15877

Attachment of Sedentary Marine Organisms to Petrolatum Surfaces.

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Independent observations, in our laboratories, in the Clapp Laboratories, and in the laboratories of the International Nickel Company, and of the Mellon Institute,† have shown that sedentary marine organisms attach much less readily to glass, metal or plastic surfaces coated with petrolatum than to similar uncoated surfaces. The present paper presents the results of an analysis of the rationale of this effect, and certain relevant data on the antifouling action of other compounds. The antifouling effect of petrolatum might be attributed to its unsubstantial character, its hydrophobic nature, or some specific repellant or toxic characteristic. We have compared petrolatum mixtures of varying consistency, and mixtures containing wetting agents to modify the hydrophobic character; we have found no clear correlation with either property.

Methods. Preliminary tests with the various materials were carried out in the laboratory. Briefly, it was found that surfaces which permitted successful attachment of sea anemones by their bases, or of mussels by their byssus pads, or which permitted successful attachment or locomotion by asteroids (sea stars) or gastropods (tectibranchs), were unsuitable for preventing attachment of sedentary organisms in general. On the other hand, surfaces which prevented attachment of the test animals *(Pisaster ochraceus, Tethys californicus, Cribrina xanthogrammica, Mytilus californianus)* in the laboratory were often effective antifoulants.

Actual exposure tests were conducted with glass or metal plates, coated with the material to be tested, and suspended either in the open sea at La Jolla or in the entrance channel to Newport Harbor at Corona del Mar. The sites and biological characteristics of the sedentary populations have been described by Coe,[1] Coe and Allen,[2] and Scheer.[3] The panels were examined at regular intervals, qualitatively at La Jolla, and semiquantitatively at Corona del Mar. Photographic records were kept of plates exposed at La Jolla.

Results. Table I gives the results of several tests with petrolatum (petrolatum white U.S.P.) In every case, coated panels were less heavily fouled than control uncoated surfaces. Two series of mixtures were then tested, to study the effects of varying consistency. These mixtures were made by diluting a crude petrolatum with lubricating oil, or with crude naphthenic acids from petroleum. The A.S.T.M. penetration values for these mixtures ranged from 93 to 450 at 77°. No consistent differences were observed in antifouling properties. However, purified white petrolatum was more effective in retarding attachment than were crude mixtures of comparable consistency.

Oil-soluble wetting agents of many different types were incorporated in petrolatum, to alter its hydrophobic properties. In an exposure at Corona del Mar, there was no relation between wettability of surface, as measured by contact angle with sea water (Adam[4]), and extent of fouling (Table II). One compound, a sodium alkyl sulfonate of uncertain composition, was markedly superior to all others tested in preventing attachment of organisms, although it was not the most effective wetting agent. Similar, though less

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† Personal communication from Dr. William F. Clapp.

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2 Coe, W. R., and Allen, W. E., *Bull. Scripps Inst. Oceanogr.*, 1937, Tech. Ser. **4**, 101.

3 Scheer, B. T., *Biol. Bull.*, 1945, **89**, 103.

4 Adam, N. K., *The Physics and Chemistry of Surfaces*, 2nd Ed., Oxford, 1938.

TABLE I.
Settlement of Organisms on Aluminum Panels (A) and on Aluminum Panels Coated with Petrolatum (P) Exposed at the Same Time. Corona del Mar.†

Duration of exposure, wks	Coating	Time for 10% coverage by ABH,* days	Avg % of area covered by Bryozoans	Maximum Bryozoans	No. Tubeworms
10	A	3	18		
	P	7	0		
28	A	2	30	3	19
	P	2	0	3	2
20	A	12	5.5	41	0
	P	3	0	1	0
24	A	6	30	39	1
	P	17	0	10	2
38	A	8	28	68	9
	P	11	0	36	18
28	A	3	47	62	14
	P	5	1.1	34	29
8	A	5	1.3	110	14
	P	10	0	1	0
14	A	2	47	129	92
	P	5	0	11	2

* ABH signifies the film of algae, bacteria, and hydroids characteristic at the early stages of fouling (Scheer[3]).
† The different panels were exposed at different seasons. This accounts for the variation of intensity of settlement.

