#### **CHAPTER 13**

# Factors Influencing the Attachment and Adherence of Fouling Organisms

Many suggestions for the control of fouling are based on an appreciation of the physiology and distribution of fouling organisms. All too often, however, they are vague and give the engineer little aid in designing structures or determining whether special methods of control are necessary. It is the purpose of this chapter to describe the physiology of the fouling larvae so that the tendency of a surface to become fouled may be appreciated, to review the factors which influence the attachment of fouling, and to assess their practical value.

The several factors which determine the tendency of a surface to foul when exposed in the sea may be divided into two main groups: 1) those which determine the numbers of larvae coming into contact with the exposed surface, and 2) those which limit the ability of these larvae to attach to the surface and grow. The physiology of the organism determines its reaction to changes in the environment, and must be understood in order to evaluate the relative importance of these factors.

The numbers of larvae coming into contact with an exposed surface depend upon the geographical location, the season of the year, the type of service for which the installation is employed, and the texture, orientation, and color of the surface. The tendency of the surface to form slime films and the degree to which the surface is wet by sea water may also have significant influences. All of these factors are, to a large extent, predetermined by engineering considerations and frequently are not subject to control or modification. Practical prevention of fouling depends upon modifications of the surface so that it repels or kills the organisms which come in contact with it. Among such surface modifications, frequently recommended, are the application of electricity and the use of exfoliating or toxic paints. Only the toxic paints have given satisfactory results, and this aspect of the control of fouling is discussed in the following chapter.

# GEOGRAPHICAL AND SEASONAL DISTRIBUTION

The seasonal and geographical distribution of fouling organisms has been discussed in Chapters 5 to 7. The geographical location determines whether a structure will be subject to intense fouling attachment, and must be appreciated in order to foretell whether special methods for the control of fouling will be necessary.

There are tremendous differences in the numbers of larvae of fouling organisms present in the water in different geographical areas, and also in any given area at different times of year. Most of the coast of the United States is in the temperate zone where marked seasonal variations in the amount of fouling occur. It is possible, in some places, that methods of control will be required during the summer months, but may be unnecessary in the fall or winter months because larvae are not present in the water or are not attaching to surfaces. It is impossible to predict the intensity of fouling solely from general considerations of distribution, since local variations are of considerable importance. Studies of each location are, therefore, necessary to determine whether special methods of control are required.

Geographical and seasonal considerations are likewise of great importance in selecting a location for the testing of antifouling surfaces or for investigation of the biology of fouling. It is futile to test antifouling surfaces under conditions of poor fouling attachment. Tests made under these conditions may appear to indicate that a surface would prevent fouling for a considerable period of time, when, if exposed to intense fouling, the same surface would foul immediately. Fouling attaches throughout the year at various locations in southern Florida and southern California, and tests made at such places give a more accurate picture of the effectiveness of the surface and of the duration of its effective life.

The concept, held by many investigators, that antifouling paints should be designed for use in certain waters is unsound. If true, it would be necessary to test all paints under as many conditions as possible. Paints which are effective under severe fouling conditions are effective wherever they may be exposed. Those which are reputed to be effective in one place but unsatisfactory in other areas are invariably borderline paints which foul anywhere when the intensity of fouling becomes high. The testing station should,

therefore, be located where the fouling intensity is great throughout the year so that a significant test of the surface may be obtained. Here, again, the exposure of nontoxic collectors to determine the intensity of fouling is essential.

The amount of fouling which will accumulate on a structure will vary depending upon its shape, the material of which it is made, and the service for which it is used. The tendency of different materials to foul, and the responses of larvae to gravity and to light and illumination, which depend upon the shape of the structure, are discussed below. In addition, differences in the character and amount of fouling depend upon the service. The difference between fouling on ships, buoys, panels, and piles has been discussed in earlier chapters.

# MOVEMENT OF WATER RELATIVE TO THE SURFACE

Among the service conditions which influence fouling is the movement of water relative to the surface, a factor important in shipbottom fouling. Visscher (50) established that ships on active duty tend to be less fouled than those which spend much of their time stationary in port. Very few of the ships which spent more than 90 per cent of their time cruising were heavily fouled, whereas most of those which cruised less than 30 per cent of the time were badly fouled. Decommissioned vessels and lightships, furthermore, frequently include in their fouling mussels, tunicates, and other species which are comparatively unimportant on more active ships in the same geographical localities.

According to Visscher (50) and Hentschel (22), fouling is most apt to occur behind the overlap of the metal plates and in dents and other protected places on active ships. This was attributed to the direct action of the water flow on the organism. Harris and Forbes (21) attribute similar results to the effect of increased turbulence in these places on the distribution of dissolved toxic in the water.

Many organisms may be found fouling the propellers of active vessels. They include algae, barnacles, tubeworms, molluscs, and encrusting bryozoa (3, 22). Differences in the amount and type of fouling between the central and peripheral regions of the propeller have been noted. Sometimes only the central portion was fouled, while the outer ends of the blades were clean. In other cases serpulid tubeworms grew over all the blades, while barnacles were limited to the areas near the

shaft. Sometimes only the bases of barnacles and oyster shells were present on the outer parts of the blades. One propeller was fouled by tubeworms, all of which were oriented with their mouths toward the axis (22).

Recent experiments have shown that fouling is influenced by the velocity of flow of water across the surface (26, 29, 46). Smith has studied the effects of different velocities on the development of fouling by two devices: graduated speed of flow through a series of tubes, and a rotating disk. In one experiment (46) glass tubes of different diameters were arranged in sequence, and sea water was then drawn through them by a pump. The velocity of flow was a function of the diameter and was estimated to range from 3.8 to 0.2 knots in the different sections. Barnacles (probably Balanus improvisus) were able to attach in currents up to about 0.5 knot; the tubeworms (Dasychone conspersa) were successful up to about 1.0 knot. Similar results have been obtained by LaQue (26).

Experiments with a rotating disk tested the ability of organisms to settle out on moving surfaces (46). An unpainted, horizontal plywood disk was rotated at various speeds under water. The nominal velocity of any point was calculated from its radius and the speed of rotation; the actual velocity relative to the water was thought to be somewhat less because of frictional drag and vorticellar flow. Barnacles attached in the center of the disk, covering an area the diameter of which was inversely related to the speed of rotation. The nominal velocity at the circumference of the fouled area in each case was close to 1.0 knot, which was taken to be the maximum rate permitting attachment. Considering that the nominal velocities of the disk and tubes are both only approximations of the true velocities, this figure is in reasonable agreement with that determined by the flow-tubes.

