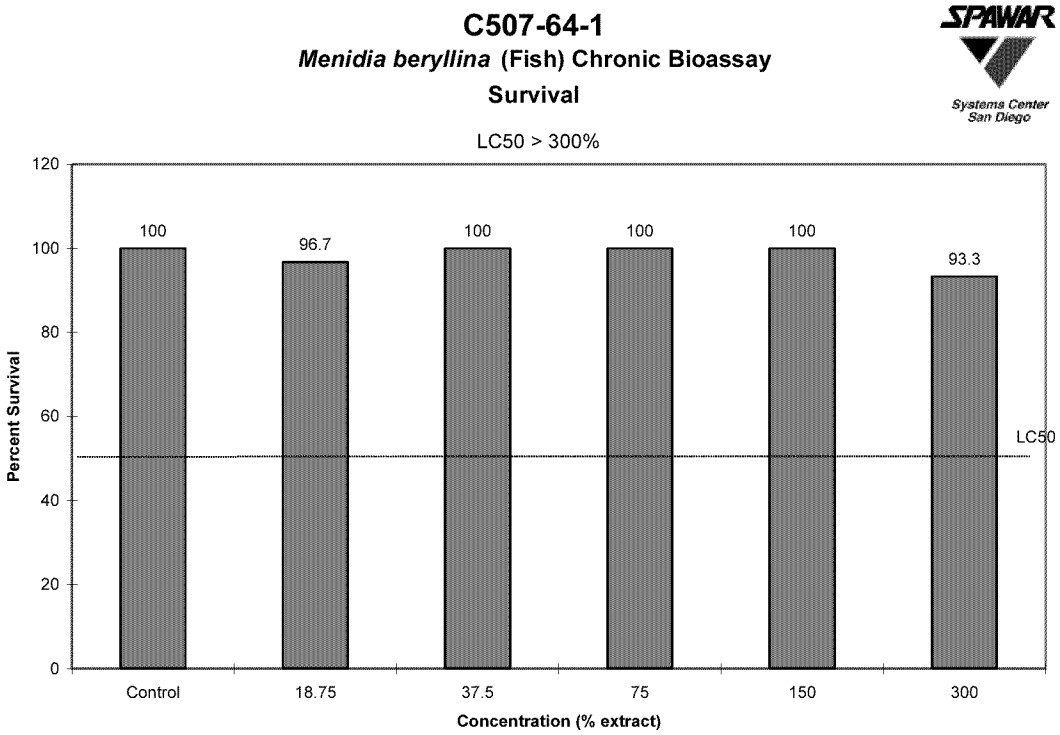

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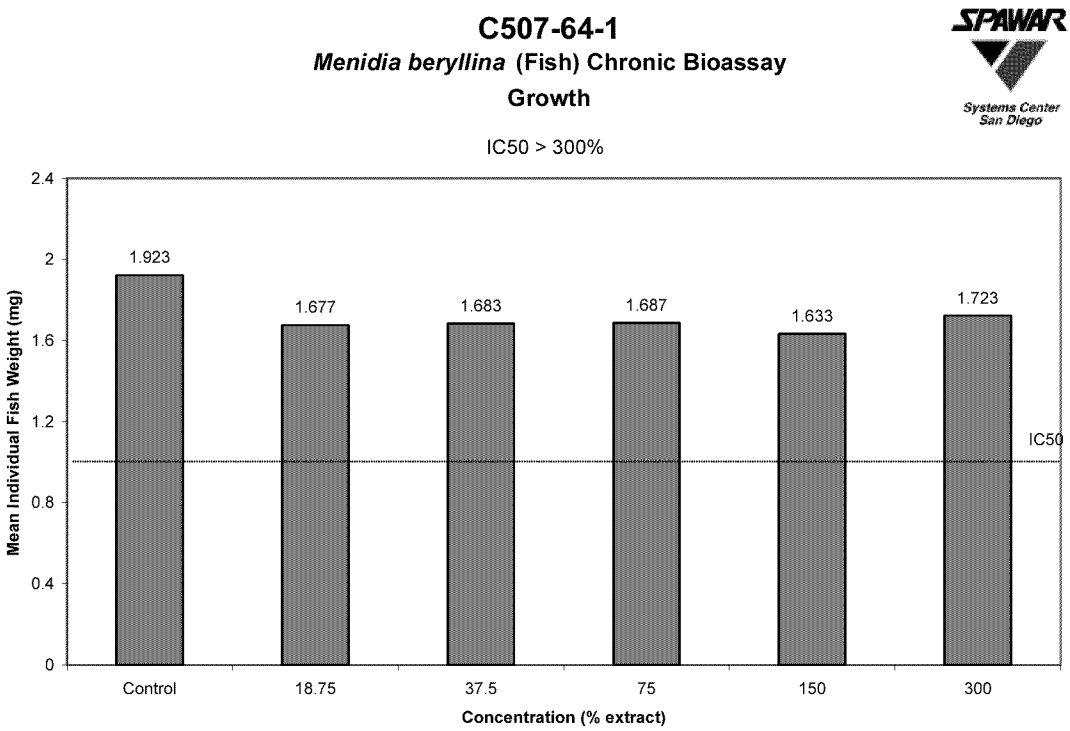

