Silicone Foul Release Coatings: Effect of the Interaction of Oil and Coating Functionalities on the Magnitude of Macrofouling Attachment Strengths

Judith Stein, Kathryn Truby, Christina Darkangelo Wood, Jeff Stein, Martha Gardner, Geoffrey Swain, Christopher Kavanagh, Brett Kovach, Michael Schultz, Deborah Wiebe, Eric Holm, Jean Montemarano, Dean Wendt, Celia Smith, Anne Meyer

GE Global Research Center, One Research Circle, Niskayuna, NY 12309, USA.
Florida Institute of Technology, Melbourne, FL 32901, USA.
Bridger Scientific, Bourne, MA 02532, USA.
NSWCCD, Bethesda, MD 20084, USA.
University of Hawaii, Honolulu, HI 96812, USA.
University of Buffalo, NY 14212, USA.

Online Publication Date: 01 January 2003


To link to this article: DOI: 10.1080/0892701031000089525
URL: http://dx.doi.org/10.1080/0892701031000089525

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article maybe used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.
# Silicone Foul Release Coatings: Effect of the Interaction of Oil and Coating Functionalities on the Magnitude of Macrofouling Attachment Strengths

**Authors:**

Naval Surface Warfare Center (NSWCCD), Carderock Division, Bethesda, MD, 20084

**Performing Organization:**

Naval Surface Warfare Center (NSWCCD), Carderock Division, Bethesda, MD, 20084

**Report Type:**

Silicone Foul Release Coatings: Effect of the Interaction of Oil and Coating Functionalities on the Magnitude of Macrofouling Attachment Strengths

**Dates Covered:**

00-00-2002 to 00-00-2002

**Distribution/Availability Statement:**

Approved for public release; distribution unlimited

**Subject Terms:**

- **Security Classification of:**
  - Report: unclassified
  - Abstract: unclassified
  - This Page: unclassified

**Language:**

English

**Report Date:**

JUL 2002

**Number of Pages:**

13
Silicone Foul Release Coatings: Effect of the Interaction of Oil and Coating Functionalities on the Magnitude of Macrofouling Attachment Strengths

JUDITH STEINa,*, KATHRYN TRUBYb, CHRISTINA DARKANGELO WOODa, JEFF STEINA, MARTHA GARDNERa, GEOFFREY SWAINb, CHRISTOPHER KAVANAGHb, BRETT KOVACHb, MICHAEL SCHULTZb, DEBORAH WIEBEb, ERIC HOLMD, JEAN MONTEMARANOd, DEAN WENDETe, CELIA SMITHe and ANNE MEYERf

aGE Global Research Center, One Research Circle, Niskayuna, NY 12309, USA; bFlorida Institute of Technology, Melbourne, FL 32901, USA; cBridger Scientific, Bourne, MA 02532, USA; dNSWCCD, Bethesda, MD 20084, USA; eUniversity of Hawaii, Honolulu, HI 96812, USA; fUniversity of Buffalo, NY 14212, USA

(Received 4 January 2002; in final form 24 July 2002)

Silicone biofouling release coatings have been shown to be an effective method of combating fouling. Nearly all silicone foul release coatings are augmented with an oil additive to decrease macrofouling attachment strength. This paper addresses the effect of the type of oil that is incorporated into the silicone coating and the type of silicone coating itself (silica vs calcium carbonate filled) on macrofouling adhesion strengths to the coating. It was found that not only are the main effects of oil type and silicone coating type important in determining the magnitude of the attachment strength of the organism, 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 (Oahu, Hawaii) which has a significance level of \( \alpha = 0.1 \). Each of the organisms exhibited a unique response to the various silicone fouling release coatings. Thus, in order to predict the effects of foul release coatings, the composition variables of the coatings and the type of target organisms must be considered.

Keywords: silicone foul release coatings; condensation cure; barnacle adhesion; tubeworm adhesion; oyster adhesion

INTRODUCTION

Biofouling is ubiquitous in the marine environment. Currently, metal containing antifouling paints are employed on seafaring vessels to reduce biofouling (Bleile & Rodgers, 1989). The negative long-term effect of antifouling paints on the environment has led the development of alternative non-metal containing paints (Cleary & Stebbing, 1985; Karnan et al., 1997). Two approaches have been taken, viz. using organic biocides in conjunction with reduced metal concentrations in antifouling paints and developing nontoxic paints in which organisms can settle but are removed by either mechanical or hydrodynamic cleaning (Swain, 1999).

