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Extended Control of Marine Fouling

Formulation of a Microencapsulated Liquid Organometallic Biocide and Vinyl Rosin Paint

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ABSTRACT

A process for microencapsulation by complex coacervation, introduced by Green and Schleider in 1957, produced a dry powder form of the liquid biocide tributyltin chloride (TBTCL). Static immersion testing of fiberglass panels painted with the shipbottom paint formulated with 14% w/w TBTCL microcapsules (10–30 μm diam.) gave excellent test results (0% fouling for up to 49 mo) when three coats of this paint were applied to panels. Rationale for the extension of protection against attachment and growth of common marine forms in this formulation are given.

Index Entries: Control, of marine fouling by microencapsulated biocide; marine fouling, control by microencapsulated biocide; fouling, microencapsulated biocide and marine; microencapsulated biocide, control of marine fouling by; biocide, organometallic, and marine fouling; organometallic biocide, control of marine fouling by microencapsulated; vinyl rosin paint, and organometallic biocide; rosin paint, and organometallic biocide; paint, organometallic biocide and vinyl rosin.

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INTRODUCTION

The attachment and growth of free-swimming marine plankton to ship hulls and causes their fouling is a problem of major economic consequence. Shipbottom fouling from surface-attaching marine organisms not only leads to loss of vessel speed and increased fuel consumption, thus causing loss of income, but also results in another important financial burden from the standpoint of lost shipping time as well as the expense incurred for recoating ship bottoms by increasing the frequency of dry docking. Because of this the worldwide demand for a high-performance ship bottom coating is ever increasing. What is needed is a formulation that will perform effectively for years without releasing deleterious levels of biocide into the environment. The modern organometallic antifoulant paint additives seem ideally suited to fill this need. The problem is to find a delivery system whereby a continuous protective surface would be proficed for at least four, and preferably more, years. Our work in the past 6 yr investigated a system that traps tiny reservoirs of concentrated liquid antigoulant in a marine coating. The liquid reservoir in this system is a microcapsule.

Hundreds of processes for the microencapsulation of bioactive agents too numerous to mention have been reported. However, our search did not locate any application of these technologies that encapsulated a liquid biocide for use in an antifoulant shipbottom paint formulation. So that full advantage might be taken of the properties of organometallic antifoulants and microcapsules, we investigated their potential in this area. This research led to the development a process for the microencapsulation of tributyltin chloride (TBTCl) and the formulation of a unique system of ship-bottom coatings (*1*).

THE DEVELOPMENT STAGE

Our first efforts involved attempting to encapsulate tributyltin oxide (TBTO). TBTO proved to be too chemically reactive and thus incompatible with the microencapsulation processes investigated, i.e., simple and complex coacervation (2). Following the suggestion of Mr. C. Beiter, M & T Chemicals, Inc., we next investigated TBTCl because of its chemical characteristics. A favorable combination of parameters allowed the production of a dry powder form of this organometallic liquid.

Microencapsulation of TBTCl follows the process introduced by Green and Schleider (3). The process of complex coacervation proceeds as follows. To gelatin type A and acacia that has been hydrated in a specific volume of water that is mixing at moderate speed at 55°C, we add TBTCl, macroemulsified in water. As the temperature is lowered, the two hydrophilic colloids, both of which are gels at room tempeature and possess an opposite charge at about pH 4.5, form coacervates (thought of as liquid precipitates) around small, microscopic droplets of the water-immiscible TBTCl. The TBTCl slightly hydrolyzes and automatically adjusts the aqueous phase to the correct pH of about 4.5. When cooled to 10°C, the encapsulated TBTCl is washed, and the capsule walls are fixed while mixing in the cold with glutaraldehyde. The fixed wall product is washed and dried to produce the loose powdered form of TBTCl. TBTCl is thus coated with a dry macromolecular membrane ready for use in a suitable coating formulation. Figure 1 shows photomicrographs of microencapsulated TBTCl before and after drying.

Formulation in Paint

Of the few marine base paint formulae investigated, a vinyl/rosin formula (Table 1) has given the best test performance. This formulation, designed for use with tributyltin fluorine was supplied by M&T Chemicals, Inc. with the biocide deleted.

