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Geoffrey W. Swain [a]; Michael P. Schultz [a]
[a] Ocean Engineering Department, Florida Institute of Technology, Melbourne, Fl, USA

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THE TESTING AND EVALUATION OF NON-TOXIC ANTIFOULING COATINGS

GEOFFREY W SWAIN and MICHAEL P SCHULTZ

Ocean Engineering Department, Florida Institute of Technology
150 West University Boulevard, Melbourne, Fl 32901, USA

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Field testing of non-toxic antifouling coatings has required the development of test protocols that can quantify their performance. This includes the evaluation of the biofouling communities, the measurement of biofouling adhesion using a calibrated water jet and the measurement of barnacle adhesion in shear. Data are presented for several test surfaces, and the results are discussed with respect to the coating characteristics.

KEYWORDS: adhesion, barnacle, biofouling, silicones, testing

INTRODUCTION

The search for an environmentally acceptable antifouling coating has directed attention away from the use of biocides to the development of non-toxic coatings which function by reducing the adhesion strengths of fouling organisms to the surface. The Office of Naval Research (USA) is actively pursuing a research program to develop such systems (Alberte *et al.*, 1992), and this has necessitated the development of field test protocols that can evaluate their performance.

Field testing provides the first opportunity to evaluate the antifouling performance of coatings in real world environments. It typically subjects coatings to a broad spectrum of physical, chemical and biological action which is difficult to replicate under laboratory conditions (Table 1). Over the years, a number of test criteria have been developed for the evaluation of antifouling coatings. These, however, were designed to test the

Table 1 Variables associated with field testing antifouling coatings

Coating	Complexity of product	Application process
		Cure time
		Edge effect
	Changes with time	Chemical composition
		Physical degradation processes
Environment	Chemical	Salinity
		Oxygen
		Nutrients
		Pollutants
	Physical	Temperature
		Water velocity
	Biological	Indigenous communities
		Succession
		Competition
		Grazing and predation

performance of coatings that contain biocides, and these tests typically characterize coating effectiveness by describing the physical condition of the coating and the type and extent of fouling that is present.

The mode of action of non-toxic coatings is different to those containing biocides (Fig. 1). Marine organisms settling on a toxic surface may survive short periods, but providing the coating is functioning, they soon die or become detached. The coating remains free of fouling. A non-toxic surface, however, may become totally covered by fouling organisms, and its effectiveness then becomes a function of the ease with which the biofouling can be removed. To improve the evaluation of coating performance, field tests have been developed to quantify the adhesion strengths of marine organisms to coating surfaces. Data are presented to demonstrate the differences in the performance of both toxic and non-toxic systems, and to set a baseline from which future research and testing of non-toxic antifouling surfaces can be made.

TEST METHODS

Candidate coatings were applied to standard 254 × 305 mm (10 × 12 in) test panels with 9.5 mm (3/8 in) holes at each corner to facilitate attachment to the test frames. These were immersed at the Florida Institute of Technology (FIT) static exposure site which is located in the Indian River Lagoon, Melbourne, Florida, USA. The exposure site has an active fouling community year-round (Fig. 2) dominated by the barnacle, *Balanus eburneus*. The following parameters were used to evaluate the coatings: biofouling and the physical condition of the coating; biofouling adhesion measurements using a calibrated water jet; and barnacle adhesion measurements in shear.

Biofouling and Physical Condition of the Coating

The biofouling and physical condition of the coating was evaluated according to ASTM D 3623 (1987). This standard was developed as a method to evaluate antifouling coatings that contain biocides as their mode of action. It describes how to organize a static immersion site, how to maintain a biofouling attachment census, and details methods to evaluate the surface for fouling and physical condition.