The effect of movement on organisms which had previously attached to a stationary surface was also studied on a rotary disk (46). The disk was divided into sectors all but one of which were covered with waterproof cloth. It was submerged stationary, and at intervals successive sectors were bared to permit fouling to settle. After 16 days, all sectors had been uncovered, and the fouling on them had been growing for respectively 6 hours, and 1, 2, 5, and 16 days. Fouling consisted of barnacles, a buguloid bryozoan, and a hydroid. The disk was then rotated at 60 r. p. m. for 19 days. Fouling toward the periphery of the

disk was removed, growth in an intermediate zone was stunted, while in the center growth, proceeded normally. The radii of the zones, and therefore the required limiting velocities, increased with the length of exposure prior to rotation, indicating that the older barnacles were more resistant. Table 1 shows the limiting water velocities for attachment and continued growth of three common forms. To remove barnacle fouling more than 16 days old, nominal velocities in excess of 4 knots were required (46).

Smith (45) has also studied the effectiveness of a stream of bubbles in preventing the attachment of fouling. Compressed air was led to the keel of a motor launch, or to the base of panels, where bubbles were released and allowed to flow over the

Table 1. Maximum Water Velocities Permitting Fouling Organisms to Remain Attached and to Grow (44)

- 0					
Sector	I	II	III	IV	V
Stationary Attachment Period —Days Maximum Velocity Permitting	$\frac{1}{4}$	1	2	5	16
Continued Attachment of Barnacles—Knots Maximum Velocity Permitting	2.3	3.0	3.3	3.3	>4.0
Normal Growth of Barnacles —Knots	1.0	1.7	1.3	2.0	2.7
Maximum Velocity Permitting Growth of Bugula—Knots	_	< 0.7	< 0.7	< 0.7	2.0
Maximum Velocity Permitting Growth of Hydroid—Knots	1.3	1.7	1.3	3.0	3.0

surface. Little or no fouling attached in the areas bathed by the rising bubbles, though control areas were densely covered with barnacles. Presumably the action of the bubbles was to cause motion of the water relative to the surface. The amount of air required was between 0.2 and 0.6 cubic feet per minute per horizontal foot of surface. The large quantity of air required makes this method of preventing fouling impractical for all but the smallest structures.

McDougall (29) has studied attachment and growth of fouling in variable currents of low velocity. Glass plates were exposed in a series of chambers through which a tidal current flowed at speeds regulated by the size of the up-stream apertures. Maximum velocity in the chamber with the largest opening was about 1.0 knot; velocity was zero in all chambers at slack water. Bugula and Balanus grew best and were most numerous at the minimum velocity. Tubularia, and the worms, Hydroides and Sabellaria, preferred maximum velocities. Sponges (Reniera), ovsters, and tunicates (Phallusia) found the intermediate conditions optimal. Except for the oyster, there was a surprising and close agreement between the optimum velocity for attachment and for growth. When the current flow is intermittent, as in the case of ships or of tidal currents, some observations indicate that moderate currents may be beneficial for the growth of the fouling organisms.

Hentschel (22) has recorded a number of instances in which the barnacles on ships attained their greatest sizes in the most exposed situations —on the stem, on the edge of the bilge keel, and on the rudder. He suggests that the difference may be due to the availability of a more abundant food supply in such places. It is commonly observed that exposed headlands with strong wave action and narrow passages carrying swift currents often support rich populations. Such fouling forms as Tubularia and other hydroids, mussels, bryozoa, and ascidians grow exceptionally well in places such as Woods Hole Passage, where tidal currents up to 4 knots are common, and where greater velocities occur on spring tides (47). Gutsell (19) concluded that scallops thrive best in rapid tide currents. Fox and Coe (13) have observed a more rapid increase in weight of Mytilus californianus in wave-washed sites than in calmer water.

Hutchins and Deevey (25) concluded that the rate of increment of mussel fouling (Mytilus edulis) on Atlantic Coast buoys, is augmented by strong tidal currents. This rate is compared with mean current velocities in Table 4 of Chapter 6. The correlation is not perfect in ranking, but all of the rates of increment greater than the Atlantic coast average were associated with mean current velocities greater than 1.0 knot. Tidal currents in general average much less than this.

Considering the evidence as a whole, it appears that relative water movement may affect fouling in two principal ways: 1) directly, by pressure and shear, and 2) indirectly, by augmenting supplies of food, oxygen, and like factors. Insofar as they are capable of withstanding the former, organisms are able to benefit from the latter. High velocity currents may prevent initial or continued attachment, or may suppress or modify growth. It is evident that any factors affecting firmness of attachment will modify the resistance to shearing, and the measurement of critical velocities must accordingly allow for such physical aspects of the surface. Because ships move rapidly and continuously for long periods, all but the most tenacious fouling tends to be removed. For such fixed installations as buoys, on the other hand, the relative movements most generally observed are of low magnitudes and of such character that the effect, if any, is to accelerate fouling growth.

There is general agreement in attributing this better growth to the increased supply of food and oxygen, and the more effective removal of metabolic wastes.

# TEXTURE OF THE SURFACE

There has always been an effort to produce paints with a smooth surface in order to keep the frictional resistance of the ship to a minimum. It has been postulated that barnacles will be unable to attach to perfectly smooth surfaces (33), and this has been suggested as a means of preventing fouling.

Wharton (55) has calculated that the pressure developed by the vacuum cup on the antennae of the cyprid barnacles is of the order of one dyne. He postulates that the cup would be least effective on a surface having projections less than 15 microns, but more than 0.1 micron in size, since these would permit water to flow into the cup, thus breaking the suction. The ultimate attachment of the barnacle, however, is by means of a cemented bond, and moderately rough surfaces should increase the strength of this bond.