Initially, both silicones and fluoropolymers were explored as fouling release surfaces as both polymers exhibit low critical surface tensions, an attribute considered essential for foul releasing ability (Goupil et al., 1973; Meyer et al., 1995). Field data indicated that silicone polymers outperformed fluoropolymers; thus, recent efforts have focused on enhancing the fouling release capability of silicone coatings (EPRI, 1989; Brady, 1997). Both Sigma Paints (Amsterdam, The Netherlands) and Akzo Nobel (Gateshead, UK) have commercialized foul release coatings based on silicone polymers.

Stein et al. (2003) report the effect of crosslink density and filler loading of silicone coatings on their fouling release properties and found an inverse correlation between fouling release performance and filler loading. However, the physical properties were enhanced by addition of filler. Therefore, the best foul release coatings had the lowest durability. It has been suggested that one way to increase foul release performance without compromising durability properties is to incorporate oil into the silicone
coating (Milne, 1977a; 1977b; Edwards et al., 1994; Nevell et al., 1996). Newby et al. (1995) suggested that interfacial slippage (friction) is an important determinant of release performance. Oils by their nature are lubricants and therefore should decrease the coefficient of friction of the coatings. Milne (1977a; 1977b) has shown that incorporation of polydimethylsiloxane oil into silicone coatings decreased the coverage of organisms on the coatings. Truby et al. (2000) reported that oil incorporation into silicone coatings decreased the attachment strength of macrofouling organisms with only moderate decreases in the modulus of elasticity of the coatings. However, these studies were limited to one type of oil and did not address compositional difference with respect to the silicone coatings themselves. Dalton et al. (2000) also reported that the effect of oil incorporation into silicone coatings on bacterial attachment indicated that the mode of attachment was dependent upon the oil type. Wynne et al. (2000) compared the foul release properties of RTV11 and a hydrosilylation cured polydimethylsiloxane and found subtle differences in their performance but did not include oil in his formulations.

In this paper, the effect of the compositional variables of model silicone systems including oil functionality and silicone coating type on macrofouling attachment strength on panels at two different sites (Indian River Lagoon, Melbourne, Florida and Ford Island, Oahu, Hawaii) is described. The response of tubeworms (*Hydroides elegans, Hydrodeta dianthus*), oysters (*Ostrea sp.*, *Crassostrea sp.*) and barnacles (*Balanus eburneus*) to coatings comprising three oil types and two filler types was determined.

### MATERIALS AND METHODS

#### Materials

ALT 251 (a decylmethylsiloxane organic compatible oil) and DMSC15 (a carbinoxil terminated polydimethylsiloxane oil) were obtained from Gelest (Tullytown, PA). Vinylterminated polydimethylphenylsiloxanes (3.0–3.5 mole% diphenylsiloxane; MW = 15,000, 27,000 and 62,000 Da) were also obtained from Gelest. SF1154 (a polydimethylsiloxane oil) was obtained from GE Silicones (Waterford, NY). Silanol polymers, tetrapropylorthosilicate, tetraethylorthosilicate, polydimethylsiloxane, dibutyldiilaurate, silica filler and calcium carbonate filler were obtained from GE Silicones. Silgan JS01 was obtained from Wacker Chemie (Munich, Germany). Amerlock 400 epoxy was obtained from the Ameron Company (Pasadena, CA).

#### Preparation of Model Foul Release Coatings

Calcium carbonate filled silicones were prepared by combining 29 g of calcium carbonate (0.287 moles), 69 g of silanol terminated polydimethylsiloxane (MW = 40,000, 1.7 mmoles), and 2.3 g of tetraetylorthosilicate (0.011 moles) in a Ross mixer. Masterbatches were stored for up to 6 months. To 100 g of the masterbatch were added 10 g of the appropriate oil. The resultant mixture was catalyzed with 0.5 g of dibutyltindilaurate (0.80 mmoles).

