Surface-Fragmenting, Self-Polishing, Tin-Free Antifouling Coatings

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Surface-fragmenting types of self-polishing tin-free resins were characterized by IR and NMR and demonstrated the successful synthesis of cupric carboxylate. According to the IR, ^{1}H-NMR and ^{13}C-NMR measurements, it is clear that the unsaturated double bonds present in the resins changed into other new bonds after drying in a manner similar to alkyd resins. These resins were used as binders to prepare antifouling paints. Scanning electron microscopy (SEM), rotary tests, raft tests, and ship tests were used to investigate the self-polishing phenomena and the antifouling ability of this type of antifouling paint. The SEM photographs obtained from the paint surfaces demonstrate self-polishing phenomena. From the rotary tests, the polishing rates of paints were measured as 10μ ~ 5.7μ/month. The results from the raft tests show that all of the paints exhibit excellent antifouling ability and are about 80 ~ 90% as effective as the conventional tin-containing antifouling paints.

INTRODUCTION

Antifouling paints can be divided into self-polishing types and dissolving-out types. Self-polishing paints result in a smooth surface which help save fuel while sailing. Also, the toxic compounds contained in self-polishing antifouling paints can be efficiently used with little residue; thus, they can maintain an antifouling effect over a long period of time. Over the past decades, self-polishing antifouling paints dominated the markets. The binders for these paints are primarily acrylic copolymers containing pendant side chains of tin acrylates, which are hydrolyzed by water to form carboxylic groups causing the copolymer to become soluble and release tin-containing toxins.[1-3] Due to pollution from the tin toxins, regulations and laws limit or prohibit the use of tin-containing antifouling paint.[4] Consequently, tin-free types of antifouling paints are now attracting a wide range of interest in both fundamental research and practical applications. Besides silicone types of antifouling coatings,[5,6] organic tin-free antifouling paints can be divided into three classes according to the mechanism of the polymers at the film/water interface: (1) self-polishing type,[7-10] (2) broken type,[11] and (3) a dissolving type of coating.[12-14] Due to the previously mentioned advantages, the self-polishing type is the most widely used. For most of the self-polishing antifouling paints described in the patent of Millichamp and Reeder,[8] the binder polymers are similar to the tin-containing copolymers where the side chains are grafted with a multi-valent metallic soap instead of an organotin compound.

In this study, we used a new approach to develop a novel self-polishing mechanism, i.e., the hydrolyzable group is built into the backbone of a crosslinked copolymer. Thus, the copolymer at the film/water interface can be expected to hydrolyze and fragment into small pieces resulting in a high self-polishing rate (*Scheme* 1). This type of copolymer binder was then used to prepare a series of antifouling paints. Scanning electron microscopy (SEM),[15] the rotary test, the raft test,[16] and tests on ships were then used to study this self-polishing phenomena and to determine the antifouling ability of this type of antifouling paint.

EXPERIMENTAL

Materials

Resins R1, R2, R3, and R4 are the products of Yung Chi Paint Co. Cupric oxide (Hurukawa), iron oxide (Bayer), zinc oxide (Lin Yi), xylene (CPC), and MIBK (Eastman) were used as supplied without further purification. A commercially available tin antifouling paint of the self-polishing type (PT) (Yung Chi), a tin-free antifouling paint of a self-polishing type (PS) (a Japanese product), and a broken-type antifouling paint (PB) (a Japanese