The texture of the surface does indeed affect the amount of fouling which may attach under comparable conditions. Coe and Allen (6) found that cement blocks were generally more densely populated with fouling forms than wood. Pomerat and Weiss (38) studied the attachment of barnacles and other fouling forms to various types of surfaces at Miami, Florida, and found that smooth, nonporous, non-fibrous surfaces, especially if also hard, were relatively poor collectors of sedentary organisms. The surface most heavily fouled was asbestos board, with 980 barnacles on an area of one square foot after three months' immersion. The most heavily fouled wooden surface had 748 barnacles per square foot. Under the same conditions, celluloid and methacrylate plastics collected only 11 barnacles, and smooth glass only 16. Glass panels with roughened surfaces were more densely fouled. The results of their exposures, given in Table 2, show that the quantity of fouling on different types of surfaces, simultaneously exposed, varies greatly. In designing experiments to study other factors which may influence attachment, it is necessary to use the same type of surface throughout.

The smoothness of the surface does not seem to offer any promise for the prevention of fouling. Though it may contribute to the success of certain preparations, it alone is not adequate to provide complete protection.

Table 2. Effect of Composition of Surface on Fouling All materials were applied to, or mounted on, wood unless otherwise noted. Exposed at South Dock, Belle Isle, Miami Beach, Florida, January 9, 1943 to April 9, 1943.

After Pomerat and Weiss (38).

	Weight of Fouling*			
Composition of Surface	Wet Grams	Dry Grams	Number* of Barnacles	
Plastics Plasticel Isobutyl Methacrylate†	24	12	124	
	15	7	70	
Formica	7	3	11	
Lucite	6	2	41	
Celluloid	4	2	11	
Glass Prestlite	57	25	176	
Pentecor	46	25	148	
Sandblasted	24	7	· 46	
Smooth	5	2	16	
Paints & Ingredients		_	10	
Asphaltum	121	34	768	
Asphaltum Varnish	68	14	256	
Anticorrosive (42A)	48	11	156	
Spar Varnish	45	7	304	
Navy Grey	42	6	150	
Paraffin	11	6	59	
Woods Gum (60 days soaked) Dade Co. Pine	452	133	686	
(60 days soaked)	395	121	748	
Gum (unsoaked)	250	44	222	
Madeira	174	84	358	
Dade Co. Pine (unsoaked) Teak Greenheart	144	27	125	
	144	89	306	
	77	41	342	
Soft Pine	58	12	184	
Balsa	3	2	5	
Metals				
Steel	224	43	88	
Nickel	43	11	126	
Lead	31	51	396	
Galvanized Iron	3	1 1 -	6	
Monel	2		6	
Zinc	1		0	
Miscellaneous Asbestos	284	66	980	
Masonite ¼ in. (heat tempered) Linoleum	138	32	594	
	80	23	193	
Sole Leather	32	12	66	
Canvas #10	5	2	7	

Corrected to an area of 144 square inches.

† Applied to glass panel.

## EFFECT OF GRAVITY

Numerous experiments have shown that many organisms, including the larvae of fouling organisms, react in a definite way to the force of gravity. For the fouling organisms this is shown by the relative intensity of fouling on panels hung in the sea at various angles. In general, the underside of a horizontal surface accumulates more fouling than surfaces exposed at any other angle. This response was found for the larvae of the Pacific Coast oyster Ostrea lurida by Hopkins (24). This larva swims with its dorsal or attaching surface upwards, and Hopkins concluded that they were thus more able to attach to the underside of an exposed surface, since they reached it in the proper position.

Other organisms also accumulate most heavily on the underside of exposed surfaces, as shown by the data in Table 3 (29, 37). Most of the organisms observed were present in greatest numbers on the undersides of plates which were horizontal or at an

Table 3. Populations of Fouling Organisms Collected on Panels Exposed at Various Angles in the Sea

The orientation is as follows. 0° (under side horizontal plate), 45° (under side 45° plate), 90° (vertical plate, both sides averaged), 135° (upper side 45° plate), 180° (upper side horizontal plate)

Numbers Attached to Plates Suspended at Various Angles

	ar 1 ar roug 22/18/00					
Organism	0°	45°	90°	135°	180°	Reference
Acanthodesia						
tenuis	165	125	7	3	6	1
Electra						
hastingseae	32	51	3	3	0	1
Barnacles	217	23	19	· 4	5	. 1
Bivalves	165	26	1	0	5 2 2	1
Hydroids	11	, <b>4</b>	1	1	2	1
Balanus					-	
eburneus	841	426	293	183	42	2
Bugula						
neritina	446	298	34	9	2	2
Hydroides						
hexagonus	776	204	96	30	10	2
Phallusia						
hygomiana	63	28	0	0	0	2
Perophora						
virides	212	5	1	17	3	2
Sabellaria		-				
vulgaris	2	22	40	321	390	2
2 5 10						

<sup>&</sup>lt;sup>1</sup> Pomerat & Reiner (37) at Pensacola, Florida. Exposure for 23 days. Numbers are for an area of 60 square inches.

angle of 45°. In contrast, the distribution of the polychaete Sabellaria vulgaris at Beaufort was just the opposite of the other forms. McDougall (29) states that the larvae of this species are apparently specially adapted to survive under conditions of heavy sedimentation. Although Table 3 indicates that Balanus eburneus is most apt to settle on the undersides of horizontal and 45° surfaces, Pomerat and Reiner (37) found that this distribution was not invariable. In many of their exposures this barnacle was nearly equally distributed on surfaces at all angles. When the larvae attaching in any brief interval were counted, approximately equal populations were found on the top and bottom of the horizontal plates. The further accumulation of larvae on the bottom increased steadily, whereas the population on the top surface increased more slowly and irregularly. At Beaufort, McDougall found that the top surface of the horizontal panel (180°) was generally covered with a layer of sediment, which might make it difficult for the cyprid larvae to attach or survive.

It can be concluded from these observations that most organisms accumulate more heavily on the underside of an exposed surface, perhaps because of a geotropic response. This effect, combined with the response of the larvae to light, probably accounts for the heavier animal fouling observed on the areas of ships between the bilges.

#### LIGHT AND ILLUMINATION

The larvae of fouling organisms are sensitive to light, and many of them tend to accumulate on darker surfaces. This reaction results in a distribution of organisms similar to that produced by gravity, since the underside of structures is also the most shaded. The plant forms, on the other hand, require light for photosynthesis, and accumulate on lighter colored surfaces in regions where the illumination is adequate for their growth. The tunicate larvae are negatively phototropic when attaching (16, 17). The larvae of Bugula are positively phototropic when first re-. leased, but become negative prior to attachment (31, 57, 58). Riley has shown that these larvae are stimulated to attach earlier than normal in dilute copper solutions, and they may then attach while still positively phototropic (39). The cyprid larvae of barnacles are also positively phototropic at first, and are most sensitive to green light (530- $545\mu\mu$ .) when different wave lengths are tested at equal intensities (51). At the time of attachment they are negative to light, and tend to move to darker areas and settle with the head end away from the source of illumination (29, 49).