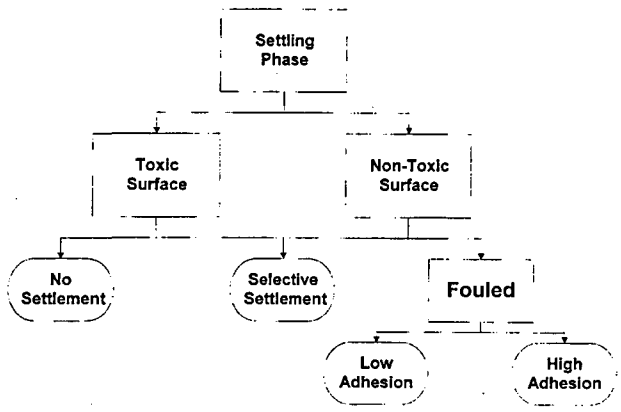

Fig. 1 Settlement matrix for toxic and non-toxic surfaces.

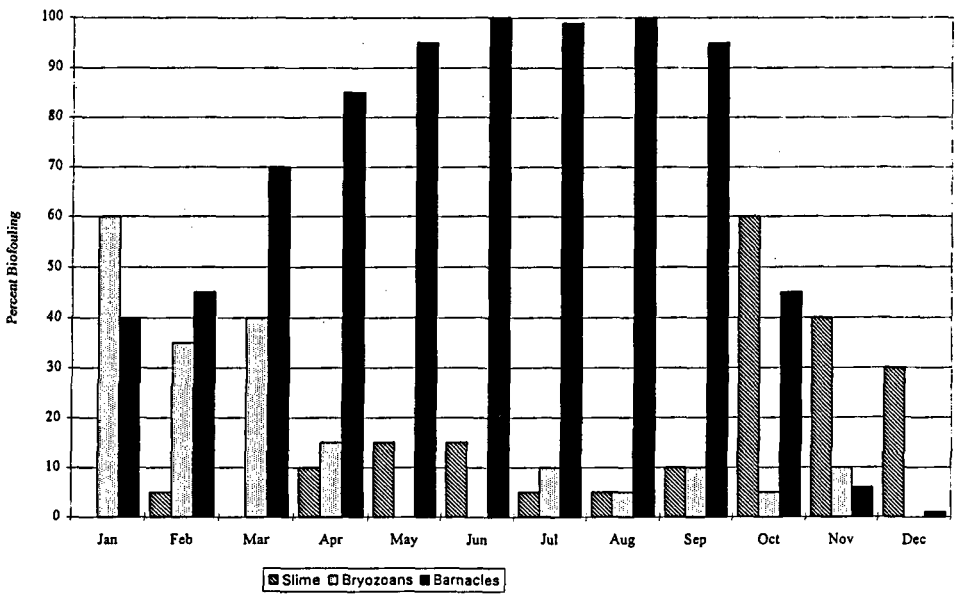

Fig. 2 Typical monthly biofouling by dominant fouling types on unglazed ceramic tiles at the FIT exposure site.

Fouling is rated according to the percentage of the intact proportion of coating or surface that is covered by a particular type of fouling organism as classified in Table 2. Fouling on portions of a panel where no test surface is present (due to coating failure, *e.g.* delamination) is ignored. The following definitions are made with regard to the reporting of fouling and coating condition: absorbed organic and inorganic chemicals, trapped silt and detritus, should be reported as "silt"; diatoms, initial algal germination and low form algae should be reported as "algal slime"; immature foulers should be reported as "incipient foulers"; mature foulers should be reported as number of individual present or as percent cover for colonial forms; the physical condition of the surface should be rated according to the percentage of surface affected by coating defects, and the type of coating deterioration should be described qualitatively.

This method then awards a rating for Fouling Resistance (FR) and Physical Rating (PR). For coating surfaces free of fouling except for the presence of algal spores and other biological slimes, a FR rating of 100 is given. This is reduced to 95 if only incipient fouling is present. When mature fouling is present, the rating is further reduced by subtracting the percentage cover or the sum of the number of individuals present from 100 or 95. The PR is obtained by subtracting the percent surface affected by defects from 100. The overall performance is obtained by awarding the coating the lowest rating from the fouling resistance and physical condition.