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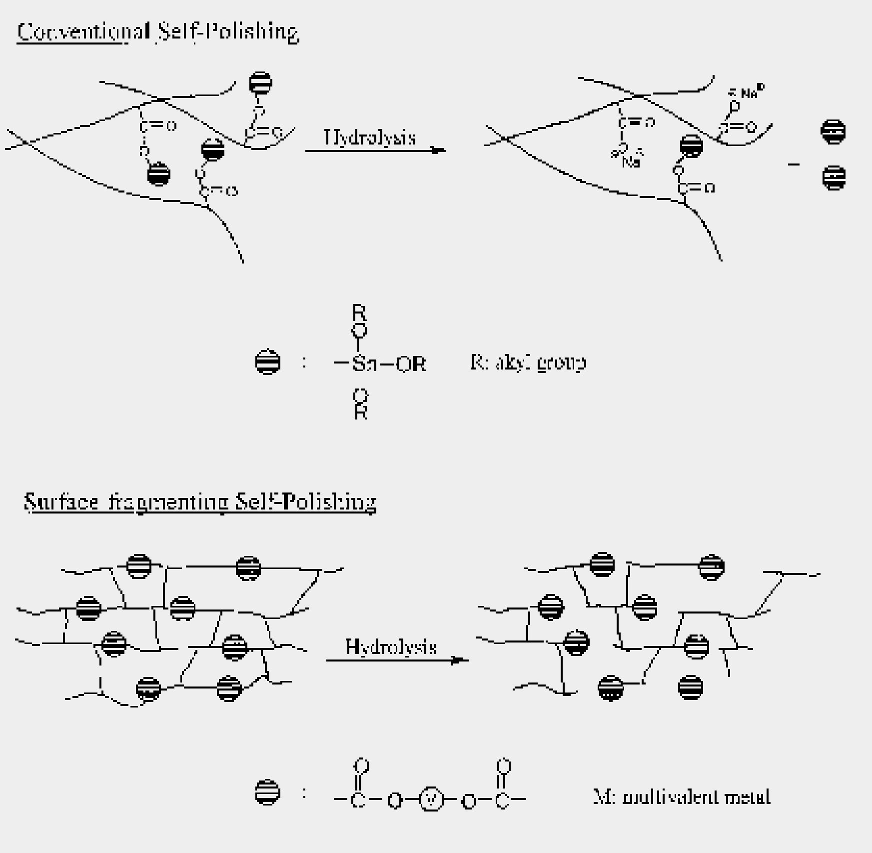

Scheme 1—The mechanisms of hydrolysis of film by water for conventional and surface-fragmenting self-polishing paints.

product) were used for the rotary test or the SEM analysis for comparison.

Resins R1, R2, R3, and R4 are the cupric salts of various unsaturated fatty acids or derivatives of organic acids. The four resins differ from each other in their molecular weight, Cu content, and viscosity. The resins are coated on polyethylene (PE) films for IR measurements. Also, they are dried and dissolved in d_6-DMSO for NMR measurements. Their compositions and properties are summarized in *Table* 1.

Methods

PREPARATION OF PAINTS: Resins R1, R2, R3, and R4 were used as the polymeric binder to prepare paints as follows: 15 g of chlorothalonil was dissolved in a 500 ml tank containing 110 g of R1 and 10 g of xylene and glass beads (with average diameters of 2 mm). Then 250 g of cupric oxide, 25 g of zinc oxide, 20 g of iron oxide, and 25 g of bentonite clay were added gradually to the tank under mechanical stirring. After mixing and milling for 60 min, 10 g of xylene and 35 g of R1 were added to the tank and mixed for another 10 min to obtain the desired paint (P1). By changing the binder to R2, R3, and R4, the corresponding antifouling paints P2, P3, P4 were obtained using the same procedure.

ROTARY TESTS: The paint was coated on the small PVC pieces (5 cm × 10 cm) of which the film thickness is c.a. 60 ~ 70 μm with area of 1.7 cm × 4 cm. The coated PVC pieces were hung on the wall of a rotary tank immersed in sea water with a speed of 20 knots. The sea water was changed every 30 days and the temperature in the container was kept at 20°C. The change in thickness was measured by the laser displacement meter.

RAFT TESTS: Steel panels were first coated with a vinyl tar type of primer (VA-10, Yung Chi) and then coated with the antifouling paints. Those panels, supported on a steel frame, were immersed in the sea in the Chayi area of Taiwan. Pictures of the panels were taken every 30 to 60 days after immersion. The antifouling effects were assessed from these pictures by observing the percentage of the area where barnacles grew on the surface of the panels.

SHIP TESTS: The P1 and P4 paints were coated on the starboard and port sides of the ship Fong Seong No. 727, while the P2 and P3 paints were coated on the starboard and port sides of the ship Fong Seong No. 747. Both are ships that normally sail at a speed of about 14 knots. After sailing in the sea around Guam for 26 months from October 24, 1992 to January 5, 1995 for Fong Seong No.

Table 1—The Properties of Four Types of Tin-Free Antifouling Paints

Paint	Resin	%Cu in Resin	Viscosity[a] (KU)	Rotary Tests[b] (μ m/month)	Raft Test[c] (%) 2	4	6	9 (month)
P1	R1	9.74	52	10.0	0	5	30	90
P2	R2	8.77	57	7.2	0	5	20	90
P3	R3	7.79	64	6.3	0	5	25	90
P4	R4	6.82	72	5.7	5	10	15	90

(a) Viscosity of the resin at 60 wt% in xylene; KU: krebs units.
(b) Polishing rate shown by the difference in the film thickness per month (see *Figure* 5).
(c) The extent of fouling was evaluated by the percentage of fouled area.