Under natural conditions the greatest fouling is generally found on the least illuminated or darker colored surfaces. McDougall (29) observed that, when a series of boxes were illuminated through glass plates of various sizes, the larvae of most species tended to attach most abundantly in the two darker chambers. The *Pelecypoda* and the sponge, *Reneira*, however, did not accumulate most heavily in the two darker chambers. These observations are reproduced in Table 4.

Visscher (50) observed in experiments with unglazed colored tiles that the lighter colors always developed smaller populations of fouling; in some experiments the population was only one-third that which developed on darker surfaces. Results

are for an area of 60 square inches.

<sup>2</sup> McDougall (29) at Beaufort, North Carolina. Exposed 88 days. Numbers are for area of 48 square inches.

with glazed tiles were contradictory, which was attributed to the reflection of light from the surface. Edmondson and Ingram (11) found that the white and green colors were more effective in discouraging attachment than the darker ones, when various paints and colored glass were exposed at Hawaii. Little difference, however, is observed, regardless of the color, after two or three months' exposure.

Pomerat and Reiner (37) experimented with black, clear, and opal glass panels at Pensacola,

It has been questioned whether the effects described above result from a true phototropic response in which the organism is guided away from the surface by the direction of the light, or whether the larva is inhibited from attachment by the general intensity of illumination. Whitney (60) and Schallek (41) maintain that, under normal aquatic conditions, light is diffused and has only a small directional component. In a diffused light, reaching the organism with equal intensity from all directions, no phototropism could occur. In an

Table 4. Numbers of Organisms Attaching in Chambers of a Light Box in Which the Illumination Progressively Decreased from Chamber No. 1 to No. 6. Exposed May 10 to August 29, 1941. After McDougall (20)

C1	T			10 to raugus	1 29, 1941. Alter	McDougaii (29).	
Chamber Numbers 1 2 3 4 5	Balanus eburneus 173 154 248 46 219 318	Bugula neritina 426 339 541 570 837 696	Schizoporella unicornis 11 4 13 19 30 23	Hydroides hexagonus 958 1,016 892 1,146 1,436 2,072	Sabellaria vulgaris 64 48 68 64 64	Pelecypoda 461 216 260 211 248	Reniera tubifera 11 17 18 23 15
				2,012	144	374	20

Florida. About twice as many barnacles were found on the black plates as on the opal or clear plates. These experiments were extended by determining attachment on moonless nights between 9 P.M. and 3 A.M. During this period of minimum illumination, remarkably similar numbers were found on the three kinds of glass. The total attachment to four plates (27.2 sq. in. each) in four of these nighttime experiments was 341 on black, 393 on opal, and 394 on clear glass.

Phelps (36) exposed panels under conditions which partially differentiated between the effects of gravity and of light. Some panels were suspended horizontally under a covered barge, where visual observations of the panels in situ showed that there was more light on the bottom of the panels than on the top. More barnacles were found attached to the top of these painted panels, and equal numbers of larvae attached to the top and bottom of the glass panels. These results indicate that when the effects of light and gravity are opposed, the organisms react primarily to light. When the clear glass panels were hung under the barge at night, however, more cyprids collected on the underside than on the top. When light was at a minimum, therefore, the organisms reacted to gravity. Panels exposed at the side of the barge during daylight collected more barnacles on the bottom of both glass and painted panels. The undersurface of these panels was also the more shaded, and the relations to light and to gravity are supplementary. These results are summarized in Table 5.

attempt to study this problem Gregg exposed black and opal glass panels which were surrounded by borders of black, opal, or transparent glass. The numbers of cyprid larvae attaching showed no correlation with the degree of contrast between the collector and the background. A decrease in the intensity of general illumination in the area occupied by the collector was found to increase the attachment. Gregg (18) suggested that "shading" acts as a stimulus which brings about favorable physiological conditions for the subsequent attachment of barnacle larvae.

Weiss (53) has extended these observations by studying the diurnal variation in attachment and the effect of artificial illumination at night on the attachment. He employed glass plates coated on the backside with a dark red paint. Greater numbers of larvae attached during the daylight hours than during the previous and succeeding nights. Artificial illumination of the panels exposed at night increased the numbers of barnacles attaching, so that the normal diurnal variation was nullified. This increase in numbers of attachments was found at light intensities of 0.03 foot-candles or more.

Table 5. Numbers of Cyprids Attaching per sq. cm. to the Top and Bottom Surfaces of Horizontal Glass Panels and of Steel Panels Painted with 15 RC, Hung Alongside and Under a Covered Barge (36)

	Alongside Barge		Unde	r Barge
Surface	Top	Bottom	Тор	Bottom
Glass	.068	. 202	.121	.125
Painted Steel	.262	. 629	.770	.549

The contrast between the dark collecting surface and the diffuse illumination coming from the surrounding water may give rise to a true phototropic response. In the absence of light at night, the number of cyprids attaching may depend solely on their chance encounters with the surface. When the water appears more luminous than the surface, during daylight or because of artificial illumination, the cyprids may be attracted to the darker area by a true negative phototropic response, and accumulate there in greater numbers.

It has been suggested that the response to illumination could be utilized as a method for the prevention of fouling. While a dark surface accumulates more fouling than a light one, it is also true that the lighter surfaces do not prevent fouling. Visscher (50) and Edmondson and Ingram (11) showed that the lighter colors became as densely fouled in time as the darker, though they foul less when initially exposed. Realizing that the color would have little effect on the numbers of larvae attaching at night, Perry (34, 35) suggested the use of luminous paints which would glow at night and thus prevent attachment at all times. Young (61), however, has exposed luminous paints in the sea and finds them ineffective. Although the color theory of preventing fouling has had great popular appeal, it has found little practical application, because it does not work.

## THE USE OF ELECTRICITY

Various suggestions have been made for the use of electricity in protecting steel ships from both corrosion and fouling. Baggs (2) took out an early patent which covered the use of electricity, however applied, for this purpose. Several more recent patents have been allowed, the most interesting of which is that of Cox (7). This patent claims that the surfaces of steel ships can be made cathodic to protect them from corrosion. Deposits form on the surface under these conditions, and it is claimed that, as these break off, all of the attached fouling will be removed.