Testing on Panels

Performing testing of TBTCl microcapsules in paint was carried out on 8 × 10 m fiberglass panels that were completely submerged in the fouling waters of Biscayne Bay, Miami Beach, Florida, where complete fouling of unprotected surfaces occurs in less than 3 months. The first test panel series compared the performance of TBTCl microcapsules of three different sizes in vinyl/rosin paint with or without the addition of liquid TBTCl and the liquid form of TBTCl alone. The TBTCl capsules were added at a concentration of 8% w/w and the liquid TBTCl at 7% w/w. These tests indicated the following: the diameter of capsules (range of 50–100, 10–30, or 1–10 μm) made little difference in performance of the tested coating. As expected, two coats of paint gave a better performance than one. The longest a test panel stayed 100% unfouled was 1.5 yr. We also saw that the liquid TBTCl adversely affected the antifouling performance of TBTCl capsules. After this test series, we chose to test only TBTCl capsules of the 10–30 μg size range.

In our next series of tests, we formulated capsules in base paint at a higher concentration. Panels with a single coat, still under test, painted with the vinyl/rosin base paint containing 14% w/w TBTCl microcapsules show a performance rating of 50% after 4.5 yr. We are investigating this higher loading of the base paint with TBTCl microcapsules and painting multiple coats on test panels to see whetehr we can extend the antifouling performance. Panels from these series are also stull under test. Figure 2 shows a comparison of performance of three such panels coated with 1, 2, or 3 coats of vinyl/rosin paint formulated with 14% w/w TBTCl capsules. Panel A with one coat of paint started to foul at less than 1 yr and was completely fouled at 2.5 yr. Panel B with two coats was recorded up to 26 months as unfouled and is now, at 4 yr, rated at 80% performance (5 medium size barnacles, 10% of the 8 × 10 in. surface cov-