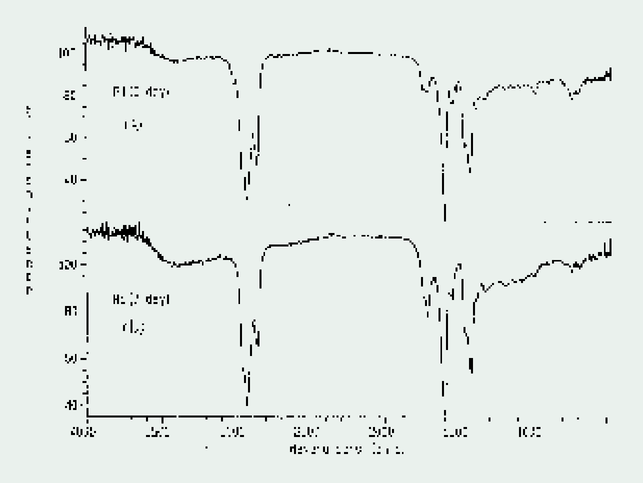

Figure 1—IR spectra for the resin R1: (a) after the evaporation of solvent in a vacuum oven; and (b) after air drying for seven days.

727 and from November 4, 1992 to February 7, 1995 for Fong Seong No. 747, pictures of the hulls were taken to assess the antifouling effects when the ships were in dry dock.

RESULTS AND DISCUSSION

The binders used in these experiments are metallic soap resins which are prepared by reacting a metal compound containing a metal having a valency of two or more with an unsaturated fatty acid having the formula[17,18] R1-A1-M-A1-R2, where R1 is an alkenyl group derived from an unsaturated fatty acid, M is a multivalent metal, A1 is a carboxyl functional group from a derived carboxylic acid, and R2 is an unsaturated or saturated organic acid. In this study, the resins R1, R2, R3, and R4 are the cupric salts of the formula with different cuprous contents and molecular weights (*Table* 1).

IR measurements of these resins were conducted either right after the evaporation of solvent in a vacuum oven (*Figure* 1a) or after drying the resin in air for seven days (*Figure* 1b). In *Figure* 1a, the peak at 1600 cm^{-1} is the carbonyl group, which is different from that found for the normal fatty acid around 1700 cm^{-1}. The shift in the IR spectra of the carboxyl group indicates that the carboxylic group from the fatty acid has been changed into the carboxylate form (i.e., metallic soap) as the resin was prepared. The peak at 3050 cm^{-1} indicates the existence of unsaturated double bonds in the resins.

After the resins were air-dried for seven days (*Figure* 1b), the peak at 3050 cm^{-1} corresponding to the unsaturated double bond disappears accompanied by the appearance of new peaks at 1720 cm^{-1} and around 1100 ~ 1200 cm^{-1}; the latter peak indicates the existence of an ether bond (C–O stretching). These phenomena demonstrate that the unsaturated double bonds were reacted to form new ether bonds on drying in the air.

The ^{1}H-NMR spectra were also recorded for the same samples either right after the evaporation of solvent in the vacuum oven (*Figure* 2a) or after drying in air for seven days (*Figure* 2b). The samples were dissolved in d_6-benzene. In *Figure* 2a, the peaks at $\delta = 5.4$ ppm and $\delta = 2.1$ ppm, are from the vinylic and allylic protons of the double bonds, respectively. The peak at $\delta = 2.8$ ppm represents the protons between the double bonds. All of these peaks shown in the NMR spectrum again indicates the existence of unsaturated double bonds. After air-drying for seven days (*Figure* 2b), the relative intensity of the peaks at $\delta = 5.4$ ppm, $\delta = 2.1$ ppm, and $\delta = 2.8$ ppm significantly decreased, indicating a decrease of the unsaturated double bonds. Next, ^{13}C-NMR spectra were