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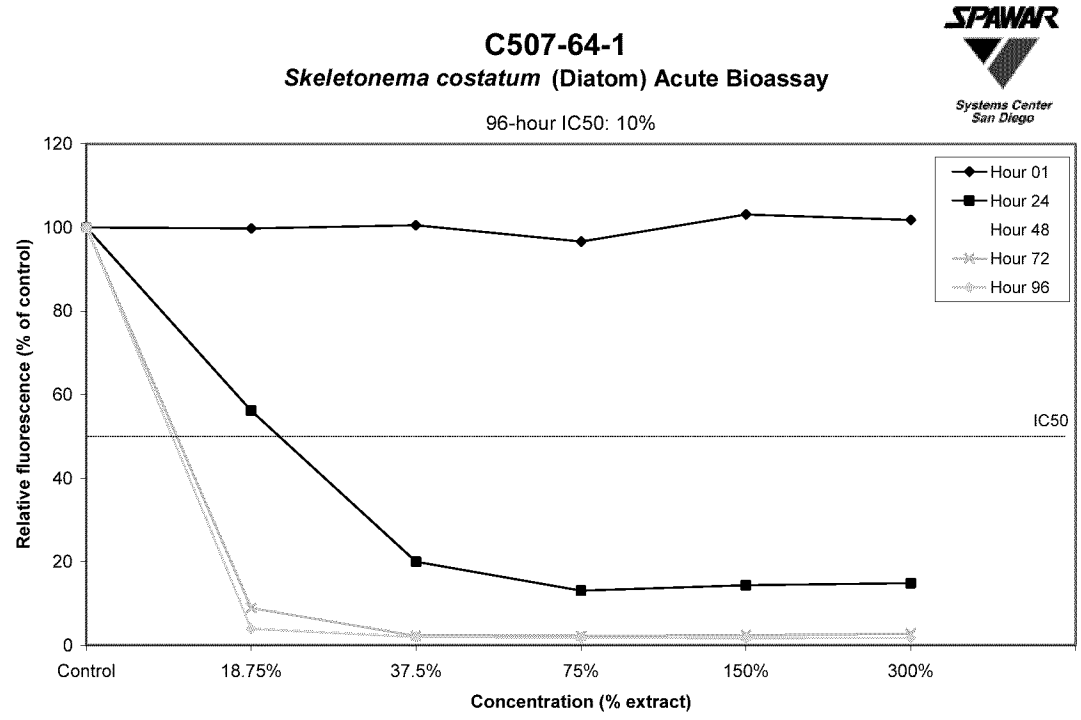

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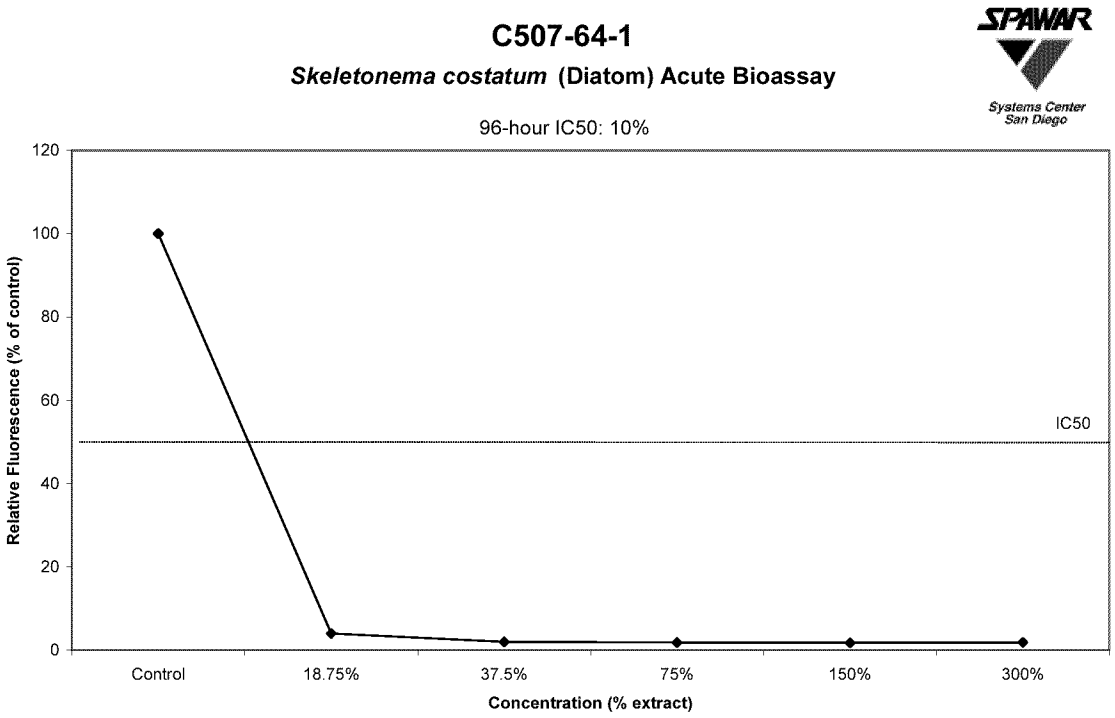