Silica filled masterbatches were prepared according to literature methods (Stein et al., 2000). To 40 g of the resultant masterbatch were added 53 g of silanol terminated polydimethylsiloxane (MW = 40,000, 1.3 mmoles), 6 g propylsilicate (0.23 mmoles) and 1 g of silanol terminated polydimethylsiloxane (MW = 500, 2 mmoles). To 100 g of the above mixture were added 10 g of the appropriate oil. The oil-amended coating was catalyzed with 0.9 g dibutyltindilaurate (1.3 mmoles).

#### Panel Preparation and Deployment Site Description

Coatings were applied as the topcoat of the NRL duplex fouling release coating system (Griffith, 1995), which consists of an anti-corrosive epoxy layer (Amerlock 400), a toughening silicone-styrene butylacrylate copolymer tie layer (Silgan J501), and the silicone topcoat. The coatings were applied to 25.4 cm × 30.5 cm (10 in. × 12 in.) steel panels using standard airless spray equipment. The wet film thickness of the silicone topcoat was 0.25–0.30 mm (10–12 mil). Two panels (four sides) were submitted for exposure at two sites, *viz.* the Florida Institute of Technology (FIT) exposure and testing platform in the Indian River Lagoon, Florida (subtropical estuarine) and the University of Hawaii Ford Island Test Site, Hawaii (tropical marine). The panels at the Indian River lagoon and the Ford Island Test sites were deployed in July 1997 and August 1997, respectively. Coverage and macrofouling attachment strengths were assessed until May 2001.

#### Coverage

The cumulative coverage at the Hawaii Ford Island test site was monitored according to the standard method for testing of antifouling panels in shallow submergence (ASTM D 3623-78a, 1978). The panels were inspected quarterly.

#### Measurement of Macrofouling Attachment Strength

The shear adhesion strengths of barnacles (*Balanus eburneus*), tubeworms (*Hydroides elegans*), oysters (*Ostrea sp.*, *Crassostrea sp.*) and barnacles (*Balanus eburneus*) to coatings comprising three oil types and two filler types was determined.
and *Hydroides dianthus*) and oysters (*Ostrea* sp. and *Crassostrea* sp.) to the silicone coatings were measured using ASTM D 5618-94 (1994), in which a force is applied parallel to the base of the hard fouling organism until the organism detaches. Cumulative adhesion strength measurements were made throughout the exposure period.

A 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 (SD) for reproducibility and repeatability of 0.007 with a repeatability SD of 0.005 and reproducibility SD of 0.005.

**Statistical Analysis**

Statistical analyses were preformed using Minitab and Design Expert. Analysis of variance (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 were 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**

**Macrofouling 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 silica or calcium carbonate fillers and oil types comprised polydimethyldiphenylsiloxane (SF1154), hydrophilic siloxane (DMSC15) and decylmethyl organic compatible siloxane (ALT251). Both silicone coating types were crosslinked *via* a condensation mechanism in which telechelic silanol polymers were reacted with tetraalkoxysilanes using dibutyltindilaurate as the catalyst in the presence of either silica or calcium carbonate fillers. Oils were incorporated at 10-wt% prior to addition of the catalyst. A general scheme for preparation of the coatings is given shown below (Scheme 1).

Coverage assays were performed at the Hawaii Ford Island test site after 12 months water immersion. Substantial differences in macrofouling coverage were seen on the different coatings (Figure 1). The benefit of oil incorporation on coverage was a function of the coating system and oil type. In general, fouling was present in greater quantities on coating systems containing silica filler than on coating systems with calcium carbonate filler. In the case of the silica filled systems, coatings amended with ALT251 outperformed coatings comprising either SF1154 or DMSC15. For the calcium carbonate filled systems, coatings amended with SF1154 had greater fouling than those containing DMSC15 or ALT251. Thus, the effect of oil was dependent upon the coating system into which it had been incorporated. Whereas the calcium carbonate filled silicone-coating system with DMSC15 oil exhibited little fouling, the comparable silica filled system was heavily fouled with oysters (*Ostrea* sp.). Conversely, the silica filled system amended with ALT251 had less fouling coverage than the comparable calcium carbonate filled system. 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.