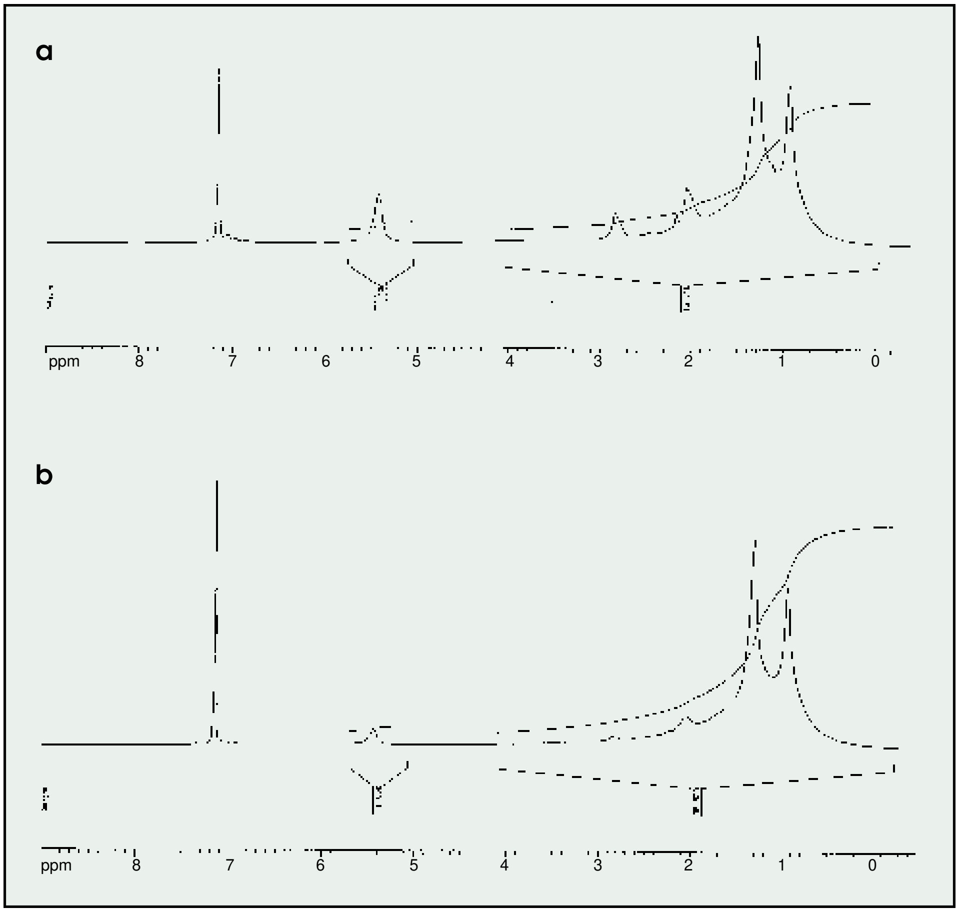

Figure 2—^{1}H-NMR spectra for the resin R1: (a) after the evaporation of solvent in a vacuum oven; and (b) after air drying for seven days.