TABLE II.
Antifouling Efficacy of Surface-active Materials Incorporated in Petrolatum. Exposed at Corona del Mar Beginning December 14, 1943, for 14 weeks.

Materials*	Chemical nature	Conc. in petrolatum %	Contact angle Out	Contact angle In	ABH Time, wks, for coverage of 10%	ABH Time, wks, for coverage of 50%	ABH Avg coverage
Aerosol-OT	Dioctyl disodium sulfosuccinate	10	45°	45°	0.65	3.2	39
Armour's AM 1180	Octadecyl amine	2	45	55	0.50	2.5	45
’’ ’’ 2180C	Octadecyl diamine and triamine	9	45	60	1.1	10.0	34
Emery's A 105 (R)	Aliphatic amine	10	45	60	0.52	2.6	48
’’ X 68 (R)	Aliphatic ester of polyglycol	20	45	50	2.0	8.8	29
Saponin	Phenanthrene glycoside	22	45	75	2.9	11.0	23
’’	’’ ’’	9	45	90	4.0	10.0	21
Aerosol-OT		4	60	65	1.1	11.0	29
Emery's X 72 (R)	Aliphatic ester of polyglycol	20	60	70	1.1	11.0	24
’’ T 333 (R)	Sodium alkyl sulfonate	20	70	70	11.0	11.0	4
Armour's AM 1120	Dodecyl amine	2	70	75	2.2	7.2	32
Emery's X 68 (R)		4	75	75	0.60	3.0	32
’’ ’’ 72 (R)		4	80	90	1.8	11.0	22
Petrolatum			90	100	1.6	11.0	22

* The trade names serve to identify the materials used; their exact composition is unknown in several instances.

clear cut, results were obtained at La Jolla.

A second series of tests, using a series of sorbitol derivatives, confirmed the lack of correlation with wettability. The results of this series are given in Table III. The time required for development of a film of algae, bacteria, and hydroids (A B H) varied considerably among different compounds, as did the intensity of coverage and the number of settlers. This variation was in no way related to the surface action of the compounds; we may note, for example, the heavy settlement on the sorbitol ether, and on the modified hexastearate, which differed markedly in their surface action.

The results obtained in these tests suggest

TABLE III.
Antifouling Efficacy of Sorbitol Derivatives. Exposed at Corona del Mar Beginning July 14, 1944, for 8 Weeks. (All compounds dissolved in petrolatum to make a 10% mixture.)

Substance	Contact angle		Time, wks, for ABH coverage of		Avg coverage, %		Maximum No.	
	Out	In	10%	50%	ABH	Bryozoans	Bryozoans	Tubeworms
Sorbitan hexaoleate, modified	35°	50°	2.2	8+	12	0	3	1
Sorbitol ether	35	60	1.8	2.7	61	11	43	112
Sorbitan distearate	60	75	0.5	8+	33	8	18	12
Sorbitan oleate, modified	70	85	2.0	8+	27	0	23	0
Sorbitan monooleate	70	85	2.0	8+	20	0	6	0
Sorbitan trioleate	80	90	4.0	8+	15	0	11	0
Sorbitan triricinoleate	80	95	1.5	4.9	52	0	34	2
Sorbitan hexastearate, modified	85	95	0.4	2.0	40	26	80	34
Sorbitan tristearate	90	95	0.4	1.9	52	2.7	51	8
Petrolatum	90	100	0.7	8+	39	0	11	0

that the antifouling action of petrolatum might better be attributed to specific chemical properties of unknown nature than to either consistency or hydrophobic properties. Certainly various modifications in chemical composition produced more startling changes in antifouling properties than did alterations in consistency or wettability *per se*.

One such chemical change appeared to be worthy of further examination. The most effective petrolatum mixtures, in the prevention of attachment, were those containing a sodium alkyl sulfonate. We accordingly tested several other compounds of a similar nature.‡ The aliphatic sulfonates were all very effective as antifoulants when incorporated in petrolatum, while the sulfated ester (Aerosol OT) was somewhat less effective; sodium hydroabietyl sulfonate was decidedly inferior.