Biofouling Adhesion Measurements Using a Calibrated Water Jet

The water jet test was developed to provide an assessment of the adhesion strength of silts, slimes, and low form fouling types to surfaces where biofouling adhesion is low. It

Table 2 Description of fouling types referenced in ASTM D 3623 (1987)

Fouling Type	Abbreviation	Definition
Incipient fouling	IF	Recently settled and juvenile forms of macrofouling
Silt	Si	Absorbed organic and inorganic chemicals, trapped silt and detritus and unidentified slimes
Slime	Sl	Diatoms, initial algal germination and low form algae
Algae	Al	Fully established alga types and larger forms, *e.g. Ulva sp., Enteromorpha sp.* and *Ectocarpus sp.*
Encrusting bryozoans	EB	Colonial animals forming an encrusting layer over the surface; these layers are generally 1–2 mm thick and have a rough texture
Bryozoans	Br	Colonial animals forming a turf like mat rarely exceeding 3 cm in length; they may be mistaken for plants
Barnacles	Barn	A hard shelled crustacean that cements itself permanently to a substrate, and is difficult to remove; the outer shell is generally whitish in color and shaped like a truncated cone. The barnacles in this area may grow to 2 cm in height and 2 cm in width at the base; the most abundant species at the FIT test site is *Balanus eburneus*
Polychaetes	PC	Worms that may form a hard calcareous exoskeleton which becomes cemented to the substrate; the individuals rarely exceed 2 cm in length and may show some coiling of the tube
Sponges	Sp	Soft animals with sponge like texture forming thin surface cover or thicker accumulations; often brightly colored
Tunicates	Tun	Soft animals that may be solitary or colonial; solitary types may reach several centimeters in height and colonial forms tend to form a thin cover over the surface
Molluscs	Mol	Animals with two hard shells, hinged along one edge; typical examples are oysters and mussels

was designed to be fully portable and self contained for field operations and is limited in the maximum water jet force that can be applied.

The apparatus consists of a SCUBA tank containing compressed air and a regulator to adjust the pressure between 0–1.65 MPa (0–240 psi), a SCUBA tank containing water, and a quick change blow gun with a 1.6 mm (1/16 in) diameter nozzle to apply the water jet (Fig. 3). A 50 × 50 mm (2 × 2 in) template is used to delineate the surface to be evaluated, and the test procedure is recorded by a video camera.

The template is placed over a representative part of the surface, and the biofouling communities in this area assessed and recorded using a video camera. The regulator is set to 0.138 MPa (20 psi) to pressurize the SCUBA tank containing water. The resulting water jet is applied to the area within the template so as to maximize fouling removal. The operator accomplishes this by changing the distance and the angle of the water jet to the surface until the maximum amount of fouling that can be removed at that setting is achieved. The biofouling cover of the surface is reassessed and recorded by video camera. The pressure in the system is increased by 0.138 MPa (20 psi) and the cycle repeated until all the fouling is removed or the maximum pressure setting is obtained.

For evaluation purposes, the biofilm is divided into silt, slime, soft and hard foulers. The water jet pressure required to remove each of these groups is recorded. The maximum true force exerted by the water jet at the surface for each pressure setting was

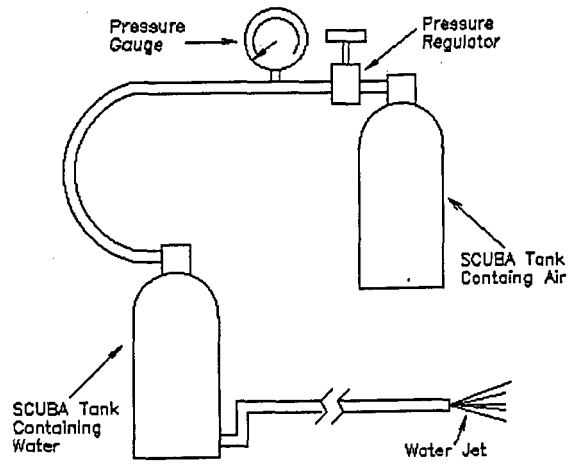

Fig. 3 Water jet apparatus.

measured using a force transducer and by observing the area over which the water exerted an effect. The relationship between the air pressure settling and the water jet force at the surface can be seen in Figure 4.