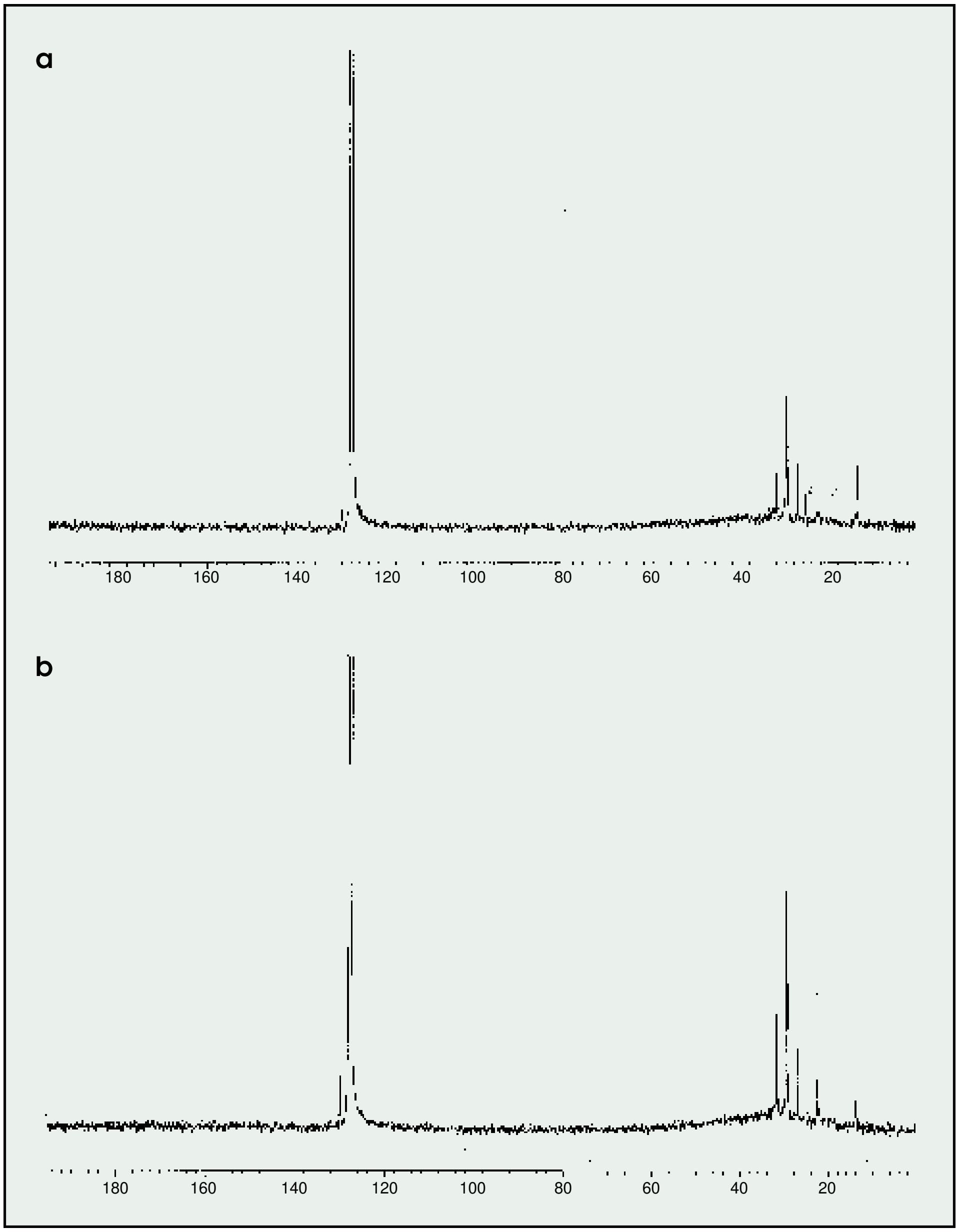

Figure 3—^{13}C-NMR spectra for the resin R1: (a) after the evaporation of solvent in a vacuum oven; and (b) after air drying for seven days.

recorded for resin R1 right after the evaporation of solvent in the vacuum oven (*Figure* 3a) or after drying in air for seven days (*Figure* 3b). The disappearance of the peaks at $\delta = 20.9$ ppm and $\delta = 26.0$ ppm in *Figure* 3a and the appearance of new peaks around $\delta = 30.0$ ppm in *Figure* 3b indicate that the double bonds of R1 have been converted into new bonds.

An alkyd resin is a polyester grafted with unsaturated oil. Normal alkyd resins or highly unsaturated drying oils are changed from liquid to dry films after exposing them to the air in the presence of a metallic soap. It has been reported that the unsaturated double bonds present in an alkyd resin react with oxygen in the air to form peroxides which in turn crosslink the ether bonds or carbon-carbon bonds to form the film[19,20] in the presence of a catalyst of a metallic soap. Resins R1, R2, R3, and R4 are themselves metallic soaps; thus, these resins serve as catalysts for the reaction of air with themselves. From the previously mentioned IR and NMR results, it is clear that the resins form films by changing the unsaturated double bond into new bonds. Therefore, it can be reasonably concluded that the resins R1, R2, R3, and R4 form films by a similar mechanism to the alkyd resins or drying oil. A proposed structure for the dried film is shown in *Scheme* 1b.

Resin R1, R2, R3, and R4 are used to make the antifouling paints of P1, P2, P3, and P4, respectively. For these paints, the carboxylate groups present in the resins at the coating film/water interface are gradually hydrolyzed to form sodium carboxylates which are more hydrophilic than the carboxylates of multivalent metals. The metal content of R1, R2, R3, and R4 are in the range of 6 ~ 10%; thus, it can be calculated that the equivalent weight of sodium carboxylate is ca 635 to 1,058, i.e., each sodium carboxylate group is attached to the hydrocarbon skeleton with carbon numbers of ca 36 to 52. Usually soaps containing sodium carboxylate have very high water solubilities as the carbon number is ca 18 to 20. Thus, the polymer shown in *Scheme* 1b is gradually hydrolyzed into small pieces by water. Once the pieces are small enough to attain high solubility in water, the polymer is polished. For the types of polymer derived from the R1, R2, R3, and R4 resins, the hydrolyzable sites are on the polymer backbone and not on the pendent side chains; therefore, the polymer skeletons at the film-water interface gradually fragment or disintegrate during hydrolysis.