An extensive study of the application of electric currents to bare iron and other metals was conducted at Miami by Castle (5), who observed that fouling developed rapidly on cathodes to which current densities of 10–300 milliamperes per square foot were applied. Fouling was delayed on coatings formed by current densities in excess of 300 milliamperes per square foot. The delay or prevention of fouling by the high current densities was attributed to the rapid formation and flaking or sloughing of the deposits formed on the surface.

Castle found no evidence that either a continuous or alternating current kept the larvae away from the electrodes or prevented their attachment. He found no feasible method for electrocuting fouling organisms after attachment, or for preventing their attachment by electrical means. Direct currents of the greatest density obtainable from storage batteries, current from the secondary of an induction coil (the so-called Harvard inductorium), 115-volt 60-cycle alternating current, and the current from the secondary of a 5000-volt transformer delivering 30 milliamperes, were all ineffective in killing barnacles when applied for durations up to 15 minutes. The method of applying sufficient currents to form heavy deposits which could be sloughed at intervals was considered too expensive to be practical.

Harkins (20) has suggested that a surface carrying a negative static charge would result in a poor bond with the barnacle cement. This was based on the observation that the fronds of seaweeds do not ordinarily become fouled. He has overlooked, however, the occurrence of bryozoans, hydroids, and some barnacles, such as Balanus algicola, on seaweeds. Sargassum is commonly heavily encrusted with growths. Certain species of algae, further, are found growing only on other algae. Extracts of algae have been used in antifouling paints with consistently poor results (14, 15, 40).

# WETTING OF THE SURFACE

It has been frequently observed that paraffin, petrolatum, and various wax or grease surfaces do not become fouled rapidly. This action has been attributed to the hydrophobic or nonwettable character of such surfaces, or to the fact that the organisms can not obtain a secure footing on such a surface (12, 42).

Scheer (43) studied the effect of adding various wetting agents to petrolatum, and found that some of these, particularly sulfonated aliphatic compounds, improved the antifouling action of the petrolatum even though they increased the degree by which the surfaces wet with water.

In a study of the prevention of fouling by waxy or non-wetting surfaces, the Naval Research Laboratory (32) prepared 25 compositions employing three samples of petrolatum of different boiling points, a Stearin Pitch Lubricant, and a hot plastic paint vehicle, each mixed with various proportions of wetting agents. Weldwood panels were coated with these compositions and exposed

<sup>&</sup>lt;sup>1</sup> This contained Stearin Pitch, caustic soda and mineral oil.
<sup>2</sup> This vehicle contained rosin, pine oil, cumarone-indene resin, and ceresein

for fouling tests at Miami Beach, Florida. None of the compositions showed any significant antifouling properties, and all were soft, sloughing from the panels and exposing in some cases large areas of bare wood. The experiment was discontinued after 30 days' exposure because all of the panels were completely fouled. Similar compositions using a petrolatum base were exposed by investigators of Mellon Institute (30) at Daytona Beach, Florida, on primed steel panels. After six months' exposure it was concluded that the compositions have little or no effect on fouling by barnacles and filamentous bryozoa, but did diminish the attachment or adhesion of molluscs, encrusting bryozoa, and hydroids, when compared to a nontoxic paint control. None of the wetting agents or even pentachlorophenol, which is a toxic agent, improved the performances over that given by petrolatum alone. The physical condition of the coatings was very poor, with much of the composition lost after six months' exposure, and with serious corrosion of the steel panels being evident. Tests of petrolatum at Kure Beach, North Carolina, by LaQue (26) demonstrated considerable suppression of fouling when exposed from November to May. Lanolin and some petrolatum base grease were, however, fouled in the same time.

The evidence available indicates that the waxy or oily surfaces may be effective in preventing the attachment of fouling for a short period of time. This action appears to be erratic and may be the result of the chemical nature of some of the ingredients, or of the unsubstantial character of the surface, rather than of the hydrophobic properties of the surface.

# **EXFOLIATION**

An exfoliating surface may be defined as one which disintegrates by loss of particles which are of more than molecular size (i.e., not by solution of ingredients). Such a surface is unsubstantial and offers the organisms an insecure footing. It has frequently been suggested that any fouling organisms which attempt to attach will be sloughed off because of the physical disintegration of the surface. Paints designed to resist fouling in this way would be the underwater counterparts of the chalking house-paints which remain clean by a similar mechanism.

The evaluation of exfoliation as a means of preventing fouling is difficult, since, though there has been much discussion, very few paints have been made and tested to prove its worth. The paints which prevent fouling and have been claimed to do

so by exfoliation all contain some toxic ingredient which may be the effective antifouling agent.

The theoretical explanation of the mechanism by which an exfoliating surface might function has been presented by Wharton (54). It is based upon the two stages of the attachment of larval barnacles. The first step of attachment is the adhesion of the antennae to the surface. This is first accomplished by means of a vacuum cup arrangement, later supplemented by the secretion of a cement. For some time the antennal attachment is the only method for holding the barnacle to the surface. In the final attachment, however, the calcareous plates become cemented directly to the surface. Wharton postulates that, as the barnacle grows, some pressure may be great enough to pull loose the antennal attachment before the plates become firmly cemented. If the surface is hard and has a loosely adhering surface layer, the barnacle may thus be sloughed off. If the surface is soft, the barnacle is able to penetrate the paint and obtain a firm attachment to the underlying structure, even though the surface layer adheres loosely. If the surface is hard and has no loosely adhering surface layer, the barnacle can maintain its attachment to the outer surface.

This ingenious explanation of the action of exfoliating paints may apply in the case of the acorn barnacle. It is difficult to see how a similar explanation could be applied to the various other important fouling forms.

Wharton (54) has devised methods for determining whether or not a paint exfoliates. The most ingenious of these involved placing a piece of transparent scotch tape on the dried paint surface. If some of the paint or surface deposit is removed with the tape, the paint is classified as exfoliating. It was found that it generally takes two or three weeks of soaking in the sea to develop the exfoliating surface. In tests of 378 paints, 300 were found to have exfoliating surfaces, and most of these, 282, gave satisfactory antifouling performance. The non-exfoliating paints were almost equally divided between satisfactory and unsatisfactory performance. All of the satisfactory paints, however, contained toxic ingredients, and may have been effective for this reason (see Chapter 14).