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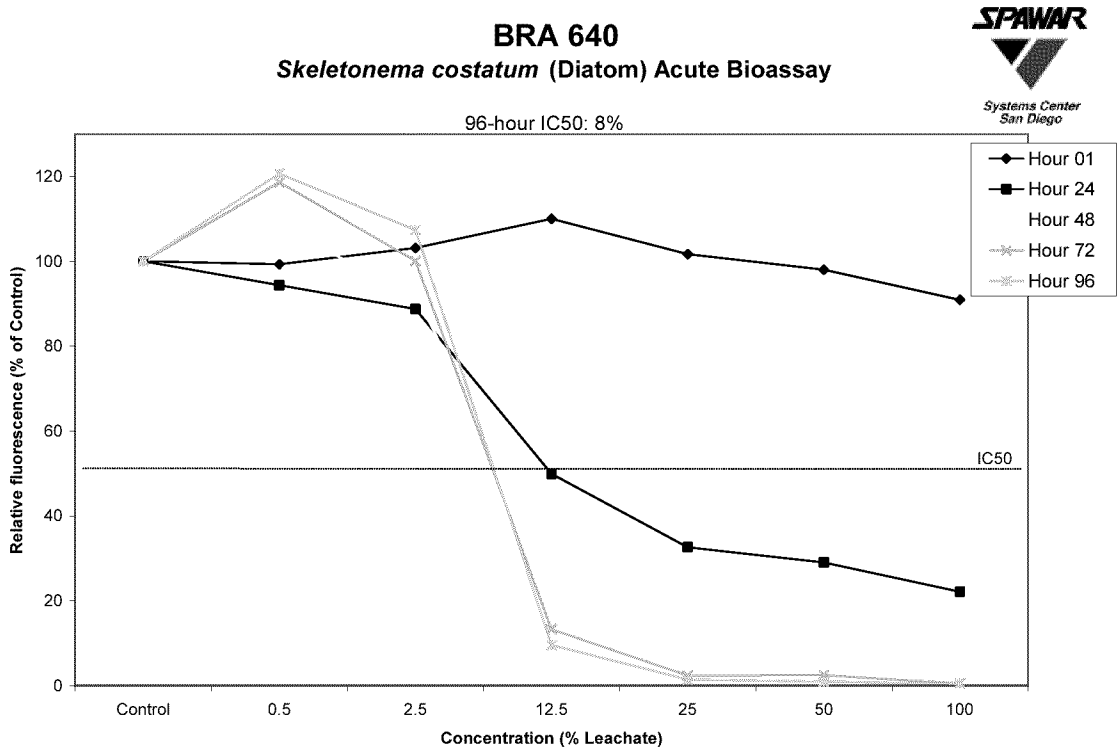