After hydrolysis, the surface of the surface-fragmenting paint P1 (*Figure* 4a) was compared with that of the broken-type of antifouling paint PB (*Figure* 4b) using SEM. Obviously, the surface of P1 is very smooth (*Figure* 4a), however, some residual materials can be observed at the surface of PB (*Figure* 4b). This result demonstrates that P1 exhibits a self-polishing phenomenon different from that of the broken-type of paint (PB). PS is a commercially available tin-free self-polishing type of paint for which the binder has pendant hydrolyzable sites on side chains. *Figure* 5 shows the results of rotary tests for

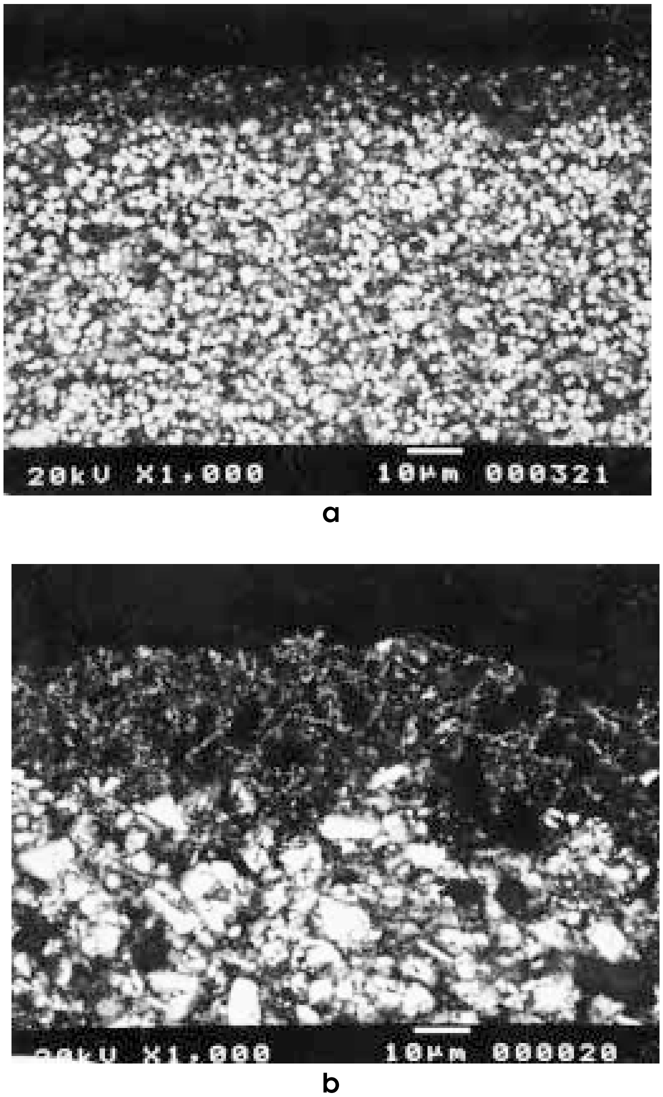

Figure 4—SEM micrographs for the surface of antifouling paints after hydrolysis: (a) the surface-fragmenting self-polishing antifouling paint, P1; and (b) the broken-type of antifouling paint.

P1, P2, P3, P4, and PS. The decreases in dry film thickness (DFT) are plotted versus the number of days immersion at a given temperature (20°C) and rotation speed (20 knots). For the first month, the thickness of all of the paints increased slightly. After the first month, the thickness of P1, P2, P3, and P4 decreased gradually. The polishing rates are in the order of P1 (10 µ/month) > P2 (7.2 µ/month) > P3 (6.3 µ/month) > P4 (5.7 µ/month). These polishing rates are higher than that of PS (1.5 µ/month). It is clear that the polishing rates of the P1, P2, P3, and P4 surface-fragmenting antifouling paints are significantly faster than that of the PS paint. For PS, the backbone of the polymer is unaffected after hydrolysis, and the hydrophilicity comes from the hydrolyzed pendant group. The polishing phenomenon occurs when

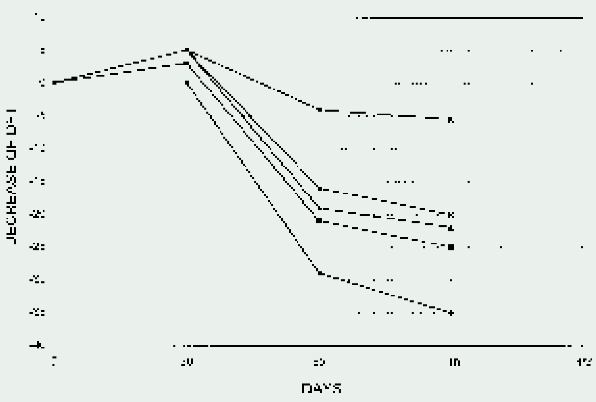

Figure 5—The results of rotary tests for five kinds of paints, P1 (◆), P2 (■), P3 (▲), P4 (×) and PS (✳). The decrease of DFT (dry film thickness) was plotted as a function of the number of days at a given temperature (20°C) and rotation speed (20 knots).

the number of hydrolyzed sites is high enough to overcome the physical interaction of the polymer backbone. Compared with this, the surface fragmenting antifouling paints (P1, P2, P3, and P4) have the hydrolyzable sites located on the polymer backbones which disintegrate into small pieces after being hydrolyzed by seawater. Therefore, the polishing rate of the surface-fragmenting type is significantly faster than the usual self-polishing type of tin-free antifouling paint.