Barnacle Adhesion Measurements in Shear

The barnacle adhesion test was developed to enable rapid and multiple measurements of barnacle adhesion strength to a coating under field conditions. It was approved as an ASTM standard in 1994 (ASTM *D5618*, 1994), and it provides quantitative data that can be used to compare the ability of surfaces to reduce biofouling adhesion. The method was based on previous research conducted on the adhesion strengths of barnacles to natural substrates (Grenon *et al.*, 1979; Bultman *et al.*, 1981; Becka & Loeb, 1984; Denny, 1988; Swain *et al.*, 1992).

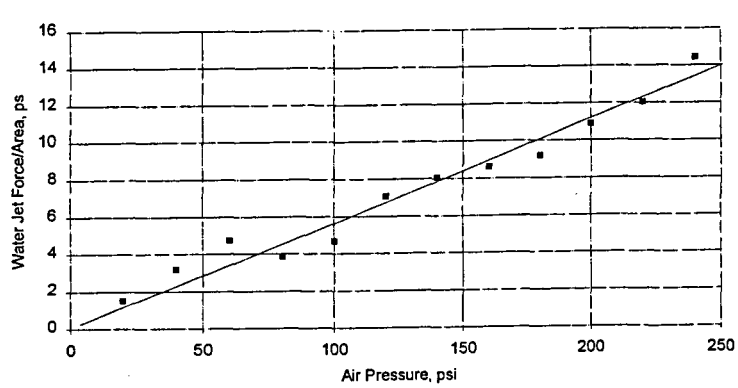

Fig. 4 Water jet calibration curve for force of water impinging on a test surface.

Test surfaces that are exposed to static immersion are monitored for barnacle settlement. To facilitate adult barnacle growth on silicones with low fouling adhesion strengths, it has been found necessary to enclose the test area with a 25 mm (1 in) mesh net that excludes larger fish and other predators which would otherwise remove the immature barnacles. When settlement is observed, the shear strength of adhesion is measured as described below. Typically, live barnacles between 5–20 mm (0.2–0.8 in) diameter at the base are selected for testing, and their species and condition are noted. They should be at least 20 mm (0.8 in) from the edges of the test panel, be attached to undamaged areas of the test surface, and not be in direct contact with other barnacles. The barnacle base is measured with calipers in four directions (0, 45, 90, 135 degrees) to obtain an average base diameter. The barnacle base plate area, A, is then estimated using the average base diameter, d_a and the formula $A = (\pi d_a^2)/4$. A shear force is then applied to the barnacle base using a hand held force measuring device at a rate of approximately 4.5N s^{-1} (1.0 lb s^{-1}) until the barnacle becomes detached or the maximum shear force is reached. The force measuring device used in this experiment was a Shimpo mechanical dial force gauge. This device had a range of 0–89 N (0–20 lb), an accuracy of ±0.3%, and a resolution of 0.45 N (0.1 lb). Care must be taken to apply the force parallel to the surface. The force (F) required for detachment is noted, and observations are made as to the mode of failure. If more than 10% of the barnacle base plate is left attached to the substrate, the test is deemed void. The strength of adhesion, τ, is then calculated by dividing the force required to remove the barnacle, F, by the area of the barnacle base plate, A.

$$\tau = F/A$$

It is recommended that, when possible, a minimum of ten measurements be made per coating, and the mean and standard deviation of the strength of adhesion, τ, are calculated. The strength of adhesion values for test surfaces are compared to control surfaces of known adhesion. Variations in barnacle adhesion strength may result from differences in species, age, time of year, and physical condition. Additionally, incomplete removal of the barnacle base plate from the surface during testing may lead to erroneous adhesion values. Care must also be taken not to dislodge the barnacle during base diameter measurements.

RESULTS AND DISCUSSION

The combined use of the aforementioned evaluation methods provides some new and interesting insights into the performance of non-toxic coatings. Biofouling data from six test surfaces (Table 3) have been selected to demonstrate the test methodologies and the differences in biofouling characteristics. These are Mil Spec F121 vinyl cuprous oxide antifouling, silicone A (commercial), silicone B (commercial), RTV 3140 (Dow Corning), FEP Teflon® (Dupont), and epoxy Mil Spec F150. F121 was chosen to represent traditional antifouling paints that use cuprous oxide as a biocide. The commercial silicones were chosen to represent the state of the art in commercial, non-toxic biofouling control. According to the patents, silicone A contained a phenyl methyl silicone fluid, and silicone B contained an organic modified partially water soluble polysiloxane fluid. RTV 3140 represented a silicone without additives. FEP Teflon® represented a non-toxic surface with low surface tension, and epoxy acted as a non-toxic high surface tension substrate.