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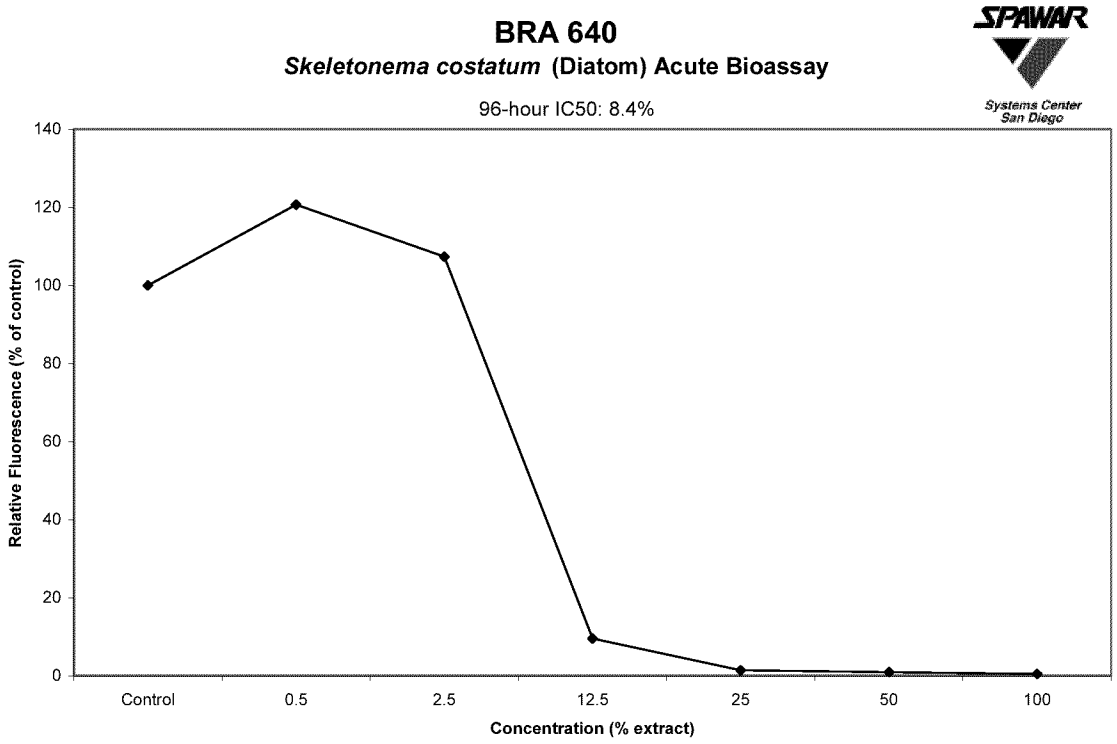

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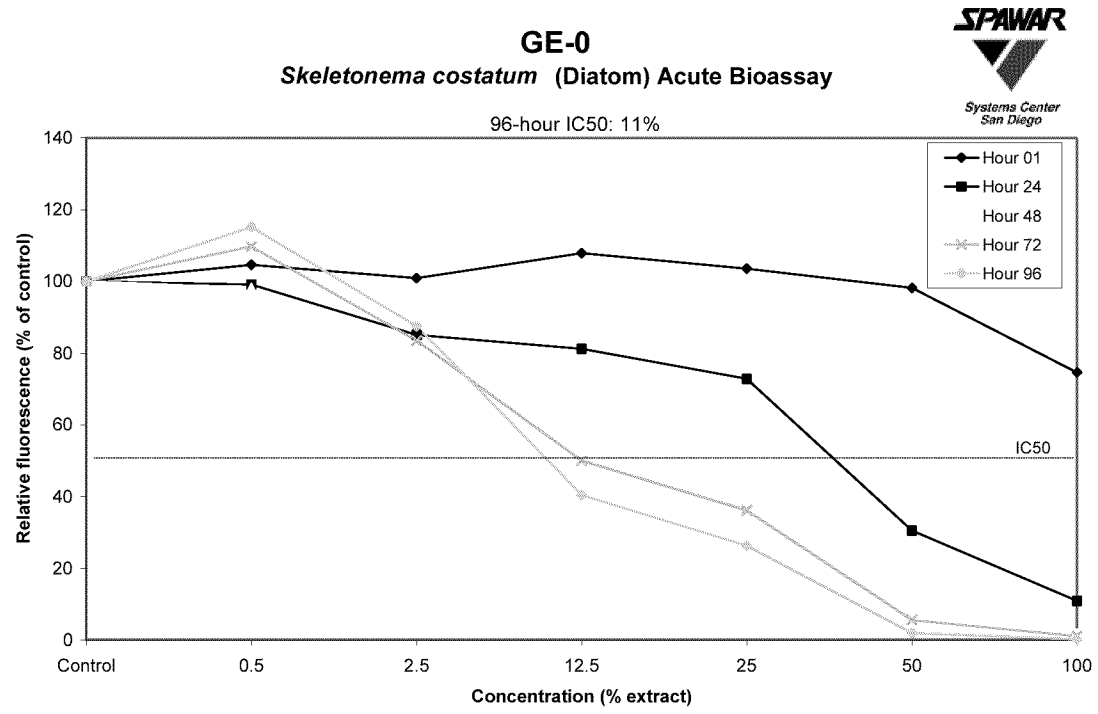