**Intrasite Comparisons of Macrofouling Attachment Strengths**

**Barnacle attachment strengths at the Indian River Lagoon test site**

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 *B. eburneus* adhesion measurements were performed on the six coatings to ensure that the means had significance levels of $\alpha = 0.05$ so that coating performance differences could be statistically distinguished. ANOVA of the attachment strengths of barnacles to the six coatings was significant ($p - value = 0000$. $F = 80.98$) (Table I, Figure 2).

Linear regression analysis was performed to determine whether the coating composition and/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 3, Table II). Thus, not only was 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 the calcium carbonate filled base than in the silica filled base. Although DMSC15 oil provided the lowest attachment strength in the calcium carbonate filled model system, its performance in the silica filled systems was comparable to ALT251. The highest attachment strength was obtained on silica filled coating systems amended with SF1154.

Attachment strengths of three species of barnacles (Balanus variagatus, Balanus improvisus, and B. eberneus) on two oil-amended coatings were obtained. However, accumulation of B. variagatus and B. improvisus was too limited on the SF1154 amended coating to provide significant barnacle

---

TABLE I ANOVA analysis for barnacle (B. eberneus) adhesion strength on the six coatings at the Indian River Lagoon test site

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acronym</td>
<td>5</td>
<td>0.226581</td>
<td>0.045316</td>
<td>80.98</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>1323</td>
<td>0.740326</td>
<td>0.000560</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1328</td>
<td>0.966908</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Individual 95% CIs for mean based on pooled SD

<table>
<thead>
<tr>
<th>Level</th>
<th>N</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>219</td>
<td>0.04241</td>
<td>0.01938</td>
</tr>
<tr>
<td>3</td>
<td>213</td>
<td>0.07339</td>
<td>0.01379</td>
</tr>
<tr>
<td>5</td>
<td>91</td>
<td>0.02371</td>
<td>0.01633</td>
</tr>
<tr>
<td>6</td>
<td>138</td>
<td>0.04116</td>
<td>0.02340</td>
</tr>
<tr>
<td>7</td>
<td>299</td>
<td>0.04055</td>
<td>0.01960</td>
</tr>
<tr>
<td>8</td>
<td>369</td>
<td>0.04157</td>
<td>0.01955</td>
</tr>
</tbody>
</table>

Pooled SD = 0.02366

---

Downloaded By: [US Naval Academy] At: 16:40 18 March 2008
attachment strength values. The attachment strengths were both a function of the species of barnacle as well as the coating type (Figure 4, Table III). However, the interaction term (barnacle species crossed with coating type) was insignificant. Thus, the order of adhesion strength among the barnacles was independent of the coating compositions. Of the three species, B. variagatus displayed the largest adhesion strength to the two surfaces.

The effect of oil molecular weight on the attachment strength of B. eberneus was probed by incorporation of vinylterminated polydimethylidiphenylsiloxanes into the coating systems. Three different molecular weights were employed that spanned the region above and below the entanglement molecular weight. Linear regression models indicated that the coating type was significant but not the oil type (Figure 5, Table IV). However, the interaction term was significant, indicating that adhesion is a function of the type of oil and into which coating it is placed.

Oyster (Crassostrea sp.) and tubeworm (H. dianthus) attachment strengths at the Indian River Lagoon site

Linear regression analyses of the adhesion strengths of H. dianthus and Crassostrea sp. at the Indian River Lagoon site indicate that both the main effects of silicone coating type and oil type are significant (Figures 6, 7, Tables V, VI). Interaction plots for both organisms show a significant dependence on the cross-term of coating type and oil type. The responses of H. dianthus and Crassostrea sp. to the coatings follow a similar trend, but very different than that of B. eberneus to the coatings. The attachment strengths of tubeworms (H. dianthus) and oysters (Crassostrea sp.) were always less on
calcium carbonate filled systems relative to silica filled coatings. For both organisms, the calcium carbonate filled coating amended with ALT251 elicited the lowest response; whereas the calcium carbonate filled coating with DMSC15 provided the lowest response against barnacles (*B. eburneus*). For all three species of macrofouling organism, the silica filled systems amended with SF1154 exhibited the worst performance. 