The test panels were exposed for a two year period at the FIT static immersion exposure site starting on 12 July 1992. The results are discussed with respect to the three methods used for evaluation.

Table 3 The antifouling mechanism and critical surface tension of unexposed surfaces, together with the barnacle adhesion strengths for the test surfaces

Surface	Antifouling Mechanism	*γ_c, mN m^{-1}	Barnacle Adhesion			
			n, # of barnacles	$\bar{x}$, MPa	± SD, MPa	Date and Days Exposure
F 121 vinyl cuprous oxide	Copper	37	0	na	na	na
Silicone A	Silicone + phenyl methyl silicone fluid	22	7	0.0593	0.0133	6/3/94 696 d
Silicone B	Silicone + organic modified polysiloxane	22	6	0.1102	0.0233	6/3/94 696 d
RTV 3140	Silicone, no fluid	25	11	0.1161	0.0392	8/5/94 759 d
FEP Teflon®	Low surface tension	17	48	0.8678	0.3345	Pooled data
Epoxy F150	None	35	15	2.2300	0.5490	9/2/92 20 d

*Approximate critical surface tension values supplied by Dr Anne Meyer.

Biofouling

Biofouling data for the test panels are presented with respect to the ASTM rating (Fig. 5) and the percentage cover by barnacles (Fig. 6). Within 100 d, the epoxy surface had a zero ASTM rating and was covered by barnacles to 100%. This condition remained constant for 300 d at which time the panel was removed. The Teflon® surface also became heavily fouled, but unlike the epoxy, the fouling was more temporary in nature, and the percentage cover by barnacles ranged from 10 to 70% during the exposure period. The three silicone surfaces all remained relatively free of fouling with slimes dominating the surfaces. Little difference could be seen between silicones A and B for the first 200 d. The oil component of these coatings appeared to prevent biofouling

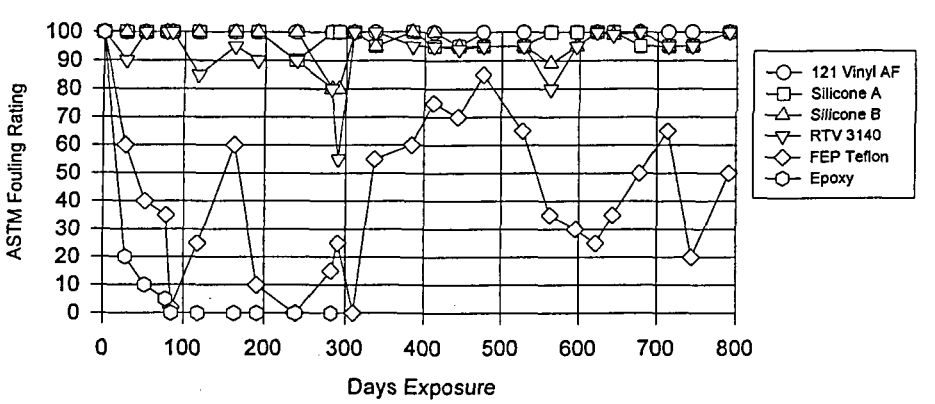

Fig. 5 ASTM fouling rating for the select test surfaces.

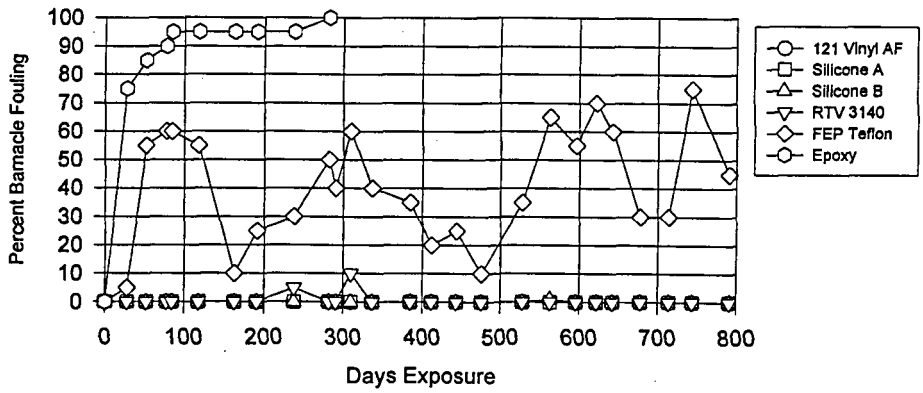

Fig. 6 Percentage biofouling by barnacles on selected test surfaces.