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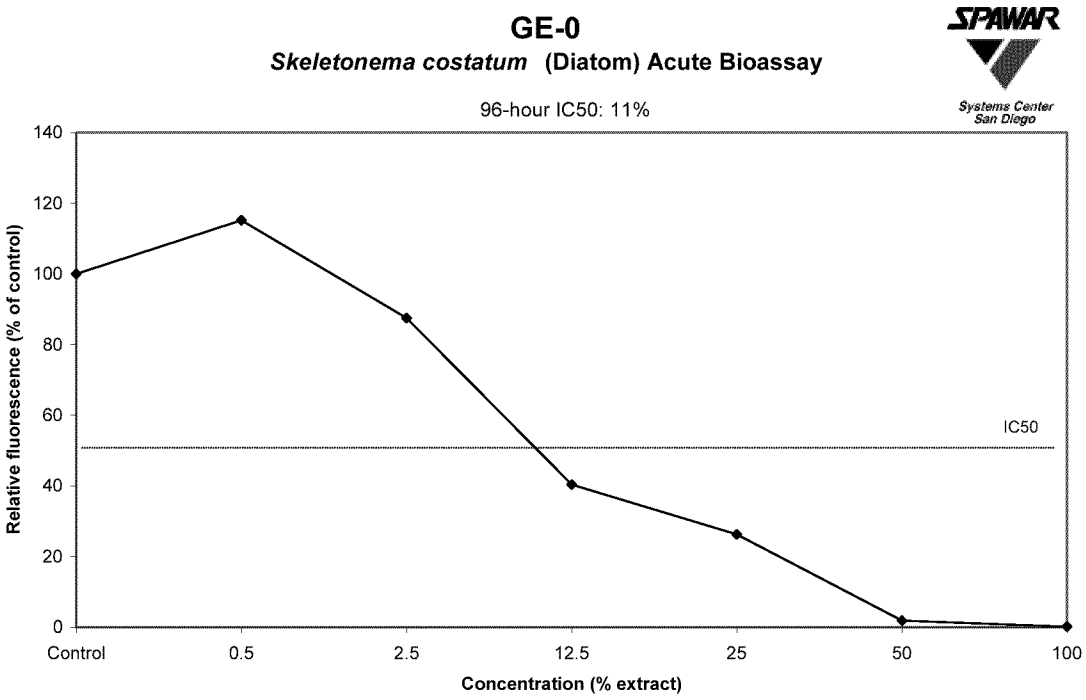

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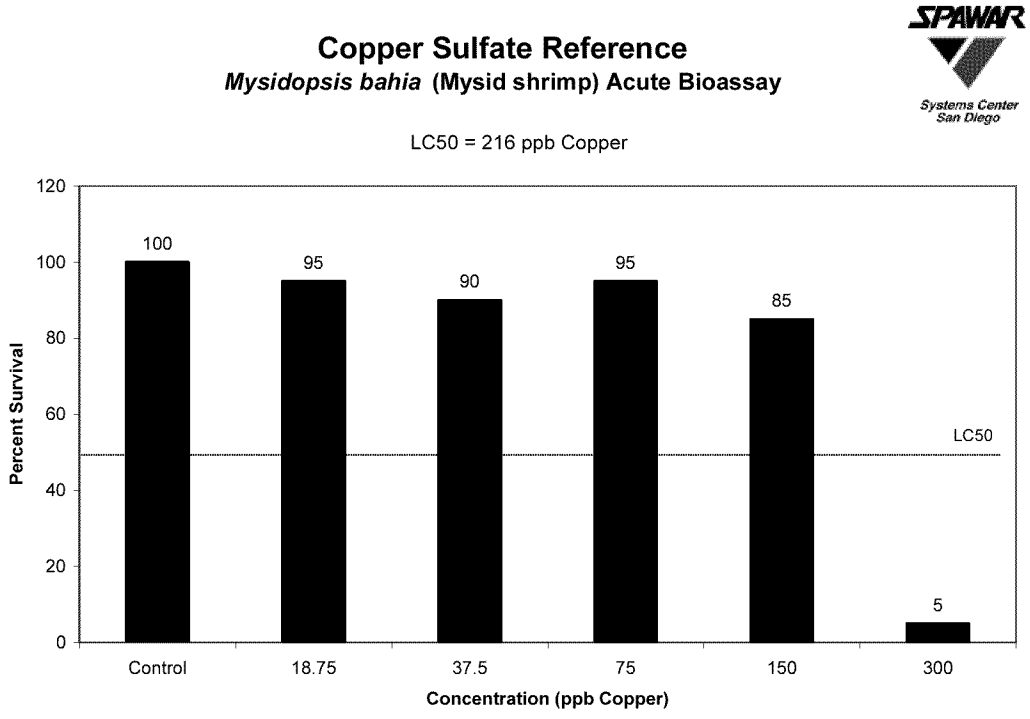