**Oyster (Ostrea sp.) and tubeworm (H. elegans) attachment strengths at the Hawaii Ford Island test site**

The attachment strengths of *Ostrea* sp. and *H. elegans* were less on calcium carbonate filled systems than on silica filled coatings. Inclusion of ALT251 in either coating resulted in the lowest adhesion values. With both organisms, the main effects were significant. However, the interaction term of oil type crossed with coating type was significant only for tube-worms at $\alpha = 0.05$. (Figures 8, 9, Tables VII, VIII). Interaction plots were similar for both organisms.

**Intersite Comparison of Tubeworm (H. dianthus and H. elegans) and Oyster (Crassostrea sp. and Ostrea sp.) Attachment Strengths**

*Crassostrea* sp. and *H. dianthus* at the Indian River Lagoon test site were similar in their responses to the oil amended coatings as were *Ostrea* sp. and *H. elegans* at the Hawaii Ford Island test site. However, the response trends were not the same between the two sites. For tubeworms (*H. dianthus* and *H. elegans*) and oysters (*Crassostrea* sp. and *Ostrea* sp.) at both sites, coatings amended with ALT251 elicited the lowest adhesion values. Calcium carbonate filled coatings outperformed silica filled coatings at both sites.

Performance differences between the calcium carbonate filled coatings amended with the three oils were less at the Hawaii Ford Island test site compared with the Indian River Lagoon test site. The worst performing coating at the Indian River Lagoon test site was the silica filled system amended with SF1154. At the Hawaii Ford Island test site, the worst coating performance depended upon the organism, the silica filled coating amended with SF1154 exhibiting the worst performance against *H. elegans* and the silica filled coating containing DMSC 15 performing the worst against (*Ostrea* sp.).

**TABLE II** Linear regression model for barnacle (*B. eburneus*) adhesion strength vs coating type and oil type at the Indian River Lagoon test site

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq. SS</th>
<th>Adj. SS</th>
<th>Adj. MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>2</td>
<td>39.451</td>
<td>45.862</td>
<td>22.931</td>
<td>101.97</td>
<td>0.000</td>
</tr>
<tr>
<td>Coating type</td>
<td>1</td>
<td>15.938</td>
<td>25.174</td>
<td>25.174</td>
<td>111.94</td>
<td>0.000</td>
</tr>
<tr>
<td>Oil × Coating type</td>
<td>2</td>
<td>20.084</td>
<td>20.084</td>
<td>10.042</td>
<td>44.66</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>1323</td>
<td>297.518</td>
<td>297.518</td>
<td>0.225</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1328</td>
<td>372.991</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE III** Linear regression model for barnacle adhesion strength vs barnacle type (*B. eburneus, B. improvisus, B. varigatus*) and coating type at the Indian River Lagoon test site

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq. SS</th>
<th>Adj. SS</th>
<th>Adj. MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating</td>
<td>1</td>
<td>0.0189</td>
<td>0.0185</td>
<td>0.0092</td>
<td>16.20</td>
<td>0.000</td>
</tr>
<tr>
<td>Barnacle type</td>
<td>2</td>
<td>0.0488</td>
<td>0.0247</td>
<td>0.0247</td>
<td>43.16</td>
<td>0.000</td>
</tr>
<tr>
<td>Coating × Barnacle type</td>
<td>2</td>
<td>0.0019</td>
<td>0.0019</td>
<td>0.0009</td>
<td>1.71</td>
<td>0.183</td>
</tr>
<tr>
<td>Error</td>
<td>622</td>
<td>0.3564</td>
<td>0.3564</td>
<td>0.0003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>627</td>
<td>0.4261</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The attachment strengths of barnacles (*B. eburneus*) at the Indian River Lagoon test site were less than that of tubeworms (*H. dianthus* and *H. elegans*) and oysters (*Ostrea* sp. and *Crassostrea* sp.) at either site (Figure 10).

The composition of the optimal coating 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 SD (Table IX). Using this method of analysis, the best performance against all organisms at both sites was exhibited by the calcium carbonate filled coating amended with ALT251.