Young and his collaborators (62) have attempted to test the importance of exfoliation by making a series of paints containing no toxic, in which the content of the pigment, barytes, varied. One paint contained no pigment; the pigment: volume ratio of the others increased up to 6:1. This variation, with a "corresponding observable"

exfoliation and erosion," had no observable effect on fouling. All of the pigmented paints fouled with barnacles, tubeworms, and hydroids as completely as the pure varnish. The paints high in pigment seemed to have some inhibitive action on bryozoa and on "algae and scum." Paints containing similar loadings of copper were much more effective in preventing attachment of all forms.

Castle (5), in his studies of the formation of deposits by means of electric currents (page 236), demonstrated that it is possible to protect a sur-

Table 6. Weight Loss and Fouling of Iron Strips Coupled to Metallic Copper Paints During 30 Days' Immersion at Miami Beach, Florida

ininiersion at 141	ann Boading Clothau
Loss of Weight	
of Iron	Fouling on
$mg/cm^2/day$	Iron
22.0	none
21.6	none
20.5	none
15.9	none
14.5	none
14.0	none
12.8	none -
9.6	none
4.1	Fouled, barnacles
	and Tunicates
3.0	Densely fouled
2.3	Densely fouled
2.1	Densely fouled
1.9	Densely fouled
1.8	Densely fouled
1.8	Densely fouled
1.8	Densely fouled

face from fouling by exfoliation. He found that fouling was prevented on cathodes to which currents in excess of 1000 milliamperes per square foot were applied. These surfaces formed deposits several millimeters thick, and underwent massive exfoliation. Unfortunately he made no quantitative determinations of the rate of weight loss necessary to prevent fouling.

Generally, the corrosion of iron in sea water is slow enough so that fouling can attach and grow on the surface; but if iron is coupled to nobler metals—copper, for example—the rate of corrosion is so rapid that no fouling can find a foothold. Presumably this protection is caused by the exfoliation of the rust on the surface.

In some experiments performed at Miami (48), strips of iron were bolted over the surface of various paints containing graded amounts of metallic copper. The rate of corrosion of the iron strip attached to these paints increased as the copper content of the paint increased. The weight losses and fouling of these iron strips are given in Table 6.

All of the iron strips which lost more than 9.6

mg/cm²/day were completely free of fouling. All of the iron strips which lost 4.1 mg/cm²/day or less were densely fouled. It is apparent from this experiment that the rate of weight loss (exfoliation) to protect iron from fouling lies between the values of 4.1 to 9.6 mg/cm²/day. A weight loss of 7.8 mg/cm²/day corresponds to a thickness of iron of about 0.01 mm. or 0.4 mil. If similar rates of loss are necessary for exfoliating paints, very thick films would be essential to give an appreciable life. For example, a film 146 mils in thickness would be necessary to last for one year.

Ever since Sir Humphry Davy (8, 9, 10) described the corrosion and fouling of copper, its action has been attributed variously to exfoliation of the corrosion products on the surface, or to the toxicity of the copper which dissolves from the surface. Both theories are equally reasonable, and both have had vigorous adherents. This subject is discussed fully in Chapter 22, but a brief review may be useful here.

LaQue (27, 28) has shown that alloys of copper and nickel which contain more than 30 per cent nickel will foul when submerged in the sea. The surfaces which do not foul lose more than 0.045–0.070 mg Cu/cm²/day. These figures are very much smaller than those necessary to protect iron from fouling. In some experiments performed at Woods Hole, the weight losses from various alloys of copper were determined. The fouling of duplicate alloys was studied at Miami (48). The results are summarized in Table 7.

In this experiment the Muntz and Monel metals fouled, even though they lost weight faster than pure copper, brass, or bronze. The weight lost

TABLE 7. Weight Losses and Fouling of Copper Alloys After Exposure for About One Year

Alloy Used	Weight Loss mg/cm²/day	Fouling
Copper	.035	None
Brass	.045	None
Muntz Metal	.107	Light and variable
Monel Metal	.060	Completely fouled
Nickel Silver	.023	Light and variable

from the pure copper surface was all in the form of copper, whereas the weight lost from the others must have contained various amounts of the alloying metals. Copper is more toxic to marine organisms than the other metals, and the effects of toxicity and exfoliation in these exposures cannot be separated. Since copper prevents fouling with much less weight loss than the other metals, it seems apparent that exfoliation alone does not explain the prevention of fouling by copper metal and its alloys.

The results of the tests of exfoliation indicate that, whereas fouling can be completely prevented by this process, it is a wasteful mechanism and would require very thick applications in order to afford prolonged protection. The fact that no paints have been discovered which prevent fouling by this mechanism alone indicates that it has not been found very useful by the paint technologist in the design and formulation of antifouling paints.

#### SLIME OR PRIMARY FILMS

A surface exposed in the sea becomes coated within a few days with a thin gelatinous or slimy film. These films are formed by bacteria and diatoms, and include considerable amounts of organic and inorganic detritus (23, 52, 56, 63-67). Several investigators have suggested that the presence of the slime film influences the subsequent attachment of macroscopic fouling forms. Information has accumulated which indicates that the presence of the slime film on nontoxic surfaces is favorable for the attachment of fouling organisms. This is discussed in Chapter 4.

The slime film was first studied in relation to the control of fouling by Bray (4), who exposed a large series of paints and observed that they slimed to markedly different degrees. Those paints which formed the heaviest slimes ultimately became the most fouled. Several later investigators have claimed a correlation between the amount of slime film and the tendency of surfaces to foul (23, 56–59), but the evidence for any such correlation is not convincing. Adamson (1) pointed out that different types of slimes form on different paints, and stated that the gelatinous slimes seem to discourage attachment, whereas the silty, granular slimes permit attachment.

ZoBell (67) studied the attachment of barnacle larvae to glass panels and concluded that the slime formed a beneficial substrate for their attachment. He suggested that the slime might favor fouling in a variety of ways: by enmeshing the larvae; by discoloring glazed or bright surfaces; by serving as a source of food; by protecting the organisms from the toxic constituents of poisonous paints; by increasing the alkalinity and thus favoring deposition of calcareous cements; or by influencing the potential of the surface.