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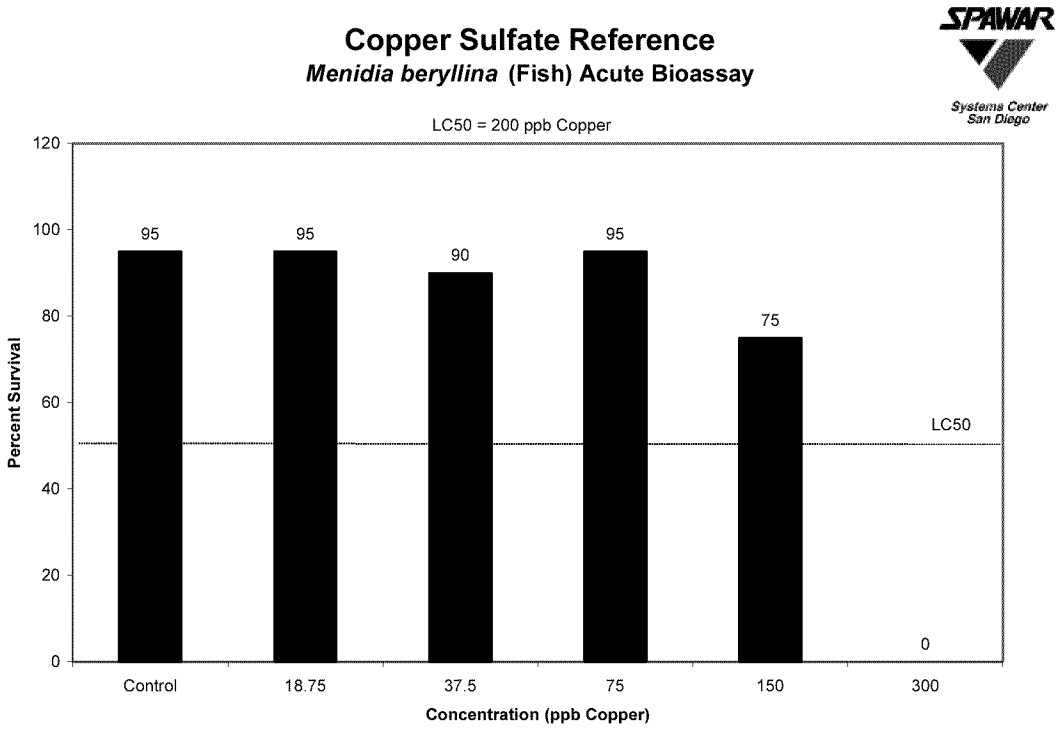

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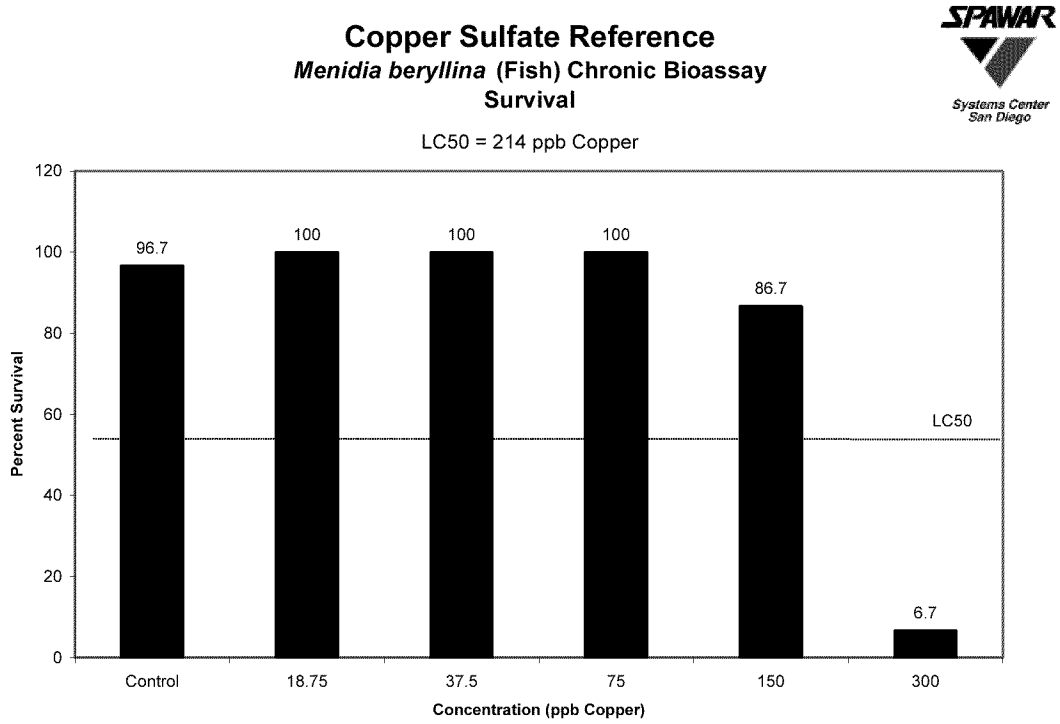