**SUMMARY**

Oil amended silicone coated panels were immersed at two aquatic sites. Macrofouling coverage was monitored visually and attachment strength determined using a calibrated force gage. This parameter was used to determine the fouling release efficacy of the coatings. The two silicone coating types were amended with a hydrophilic carbinol terminated silicone oil (DMSC 15), a phenylmethylsiloxane oil(SF1154) or a decylmethyl siloxane oil(ALT 251). The attachment strength of three organisms, barnacles (*B. eburneus*), tubeworms (*H. dianthus* and *H. elegans*) and oysters (*Ostrea* sp. and *Crassostrea* sp.) was measured with respect to each of the six coatings. In general, the performance of calcium carbonate filled systems was superior to silica filled systems for each of the targeted organisms.

Wynne et al. (2000) also observed better fouling release properties on calcium carbonate filled systems compared with silica filled systems for each of the targeted organisms. Wynne et al. (2000) also observed better fouling release properties on calcium carbonate filled coatings compared with silica filled systems. They suggested that calcium carbonate filled coatings have lower surface moduli than silica filled coating since calcium carbonate has been proposed to deplete from the surface of the coating. They suggested that a lower surface modulus would result in smaller attachment strengths.

**FIGURE 5** Interaction plot of barnacle (*B. eburneus*) adhesion strength vs coating type and oil molecular weight at the Indian River Lagoon test site.

**TABLE IV** Linear regression model of barnacle (*B. eburneus*) adhesion strength vs oil molecular weight and coating type at the Indian River Lagoon test site

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq. SS</th>
<th>Adj. SS</th>
<th>Adj. MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating type</td>
<td>1</td>
<td>3.51</td>
<td>3.3815</td>
<td>3.3815</td>
<td>16.11</td>
<td>0.000</td>
</tr>
<tr>
<td>Oil MW</td>
<td>2</td>
<td>0.0093</td>
<td>0.0557</td>
<td>0.0278</td>
<td>0.13</td>
<td>0.876</td>
</tr>
<tr>
<td>Coating type x Oil MW</td>
<td>2</td>
<td>2.6190</td>
<td>2.6190</td>
<td>1.3095</td>
<td>6.90</td>
<td>0.001</td>
</tr>
<tr>
<td>Error</td>
<td>309</td>
<td>64.8718</td>
<td>64.8718</td>
<td>0.2099</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>314</td>
<td>71.0101</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In the present study it was found that both the coating type and oil type were significant parameters for quantification of attachment strengths for all organisms. The interaction term of coating type and oil type was significant for all species at $\alpha = 0.05$ except oysters (Ostrea sp.) at the Hawaii Ford Island test site, which was significant at $\alpha = 0.1$. The calcium carbonate coating amended with DMSC15 exhibited the best fouling release properties against barnacles (B. eburneus). However, this coating was the worst of the calcium carbonate filled coatings with respect to attachment strengths of tubeworms (H. elegans and H. dianthus) and oysters (Ostrea sp. Crassostrea sp.) at both sites. The best performing coatings against H. elegans and H. dianthus and Ostrea sp. and Crassostrea sp. were coatings amended with ALT251. Thus, not all oils exhibited the same performance benefit and the overall efficacy was a function of oil functionality, coating type, and the interaction of the oil with the coating.

**FIGURE 6** Interaction plot of tubeworm (H. dianthus) adhesion strength vs coating type and oil type at the Indian River Lagoon test site.

**FIGURE 7** Interaction plot of oyster (Crassostrea sp.) adhesion vs coating type and oil type at the Indian River Lagoon test site.
Kendall (1971) developed an equation for reversible adhesion of a rigid punch to an elastomer in tension that the authors have modified to include both reversible and nonreversible terms as components of the fracture energy, \( G_a \) in shear:

\[
\sigma = \left(\frac{2G_0G'}{t}\right)
\]