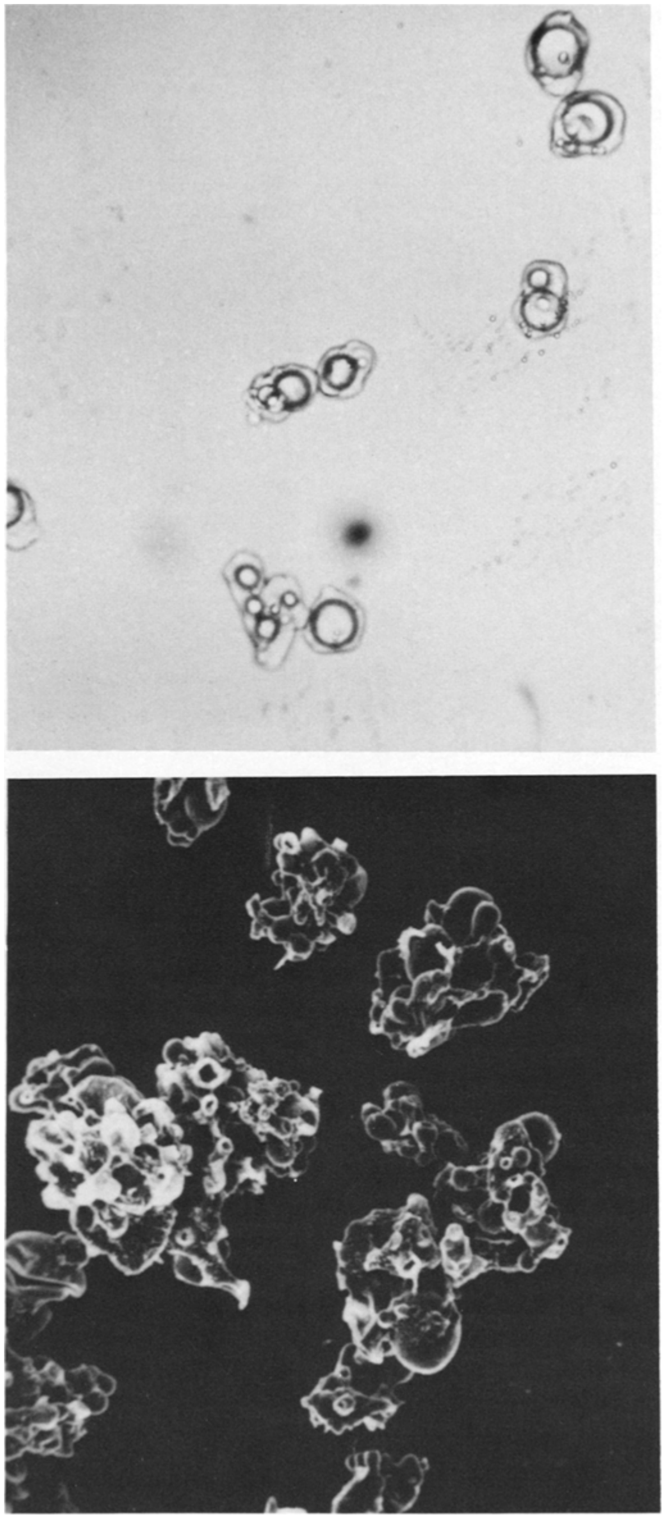

Fig. 1. TBTCl microcapsules: Top, before drying, ×250. Bottom, dry capsules, ×450. Scanning electron micrograph.

TABLE 1
Formula for Vinyl/Rosin Paint

Ingredients	Parts by wt
Red iron oxide	15.12
Talc	11.22
Zinc oxide	7.08
Rosin	3.73
MIBK	13.31
Cyclohexanone	13.00
Xylene	12.84
Bentone 27 } prewet	0.51
Methanol } prewet	0.15
VAGH (Union Carbide)	11.16

ered with encrusting bryozoans). Panel C with three coats of paint was performance rated after 4 yr exposure as 100% unfouled. Figure 3 is a photo of this panel after 40 months immersion. The graph in Fig. 4 demonstrates the adverse effect that adding liquid TBTCl to this paint formulated with 14%, w/w, TBTCl microcapsule had on antifouling performance.

DISCUSSION

The mechanism for prolonged release from encapsulated liquid TBTCl in paint is not clear. The quality of the membrane around these microcapsules cannot be thought of as adequate to effect long-term slow

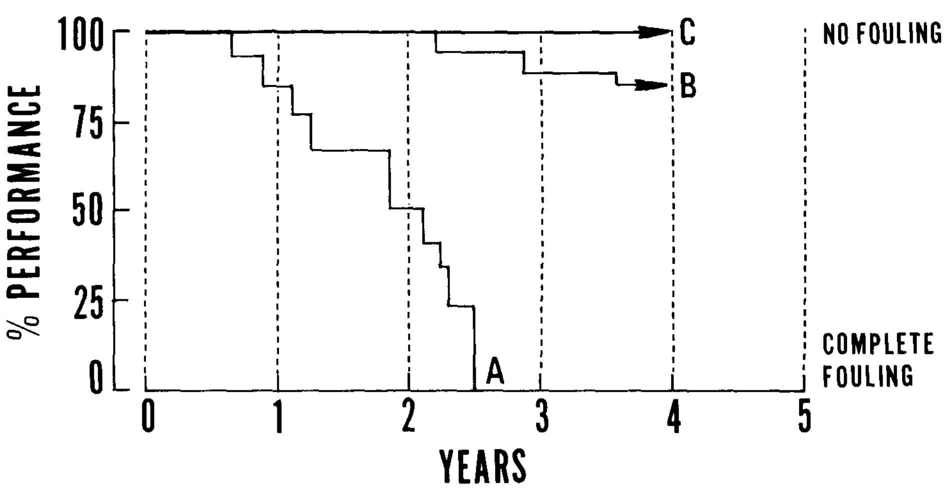

Fig. 2. Comparison of antifouling performance rating of fiberglass panel surfaces coated with vinyl/rosin paint that was formulated with TBTCl microcapsules, 14% w/w. Panel A received one coat, panel B two coats, and panel C three coats.