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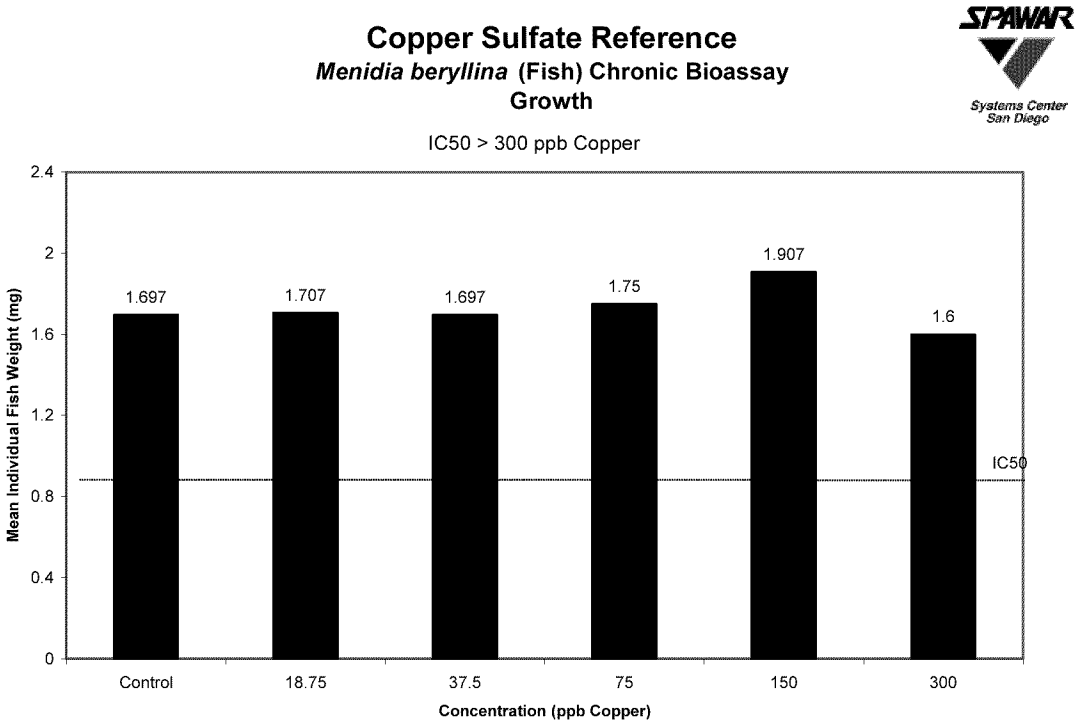
Copper Sulfate Reference
Menidia beryllina (Fish) Chronic Bioassay
Growth
SPAWAR
Systems Center
San Diego
IC50 > 300 ppb Copper
Mean Individual Fish Weight (mg)
2.4
2
1.6
1.2
0.8
0.4
0
1.697
1.707
1.697
1.75
1.907
1.6
IC50
Control
18.75
37.5
75
150
300
Concentration (ppb Copper)

Figure 3.B.64

APPENDIX 4. VALIDATION TRIALS

Appendix 4.A. Large-scale validation report

APPLICATION OF A FOUL-RELEASE COATING SYSTEM (RTV11 WITH SF1147 TOPCOAT OVER SEA/SCM TIE COAT) ON USS WYOMING (SSBN-742) DURING REFIT# 12 AT TRIDENT REFIT FACILITY (TRF), KINGS BAY, GEORGIA

Place Visited: Trident Refit Facility, Kings Bay, GA

Dates Visited: 11-18 October 2000

Visited by: Thomas Radakovich
Code 641
Naval Surface Warfare Center,
Carderock Division (NSWCCD)
Bethesda, MD

Purpose: The purpose of this trip was to document the application of a silicone-based foul-release coating system on a test area on the USS WYOMING (SSBN-742) at TRF, Kings Bay, Georgia. Foul-release coatings are designed to control fouling by creating a slick, low energy surface to which fouling organisms cannot tenaciously attach.

Application: The foul release system applied was RTV11® with 10% SF1147 over an SEA/SCM tie coat. General Electric Company (GE) manufactures RTV11®, SF1147 oil, and the tie coat system components. The system was applied on a test area on the port side of the ship. Most of the test area is located just below maximum beam between frames 42 and 53. This section is about 30 ft long (9.1 m) and 20 ft (6.1 m) high. A portion of the test area extends up above maximum beam between frames 51 and 53 and measures about 5 ft by 5 ft (1.5 m x 1.5 m).

Surface preparation, accomplished by TRF, Shop 71A, consisted of wet grit blasting the surface to a near white metal finish (SSPC-SP-10 according to "Standards of Surface Finish" published by Steel Structures Painting Council). The blast media, Black Beauty coal slag, was mixed with water at the blast nozzle to reduce dust. Rust-Lick B (ITW Fluid Products Group) rust inhibitor was used to prevent flash rusting.