where \( \sigma \) is the removal stress, \( G' \) is the shear modulus of the coating and \( t \) is the thickness of the coating (Stein et al., 2003). The fracture energy, \( G_a \), is composed of contributions from the coating, adhesive and interfacial surface tension terms (Dupree work of adhesion), viscoelastic energy dissipation, pullout of polymer chains and energy required to break chemical bonds. For the series of coatings, oil incorporation can change the dissipative forces of the coating (reflected in the value of \( \tan \delta \) for the coating), \( G' \) and the critical surface tension. Oil incorporation into a silicone coating may also increase interfacial slippage, thereby reducing attachment strengths of organisms. Each of these parameters remains constant for a particular coating. However, each macrofouling
organism has a unique response to the coatings. For example, knowledge of barnacle (B. eburneus) adhesion strength as a function of coating type and oil type at the Indian River Lagoon test site does not allow prediction of the response of tubeworms (H. dianthus) or oysters (Crassostrea sp.). In addition to inherent attributes of the coating, large performance differences of the coatings must be attributed to the nature of the probe organism, i.e., the attachment strength of the average tubeworm (H. dianthus and H. elegans) is three times greater than that of the barnacle B. eburneus (0.15 mPa vs 0.05 mPa). Thus the interfacial interaction of the adhesive secreted by the target organism and the coating is also an important determinant of the efficacy of a coating as well as coating attributes such as coating type, incorporated oil type, and the interaction of the coating with the oil.

A subsequent paper will address the mechanical properties of these coatings and will define the relationship between interfacial slippage, modulus, and oil layer thickness on pseudobarnacle adhesion strength. The results of nanoadhesion measurements on these surfaces will also be reported.

### TABLE VII

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq. SS</th>
<th>Adj. SS</th>
<th>Adj. MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>2</td>
<td>12.1003</td>
<td>14.2154</td>
<td>7.1077</td>
<td>16.75</td>
<td>0.000</td>
</tr>
<tr>
<td>Coating type</td>
<td>1</td>
<td>8.1777</td>
<td>9.7972</td>
<td>9.7972</td>
<td>23.08</td>
<td>0.000</td>
</tr>
<tr>
<td>Oil × Coating type</td>
<td>2</td>
<td>12.0800</td>
<td>12.0800</td>
<td>6.0400</td>
<td>14.23</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>162</td>
<td>68.7524</td>
<td>68.7524</td>
<td>0.4244</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>167</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE VIII

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq. SS</th>
<th>Adj. SS</th>
<th>Adj. MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>2</td>
<td>10.6671</td>
<td>6.8606</td>
<td>3.4303</td>
<td>13.59</td>
<td>0.000</td>
</tr>
<tr>
<td>Coating type</td>
<td>1</td>
<td>13.2648</td>
<td>10.3216</td>
<td>10.3216</td>
<td>40.88</td>
<td>0.000</td>
</tr>
<tr>
<td>Oil × Coating type</td>
<td>2</td>
<td>1.4699</td>
<td>1.4699</td>
<td>0.7349</td>
<td>2.91</td>
<td>0.059</td>
</tr>
<tr>
<td>Error</td>
<td>110</td>
<td>27.7725</td>
<td>27.7725</td>
<td>0.2525</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>115</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE IX  Taguchi Analysis of Design of Experiments to determine optimal coating composition

<table>
<thead>
<tr>
<th>Coating type</th>
<th>Oil</th>
<th>Overall average adhesion strength (mPa)</th>
<th>Overall SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium carbonate</td>
<td>SF1154</td>
<td>0.081</td>
<td>0.021</td>
</tr>
<tr>
<td>Silica</td>
<td>SF1154</td>
<td>0.206</td>
<td>0.043</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>DMSC15</td>
<td>0.099</td>
<td>0.027</td>
</tr>
<tr>
<td>Silica</td>
<td>DMSC15</td>
<td>0.204</td>
<td>0.052</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>ALT251</td>
<td>0.058</td>
<td>0.021</td>
</tr>
<tr>
<td>Silica</td>
<td>ALT251</td>
<td>0.086</td>
<td>0.017</td>
</tr>
</tbody>
</table>

Acknowledgments

Tim Burnell, Owen Harblin, Jim Resue, and Gosia Rubinsztajn are thanked for panel preparation. We gratefully acknowledge support of this research by DARPA (contract number N 10017-96-C0145).

References


Brady R (1997) In search of non-stick coatings. Chem Ind (Lond) 6: 219–222


FIGURE 10  Mean macrofouling attachment strengths at the Indian River Lagoon and Hawaii Ford Island test sites for barnacles (B. chomneus), tubeworms (H. dianthus at Indian River and H. elegans at Ford Island), and oysters (Crassostrea sp. at Indian River and Ostrea sp. at Ford Island).