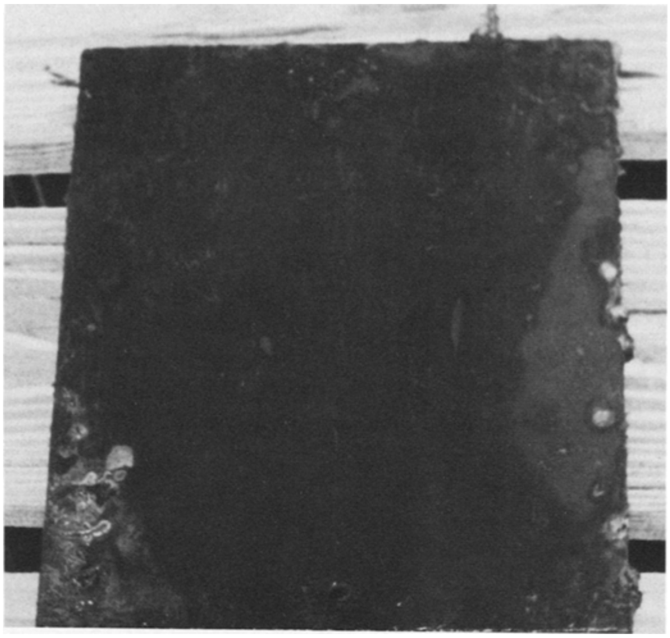

Fig. 3. Photo of test panel C after 40 months immersion in Biscayne Bay, Miami Beach, Florida.

release of the biocide inasmuch as the dried plant, in effect a second encapsulating coating of the liquid, should be, by far, a more stable and impervious material for the prevention of early escape of this bioactive agent from the coating. One theoretical view of how TBTCl microcapsules affects extended protection from fouling is that the mole-

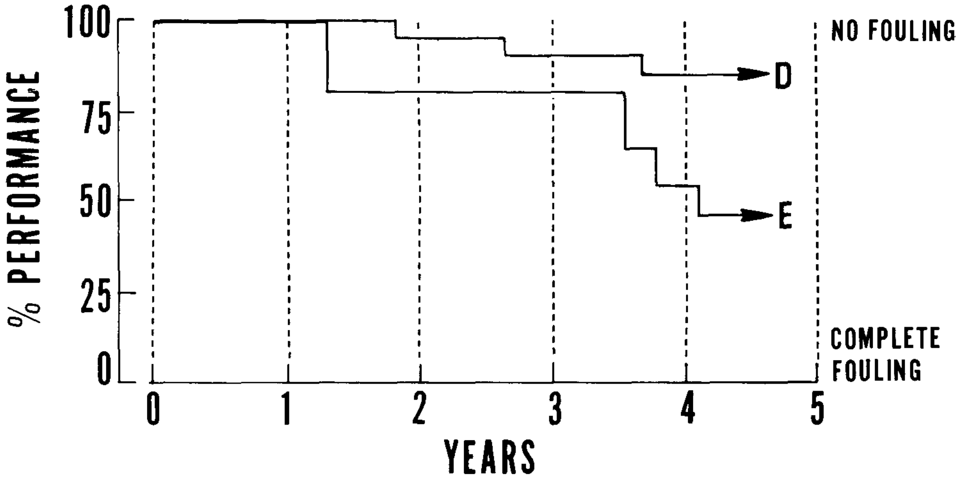

Fig. 4. Comparison of antifouling performance rating of fiberglass panel surfaces painted with two coats vinyl/rosin paint that was formulated with TBTCl microcapsules, 14% w/w. The surface of panel D outperformed panel E. Panel E had in addition to the microcapsules 10% v/v TBTCl liquid.

cules of TBTCl in microcapsules leach out from their entrapped 100% concentration pinpoints in the paint against a much different diffusion gradient than when TBTCl is evenly distributed throughout the matrix of the coating. That is, the release from the paint begins from whatever concentration is optimal, say 10–11% when mixed directly into the formulation as a liquid, but begins to leach from the concentrated stuff in the microcapsule and requires a longer time to reach subtoxic levels at the surface of the paint.

Another theory holds that TBTCl has a modifying effect on its own leach rate from vinyl/rosin paint. Therefore, when the microencapsulated form of TBTCl is used in a paint formulation the coating does not experience as much of the modifier and thus resists the loss of the biocide. Microencapsulation may also allow for a more optimal loading of this liquid antifouling agent in marine paint formulations. The mechanism for sustained release is not clear but the extended performance is.

ACKNOWLEDGMENT

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