adhesion. They both performed better than RTV 3140 which contained no additive. After 200 d, silicone B showed a decline in performance that, from visual inspection, appeared to be associated with a reduction in the oil component at the surface. Its performance then more closely matched that of RTV 3140. With the exception of slimes, F121 remained relatively free of fouling during the entire exposure period.

Barnacle spat were frequently observed on all three silicone coatings. However, they rarely matured into adults. Observations suggest that this was caused by grazing from local fish populations which continually removed juvenile sedentary organisms from the silicone surfaces. It appears that grazing is a determining factor in the fouling communities that develop on low adhesion surfaces, and experiments are being conducted to further investigate this phenomenon.

Biofouling Adhesion Measurements Using a Calibrated Water Jet

The calibrated water jet provides a measure of the force required to remove biofilms from a test surface. When interpreting these data, it must be remembered that silt, slime, and low form foulers can be ephemeral in nature, and there may be temporal differences in their structure and adhesion strengths. Comparison of biofouling adhesion strengths using these organisms should therefore only be made for the same site and date. Data for different days should not be compared.

Data for the water jet pressure to remove slimes from the test panels are presented in Figure 7. The epoxy surface became covered by a well adhered layer of slime within a short period of time reflecting the non-toxic and relatively high critical surface tension of the original substrate. The adhesion of slime to Teflon® was initially more tenaceous than to the silicones. However, this changed with time, and after about one year, the Teflon® surface exhibited superior foul-release properties to these organisms than did the other coating types. No explanation for this behaviour is available at the present time. Initially the best performer was silicone B. For the first 200 d, the oil component was sufficiently active to prevent even slimes from becoming firmly established. After that time, however, the oil appeared to be depleted, and fouling became better established. This coating then performed in a similar manner to RTV 3140. Silicone A showed the best long-term performance, possibly indicating that the phenyl methyl silicone fluids have longer term effectiveness than the organic modified partially water soluble

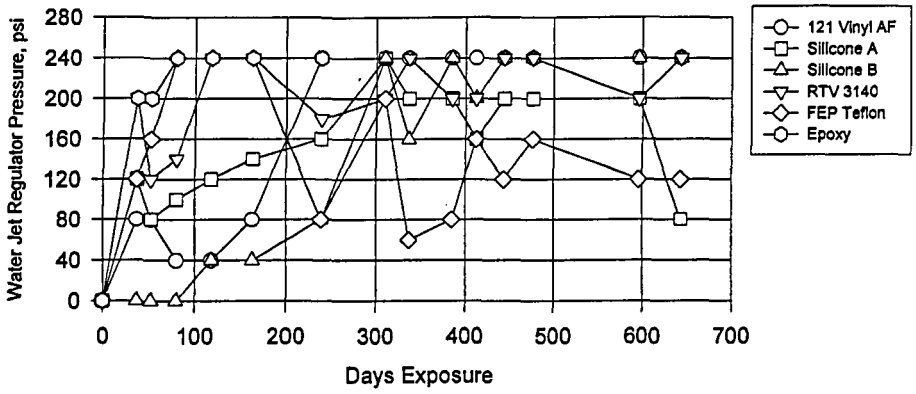

Fig. 7 Water jet pressure to remove slime fims.

polysiloxane fluids. Although F121 did not develop any macrofouling, the slimes that formed on its surface were very tenacious, and the coating exhibited no foul-release properties.