On antifouling surfaces the slime has been stated variously to favor, to interfere with, or to have no effect on the attachment of fouling forms. Much of the confusion has resulted from the use of a variety of different paints having different toxic properties. In the early investigations it was

impossible to differentiate between the contribution of the slime and the toxicity of the surface. With the development of the leaching rate technique as an independent measure of toxicity, it became apparent that the slime film might contribute to the effectiveness of an antifouling paint by influencing its toxicity. This is discussed in detail in the next chapter, which includes other investigations of the toxicity of metallic poisons to organisms.

# REFERENCES

- Adamson, N. E. Technology of Ship Bottom Paints and Its Importance to Commercial and Naval Activities. Bureau Construction and Repair Bull. No. 10, U. S. Govt. Printing Office. 1937.
- 2. Baggs, J. British Patent 2295. September, 1863.
- Bengough, G. D., and V. G. Shepheard. The Corrosion and Fouling of Ships. Jour. Inst. Iron & Steel, 147, 339-451. 1943.
- Bray, A. W. L. A Preliminary Investigation into the Fouling of Ships' Bottoms by Marine Growth. Bureau Construction and Repair, U. S. Navy Dept., 1923. (Unpublished.)
- CASTLE, E. S. Electrical Control of Marine Fouling. Ind. and Eng. Chem., 43, 901-904. 1951.
- COE, W. R., and W. E. ALLEN. Growth of Sedentary Marine Organisms on Experimental Blocks and Plates for Nine Successive Years at the Pier of the Scripps Institution of Oceanography. Bull. Scripps Inst. Oceanog., Tech. Ser., 4, 101-136. 1937.
- Cox, G. C. Anticorrosive and Antifouling Coating and Method of Application. U. S. Patent 2,200,469. 1940.
- 8. DAVY, SIR HUMPHRY. On the Corrosion of Copper Sheathing by Sea Water, and on Methods of Preventing this Effect; and on their Application to Ships of War and other Ships. Phil. Trans. Roy. Soc. London, 114, 151-158. 1824.
- DAVY, SIR HUMPHRY. Additional Experiments and Observations on the Application of Electrical Combinations to the Preservation of the Copper Sheathing of Ships, and to Other Purposes. Phil. Trans. Roy. Soc. London, 114, 242-246. 1824.
- DAVY, SIR HUMPHRY. Further Researches on the Preservation of Metals by Electro-chemical Means. Phil. Trans. Roy. Soc. London, 115, 328-346. 1825.
- EDMONDSON, C. H., and W. H. INGRAM. Fouling Organisms in Hawaii. Bernice P. Bishop Mus., Occas. Papers 14 (14), 251-300. 1939.
- 12. Fox, D. L. Personal Communication.
- Fox, D. L., and W. R. Coe. Biology of the California Sea Mussel (*Mytilus californianus*). II, Nutrition, Metabolism, Growth and Calcium Deposition. J. Exp. Zool., 93, 205– 249. 1943.
- GARDNER, H. A. Letter to Bureau of Yards and Docks, July 27, 1934; August 23, 1934; November 7, 1934. (Unpublished.)
- GARDNER, H. A. Letter to Bureau of Construction and Repair. Report on Brief Exposure of Paints, January 4, 1935. (Unpublished.)
- GRAVE, C. A. Continuation of Study on the Influence of Light on the Behavior and Metamorphosis of the Larvae of Ascidians. Yearbook Carnegie Inst. Wash., 27, 273-275; 28, 284-286, 1928-1929.
- Grave, C. A. Notes on the Culture of Eight Species of Ascidians, 560-564 in Culture Methods for Invertebrate Animals. Comstock Publ. Co., Inc., Ithaca, N. Y. 1937.
- GREGG, J. H. Background Illumination as a Factor in the Attachment of Barnacle Cyprids. Biol. Bull., 88, 44-49.

- 19. GUTSELL, J. S. Natural History of the Bay Scallop. Bull. U. S. Bur. Fish., 46, 569-632. 1930. 20. HARKINS, H. H. Theory of Fouling. Letter to Bureau of
- Ships. July 22, 1941. (Unpublished.)
- 21. HARRIS, J. E., and W. A. D. FORBES. Under-water Paints and the Fouling of Ships, with Reference to the Work of the Marine Corrosion Sub-committee of the Iron and Steel Institute and the Admiralty Corrosion Committee. Inst. Nav. Arch., London. April 12, 1946.
- 22. HENTSCHEL, E. Der Berwichs an Seeschiffen. Int. Rev. Hydrobiol. Hydrogr., 11, 238–264. 1923.

  23. Herpin, R., and R. Duliscouet. Le rôle d'une membrane
- microbienne dans l'efficacité des peintures destinées à protéger les carènes de bateaux contre les organismes encrassants. Compt. rend. Acad. Sci. (Paris), 207, 193-195. 1938.
- 24. HOPKINS, A. E. Factors Influencing the Spawning and Setting of Oysters in Galveston Bay, Texas. Bull. U. S. Bur. Fish., 47, 57-83. 1931.
- 25. HUTCHINS, L. W., and E. S. DEEVEY, JR. Estimation and Prediction of the Weight and Thickness of Mussel Fouling on Buoys. Interim Report I for 1944 from Woods Hole Oceanographic Inst. to Bureau of Ships. 1944. (Unpublished.)
- 26. LAQUE, F. L. Personal Communication. 1945.
- 27. LAQUE, F. L. Bio-fouling Characteristics of Some Common Metals and Alloys. Report Prepared for the N.D.R.C. Advisory Committee on Marine Coatings and Corrosion. January 2, 1945. (Unpublished.)
- 28. LAQUE, F. L., and W. F. CLAPP. Relationships between Corrosion and Fouling of Copper Nickel Alloys in Sea Water. Trans. Electrochemical Soc., 87, 165-184. 1945.
- 29. McDougall, K. D. Sessile Marine Invertebrates at Beaufort, N. C. Ecol. Mon., 13, 321-374. 1943.
- 30. Mellon Inst. (Norman Ellis). Antifouling Studies for Scripps Institution. Special Report, Stoner-Mudge, Inc. Industrial Fellowship No. 258-10. February, 1945. (Unpublished.)
- 31. MILLER, M. A. Toxic Effects of Copper on Attachment and Growth of Bugula neritina. Biol. Bull., 90, 122-140. 1946.
- 32. Naval Research Laboratory (R. L. Benemelis). Report on a Study of Non-Toxic Composition for the Prevention of Fouling. (N.R.L. Report #P-2444, Problem #P-90). January 26, 1945. (Unpublished.)
- OSHIMA, S. Research on Antifouling Paints Containing No Mercury. VI-VIII, J. Soc. Chem. Ind. Japan, 38, 170B.
- 34. PERRY, E. The Fouling of Ships' Bottoms. Pacific Marine
- Review, 28, 202-203; 244-245. 1931.
  35. Perry, E. A Study of the Preventive Effect of Light Colors on the Fouling of Ships' Bottoms. Paint and Varnish Production Manager, 7, 10-16. 1932.
- 36. PHELPS, A. Observations on Reactions of Barnacle Larvae and Growth of Metamorphosed Forms at Beaufort, N. C., June, 1941, to Sept., 1941. Paper 7, Fourth Report from Woods Hole Oceanographic Inst. to Bureau of Ships. March 27, 1942. (Unpublished.)
- 37. POMERAT, C. M., and E. R. REINER. The Influence of Surface Angle and of Light on the Attachment of Barnacles and Other Sedentary Organisms. Biol. Bull., 82, 14-25. 1942.
- 38. POMERAT, C. M., and C. M. Weiss. The Influence of Texture and Composition of Surface on the Attachment of Sedentary Marine Organisms. Biol. Bull., 91, 57-65. 1946.
- 39. RILEY, G. A. The Toxicity of Heavy Metals to Fouling Organisms. Paper 12, Sixth Report from Woods Hole Oceanographic Inst. to Bureau of Ships. May 1, 1943. (Unpublished.)
- 40. San Diego. Reports on Exposure of Paints Submitted by H. A. Gardner. January 4-May 5, 1935.
- 41. SCHALLEK, W. The Reaction of Certain Crustacea to Direct and Diffuse Light. Biol. Bull., 84, 98-105. 1943.
- 42. SCHEER, B. T. Personal Communications.
- 43. SCHEER, B. T., and D. L. Fox. Attachment of Sedentary