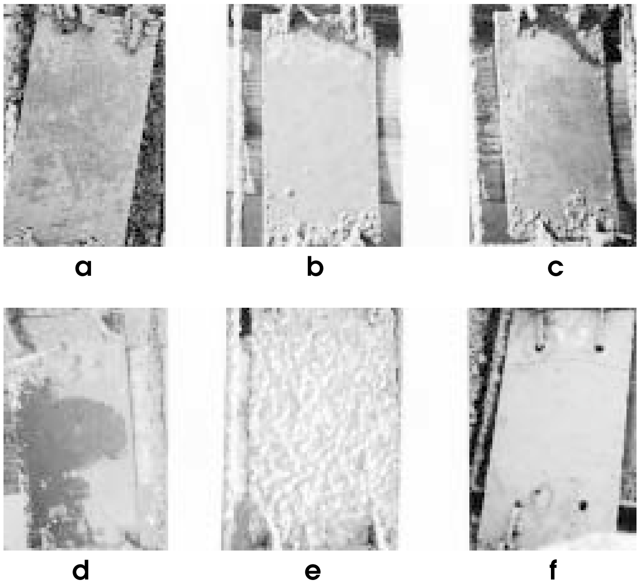

Figure 6—Photographs obtained from a raft test after dipping panels coated with: (a) paint P1, (b) paint P2, (c) paint P3, (d) paint P4, (e) non-antifouling paint PN, and (f) tin-containing antifouling paint PT, over a six-month period.

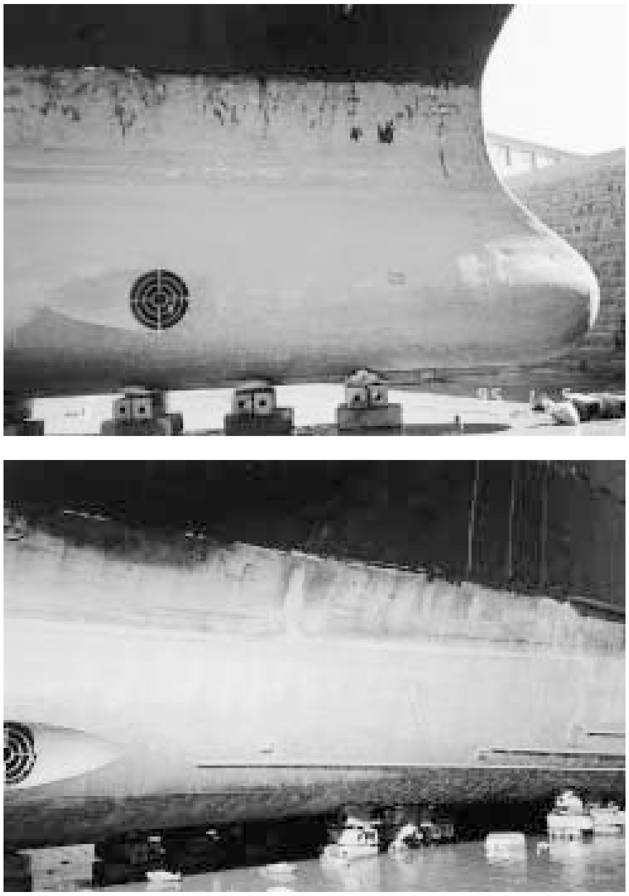

Figure 7—Pictures obtained from the ship test for the Fong Seong No. 727 ship, which had sailed 26 months in the sea around Guam.