A possible explanation of the effectiveness of the aliphatic sulfonates might be the following: The sulfonic acid radical is polar and strongly acidic. Accordingly, at an oil-water interface, we would expect orientation such that the sulfonate radical will lie in the aqueous phase and will be ionized. This ionization will be accentuated if the solution is buffered to an alkaline pH, as is the case with sea water. This will provide, in effect, an acidic or negatively charged oil surface.

We were able to show that such orientation does occur by immersing panels coated with petrolatum-sulfonate mixtures in sea water, and measuring the change in wettability (contact angle) with time. With concentrations of sulfonate from 5 to 40%, wettability increased during the first 4 hours of immersion, rapidly at first and then more slowly. No further increase occurred during 20 hours of immersion. The importance of this orientation in prevention of fouling was shown in an experiment in which sulfonated material was mixed with a black asphalt paint. One panel was treated with this mixture and allowed to dry before immersion in sea water; a second panel was immersed in sea water for 2 hours immediately after preparation, and then allowed to dry. The second panel was distinctly superior in antifouling efficacy to the first (Table IV).

Summary. The action of petrolatum in delaying or preventing the attachment of sedentary marine organisms to submerged surfaces is not consistently altered by changes in consistency, produced by dilution with miscible liquids, or in wettability, produced by incorporation of wetting agents. The alterations observed appear rather to be the result of unknown chemical differences in the coatings. One such difference, characteristic of mixtures of petrolatum with aliphatic sulfonates, was shown to be related to orientation at the surface. It is suggested that the

‡ Aerosol OT (dioctyl disodium sulfosuccinate); T-333 (R), T-284 (R), T-285 (R), T-286 (R) (aliphatic sulfonates, Emery Industries, Inc.); Gamonol X, Sulfoline P (sulfonated petroleum products); Sodium hydroabietyl sulfonate (Hercules Powder Co.).

TABLE IV.
Effect of Immersion in Sea Water on Antifouling Efficacy of a Paint-Sulfonate Mixture. Panels exposed at Corona del Mar for six weeks beginning October 17, 1944.

Material	Time for 10% ABH coverage, days	Avg coverage		Maximum No.		
		ABH	Bryozoans	Bryozoans	Tubeworms	Barnacles
Black asphalt paint	6	24	0	44	6	16
Same + 30% T-333	5	37	0	0	0	0
Same + 30% T-333, soaked 2 hr in sea water	14	23	0	1	0	0
Same + 50% T-333, soaked 2 hr	42+	5	0	0	0	0

interface between such a mixture and sea water has a negative charge, and that this may be important in its antifouling properties.

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15878 P

Effect of Drugs on Gastric Motility Following Vagotomy.

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During the past 4 years, reports by Dragstedt,[1] Grimson,[2] Moore[3] and their associates have renewed interest in vagotomy for the management of patients with peptic ulcer. Although prompt relief from symptoms and healing of ulcer usually follow vagus resection, adverse complaints may develop because of reduced gastric peristalsis with retention or delayed emptying of stomach contents. Investigation of this retention phenomenon led to studies of gastric motility and tone as shown by variations of intragastric pressure in rabbits and in patients before and after vagotomy and after drugs.

Methods. Experiments were performed on rabbits after bilateral cervical vagotomy using local anesthesia and frequently inserting tracheotomy tubes. Intragastric pressures were recorded graphically by water manometers connected through small catheters to stomach balloons inflated with 30 to 50 cc of air. Drugs were administered hypodermically 30 minutes to 2 hours after vagotomy. Records of gastric motility and of resting intragastric pressure or "tone" were made for periods of 2 hours or longer. Experiments were also performed in rabbits one day to 8 months after transthoracic vagotomy done through a left thoracotomy wound. Studies on patients were obtained before and at intervals after transthoracic vagotomy for peptic ulcer. The balloons used in patients were inflated by 300 cc of air and pressures

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