- Marine Organisms to Petrolatum Surfaces. Proc. Soc. Exp. Biol. and Med., 65, 92-95. 1947.
- 44. SMITH, F. G. W. The Effect of Water Currents upon Growth of Fouling Organisms Subsequent to Attachment. Interim Report III for 1945 from Woods Hole Oceanographic Inst. to Bureau of Ships. February 19, 1945. (Unpublished.)
- 45. SMITH, F. G. W. Mechanical Control of Ship-Bottom Fouling by Means of Air Bubbles. Quart. Jour. Fla. Acad. Sci., 9, Nos. 3-4, 153-161. 1946.
- 46. SMITH, F. G. W. Effect of Water Currents upon the Attachment and Growth of Barnacles. Biol. Bull., 90, 51-70. 1946. 47. Sumner, F. B., R. C. Osburn, and L. J. Cole. A Biological
- Survey of the Waters of Woods Hole and Vicinity. Bull. U. S. Bur. Fish., 31, 5-442. 1911.
- 48. Unpublished Results of Tests Conducted at Miami. These are described in Chapter 22.
- 49. Visscher, J. P. Reactions of the Cyprid Larvae of Barnacles at the Time of Attachment. Biol. Bull., 54, 327-335. 1928.
- 50. VISSCHER, J. P. Nature and Extent of Fouling of Ships' Bottoms. Bull. Bur. Fish., 43, 2, 193-252. 1928.
- 51. VISSCHER, J. P., and R. H. LUCE. Reactions of the Cyprid Larvae of Barnacles to Light, with Special Reference to Spectral Colors. Biol. Bull., 54, 336-350. 1928.
- 52. Waksman, S. A., and Collaborators. Reports from Woods Hole Oceanographic Institution to Bureau of Ships, 1940-
- 53. Weiss, C. M. The Effect of Illumination and Stage of Tide on the Attachment of Barnacle Cyprids. Biol. Bull., 93, 240-249 1947.
- 54. Wharton, G. W. Report of the Biologist. Norfolk Navy Yard. June, 1941-August, 1942.
- 55. WHARTON, G. W. The Primary Attachment of Balanus eburneus. Progress Report of the Biologist, Norfolk Navy Yard. April 19, 1943. (Unpublished.)
- 56. Whedon, W. F. La Jolla Investigations. 1937-1941. Naval Biological Laboratory Investigations. 1941-1943. Reports to Bureau of Ships.
- 57. WHEDON, W. F. Investigations Pertaining to the Fouling of Ships' Bottoms. Semi-Annual Report for 1941-1942 from Naval Biological Lab., San Diego, Cal., to Bureau of Ships. April 30, 1942.
- 58. WHEDON, W. F., and Collaborators. Investigations Pertaining to the Fouling of Ships' Bottoms. Annual Report 1941-1942 from Naval Biological Lab., San Diego, Cal., to Bureau of Ships. October 24, 1942.
- 59. WHEDON, W. F. Investigations Pertaining to the Fouling of Ships' Bottoms. Annual Report 1942-1943 from Naval Biological Lab., San Diego, Cal., to Bureau of Ships. June, 1943.
- 60. WHITNEY, L. V. The Angular Distribution of Characteristic Diffuse Daylight in Natural Waters. Jour. Mar. Res., 4. 122-131. 1941.
- 61. Young, G. H. Personal Communication.
- 62. YOUNG, G. H., W. K. SCHNEIDER, and G. W. SEAGREN. Antifouling Paints-Effect of Inert Pigment on Antifouling Action. Ind. Eng. Chem., 36, 1130-1132. 1944
- 63. ZoBell, C. E. The Sequence of Events in the Fouling of Submerged Surfaces. Fed. Paint Varn. Prod. Clubs, No. 178, 379-385. 1938.
- 64. ZoBell, C. E. The Biological Approach to the Preparation of Antifouling Paints. Scientific Section, National Paint, Varnish and Lacquer Assoc., Circ. 588, 149-163. 1939.
- 65. ZoBell, C. E. The Role of Bacteria in the Fouling of Submerged Surfaces. Biol. Bull., 77, p. 302. 1939.
- 66. ZoBell, C. E. Primary Film Formation by Bacteria and Fouling. Collecting Net, 14, 105-106. 1939.
- 67. ZoBell, C. E. Fouling of Submerged Surfaces and Possible Preventive Procedures. The Biological Approach to the Preparation of Antifouling Paints. Paint, Oil and Chemical Review, 101, 74-77. 1939