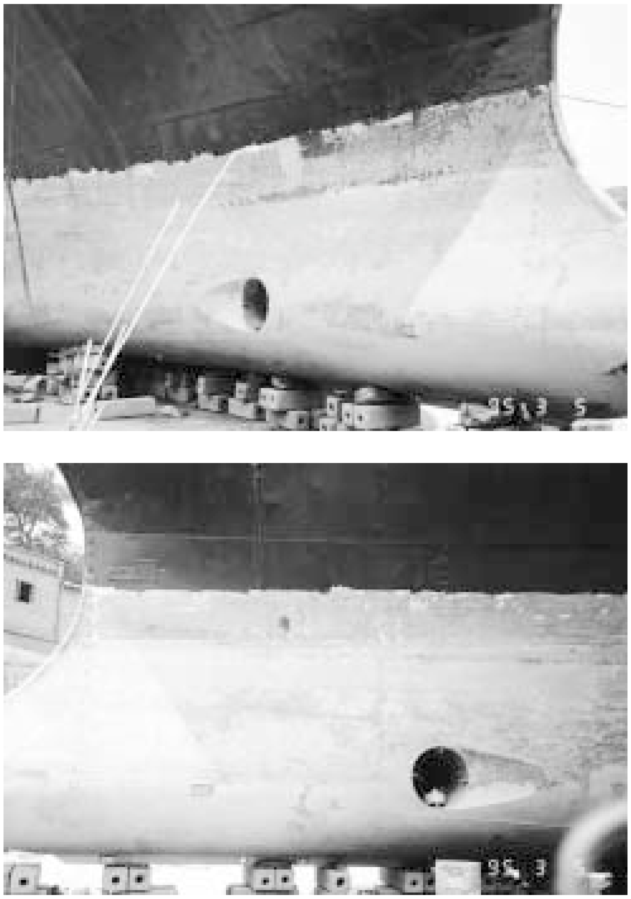

Figure 8—Pictures obtained from the ship test for the Fong Seong No. 747 ship, which had sailed 28 months in the sea around Guam.

For the surface-fragmenting antifouling paints, two special characteristics can be summarized as follows:

(1) The hydrolyzable sites are connected to monomeric molecules; however, the latter become crosslinked in air to form a coating film possessing the required mechanical strength.

(2) The hydrolyzable groups are separated in the polymer backbone over very short distances. Thus, the polymer at the surface in contact with water disintegrates into small pieces after being hydrolyzed as shown in *Scheme* 1.

By the raft tests, the fouling of the test panel surfaces was assessed after immersing the panels over a two-month, four-month, six-month, or nine-month period (*Figure* 6) for P1, P2, P3, and P4 paints, compared with two control panels (conventional tin-type self-polishing antifouling paint, PT, and the non-antifouling paint, PN).

After two months, the paints P1, P2, P3, and PT are free of barnacles with a slight degree of slime, but the area of the panel coated with P4 paint is covered 5% with barnacles. Compared to these paints, the panel coated with PN was full of barnacles even after one month of immersion. After four months, barnacles covered 5, 5, 5, and 10% of the test panels coated with paint P1, P2, P3, and P4, respectively, compared to barnacle coverage of 5% for tin-containing paint PT. After six months, barnacles covered 30, 20, 25, and 15% of the panels coated with paints, P1, P2, P3, and P4, respectively, compared to 10% barnacle coverage for the tin-containing paint PT. After nine months, 90% of the test panel area was contaminated with barnacles for the P1, P2, P3, and P4 paints. Under the same conditions, the PT panel exhibited 80% barnacle coverage. The testing site is warm and close to the area where oysters grow. The testing conditions are severe and accelerate the antifouling phenomena. From *Figure* 6, it can be concluded that the antifouling abilities of tin-free paints P1, P2, P3, and P4 are roughly 80-90% as effective as that of the conventional tin-type of antifouling paints (PT), for which its antifouling ability can last 30 months (with a 150 μ coating) on normal sailing ships.

The sailing speed and the sailing area influences the results of ship tests. Faster sailing speed and the colder weather make it more difficult for the barnacle organisms to become deposited on the ship's hull. The ship tests of this experiment were conducted on two 1,000 ton fishing ships with average sailing speed of 14 knots.

Figure 7 shows the pictures obtained from the ship tests for one ship which had sailed 26 months in the sea area around Guam. For the side painted with P1, no barnacles were found; however, the paint cracked after dry docking. For the other side painted with P4, no barnacles as well as no cracking were found. *Figure* 8 shows the pictures of the other ship which had sailed 28 months in the sea around Guam. For both sides of the hull painted with P2 and with P3, barnacles or other sea life were observed. From the results of the ship tests, it can be concluded that the antifouling abilities of P1, P2, P3, and P4 last at least 26 months in the sea around Guam.

CONCLUSIONS

From the IR and NMR characterization, it is clear R1, R2, R3, and R4 are polymers of metal carboxylates containing unsaturated double bonds. They are cured by reaction of the double bond upon drying in air. SEM photographs from the surface of this new type of tin-free antifouling paint show obvious self-polishing phenomena. From the results of rotary tests, the polishing rates change with the compositions of paint (between 10 μ/month and 5.7 μ/month). The results of raft tests show that all the paints exhibit excellent antifouling ability, and are 80-90% as effective as the conventional tin-containing antifouling paints. From the tests on two fishing ships, no barnacles or other sea life were observed after 26 months.

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