Barnacle Adhesion Measurements

Barnacle adhesion measurements were obtained for all the test surfaces except F121 which, because of its toxicity, did not become fouled by barnacles (Fig. 8, Table 3). The number of days exposure prior to measurements was determined by the availability of barnacles on the surfaces, and this is given in Table 3. The barnacle adhesion data for Teflon® were pooled from measurements taken at 30, 57, 197, 291, 385, and 399 d exposure. When the adhesion strengths of the barnacles to all the surfaces were analyzed

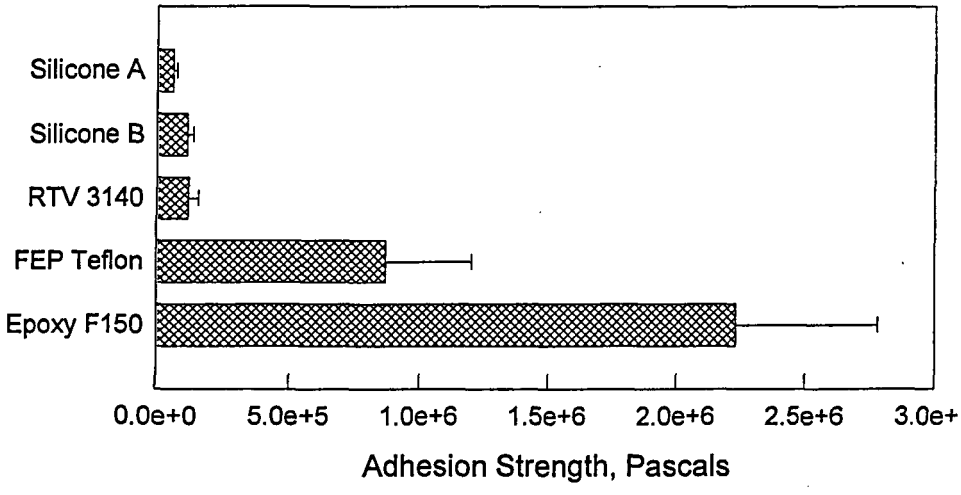

Fig. 8 Mean barnacle adhesion data ± SD for test surfaces.

using the Kruskal-Wallis test, a significant difference was observed ($p < 0.001$) between the means. Dunn's Test was then used to make pairwise comparisons. A significant difference ($\alpha = 0.05$) was noted between the epoxy, Teflon®, and the silicone surfaces. No significant difference was observed among the silicones.

The barnacle adhesion strengths for the silicones were then analyzed separately because the variances for the epoxy and Teflon® surfaces were much greater. A one way parametric ANOVA was carried out on these data, and a significant difference in the means was found ($p = 0.002$). Student-Newman-Keuls Method was used to make pairwise comparisons between the silicones. A significant difference in adhesion strength ($\alpha = 0.05$) was found between silicone A and silicone B. A significant difference was also noted between silicone A and RTV 3140. However, no significant difference was observed between RTV 3140 and silicone B. This may have resulted from a depletion of fluid in silicone B at the time the adhesion measurements were made.

CONCLUSIONS

Field testing of non-toxic coatings has required the establishment of new criteria for their evaluation. Observations of biofouling accumulations can no longer be the sole criteria on which the performance of a surface is judged. More quantitative evaluations are required. The two methods presented here, the calibrated water jet and a direct measure of barnacle adhesion, have provided useful data enabling the performances of test surfaces to be differentiated.

The epoxy F150 surface acted as a control and, as such, became rapidly fouled by tenacious and well adhered organisms. The Teflon® surface exhibited lower fouling and fouling adhesion. It appeared to provide the best long-term surface against the adhesion of slimes, although barnacle settlement and resulting adhesion values were high. RTV 3140 had reduced fouling and bioadhesion but did not provide the same level of performance as silicone A and silicone B. Silicone A, with the phenyl methyl silicone fluid, provided longer term performance than silicone B, whose fluid appeared to become exhausted after about 200 d. The F121 cuprous oxide coating prevented macrofouling but developed slime films which adhered tenaciously to the surface.

Observations suggest that the structure and quantity of biofouling on surfaces with low bioadhesion will be influenced by grazing pressures, and these may limit the communities that ultimately become established. These interactions must be taken into account when addressing the performance of test surfaces under static immersion.

Acknowledgements

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