The complete coating system, beginning with the first coat applied to the steel hull, is shown in Table 4.A.1. The first two coats were applied by TRF, Shop 71A. The third, fourth, and fifth coats were applied by GE personnel.

Table 4.A.1. Foul-release coating system

Coat	Coating System
1st-2nd	MIL-P-24441, Type III
3rd	Ameron Marine Coatings Amerlock 400 (Gray epoxy; two components) Batch Nos. Base – LR2000030194 Hardener – LR2000030252
4th	GE Silicones Base – SEA 210A (Batch No. JK071) Thinned with Sherwin-Williams Retarder Thinner K27 (20% by weight) and VM&P Naphtha (20% by weight) Catalyst – SCM 501C (Batch No. KD901) (Approximately 3% by weight)
Topcoat	GE Silicones RTV11 Silicone Rubber Compound Batch number – JN861 (With approximately 0.5% catalyst and 10% SF-1147 oil)

Wet and dry bulb temperatures were measured using a sling psychrometer prior to coating application. Dew point was calculated from the wet and dry bulb temperatures. Surface temperature was measured using a surface temperature thermometer. The dew points, corresponding surface temperatures, and relative humidities are shown in Table 4.A.2.

Table 4.A.2. Environmental conditions

	Coating Applied	***Dew Point (^oF)***	***Surface Temperature (^oF)***	***Relative Humidity (%)***	***Wet Film Thickness (mils)***
Day 1	Amerlock 400 (gray)	57	63	64	6-8
Day 2	SEA/SCM Tie Coat	55	63	59	16-18
Day 3	RTV-11 + 10% SF1147	53	62	69	12-14

Table 4.A.2 shows that the surface temperature always exceeded the dew point by at least 5 ^oF (-15 ^oC). This means that no moisture was present on the surface during paint application.

Christina Darkangelo-Wood, Owen Harblin, and Jim Resue, technical representatives from General Electric Company, were on-site during the application. Airless spray equipment was used to apply all coats. Table 3 summarizes the equipment used during application.

Table 4.A.3. Spray equipment data

Coating Applied	*Tip Size (in.)*	*Pump Ratio*	*Line Specs (Length; Inside Diameter (ID))*
Amerlock 400 (gray)	0.017	30:1	50 ft.; 3/8 in. ID + 6 ft; 3/8 in. ID (whip)
SEA/SCM Tie coat	0.021	40:1	50 ft.; 3/8 in. ID + 6 ft; 3/8 in. ID (whip)
RTV-11 + 10% SF1147	0.017	74:1	50 ft; 1/2 in. ID + 6 ft; 3/8 in. ID (whip)

All coats showed good sprayability. The Amerlock 400 epoxy was thinned by about 5% with Sherwin-Williams K10 lacquer thinner. The topcoat (RTV-11 with 10% SF1147) was thinned by about 20% with VM&P naphtha. All coatings were strained prior to application.

Wet film thickness (WFT), measured by the applicator during coating application, was used to attain proper thickness. Dry film thickness (DFT) was measured to document final coating thickness. An electronic DFT gauge, calibrated to 15 mils, was used to measure DFT of the first three coats, which comprise the epoxy anticorrosive (AC) system. The gauge was calibrated to 35 mils to measure DFT of the entire system. Table 4 below shows results of the DFT survey.

Table 4.A.4. Dry film thickness data

	#Readings (mils)	**Average (mils)**	**Standard Deviation**	**Median (mils)**	**Maximum (mils)**	**Minimum (mils)**
First 3 coats	300	17.7	2.7	17.5	29.6	11.3
Complete System	300	35.4	5.6	35.2	50.2	23.6

Observations: During application of the SEA/SCM tie coat, a narrow stream of water, emanating from the superstructure, ran through the test area. The stream was about two inches wide and occurred at frame 49. The stream had completely stopped by the next day when the topcoat (RTV11® with 10% SF1147) was applied. The topcoat (RTV11® with 10% SF1147) completely covered all traces of the stream.

During application, the topcoat (RTV11® with 10% SF1147) showed extensive runs, probably caused by excessive thickness, along the top of the test area. The runs were smoothed out with a roller. The rolled areas leveled well during the curing process. The cured coating appeared to be tightly adhering.
Toluene was used as a cleaning solvent for the silicone coatings. The industrial hygienist from the TRF Safety Office and the hazardous materials representative from Shop 71A stated that

toluene is banned as a cleaning solvent at Navy installations and strongly urged finding a suitable replacement.

Recommendations:

- Annual evaluations should be conducted based on availability.
- Identify a replacement clean-up solvent for toluene.

For questions about this report, call Tom Radakovich at (301) 227-4786.