Designation: D5108 – 90 (Reapproved 2007)

Standard Test Method for Organotin Release Rates of Antifouling Coating Systems in Sea Water[1]

This standard is issued under the fixed designation D5108; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the laboratory determination of the rate at which organotin expressed as tributyltin (TBT) is released from an antifouling (AF) coating in synthetic sea water using graphite furnace atomic absorption spectrophotometry (GF-AAS). This does not exclude the use of other analytical methodology for measurement of organotin in sea water such as gas chromatography.

1.2 The values stated in SI units are to be regarded as standard. The inch-pound units given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1141 Practice for the Preparation of Substitute Ocean Water

D1212 Test Methods for Measurement of Wet Film Thickness of Organic Coatings

D4138 Practices for Measurement of Dry Film Thickness of Protective Coating Systems by Destructive, Cross-Sectioning Means

3. Summary of Test Method

3.1 The candidate paint system is applied to cylindrical test specimens. The coated specimens are placed in a tank of synthetic sea water where the tin levels are kept low by circulating the sea water through a carbon filter. At specified intervals, each specimen is placed in 1500 mL of unused sea water and is rotated for 1 h. The rate of tributyltin release from the paint is determined by measuring tributyltin concentrations in the sea water.

3.2 Analysis of sea water for tributyltin is conducted by extracting the organotin with toluene, washing with sodium hydroxide, and measuring for total tin using (GF-AAS).

4. Significance and Use

4.1 This test method is designed to provide a laboratory procedure to measure changes in the release rates of solvent soluble tin (tributyl- and triphenyltin) that occur during a period of immersion under specified conditions of constant temperature, pH, salinity, and low heavy-metal concentrations in the surrounding sea water. Quantitative measurement of the release rate is necessary to help in selection of materials, in providing quality assurance, and in understanding the performance mechanism.

4.2 This test method serves only as a guide for organotin release rates in service. Organotin release rates of antifouling (AF) paint systems in service can vary over the life of the coating system depending on the formulation and the environment. Differences in berthing locations, operating schedules, length of service, condition of paint-film surface, temperature, pH, and salinity can affect results, Results obtained may not necessarily reflect actual tributyltin release rates that will occur in service, but provide reliable comparisons of the release rate characteristics of different antifouling formulations.

4.3 This test method will serve to characterize the early release rate pattern, as well as estimate the steady state release, of tributyltin from both self-polishing copolymer and free-association antifouling paints.

5. Apparatus

5.1 *Release-Rate Measuring Container*—A 2-L (nominal ½ gal) polycarbonate container,[3] approximately 13.5 cm (5.5 in.)

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[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.45 on Marine Coatings.

Current edition approved June 1, 2007. Published August 2007. Originally approved in 1990. Last previous edition approved in 2002 as D5108 - 90 (2002). DOI: 10.1520/D5108-90R07.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] A Nalgene Container, available from Cole-Palmer, 7425 N. Oak Ave., Chicago, IL 60648, catalog number R-6761-20, or equivalent, has been found satisfactory for this purpose.

in diameter and 19 cm (7.5 in.) high, fitted with three polycarbonate rods approximately 6 mm (nominal 1/4 in.) in diameter to serve as baffles. Rods shall be evenly spaced on the inside circumference of the container to prevent swirling of water with the test cylinder during rotation. The rods will be secured to the container walls using acetone or methylene chloride.

5.2 *Constant Temperature Bath*—A temperature controlled water bath capable of maintaining a temperature of 25 ± 2°C into which one or more release rate measuring test containers can be placed.[4]

5.3 *Holding Tank*—A container of such dimensions so as to permit immersion of four or more test cylinders; must be equipped with a system to continuously circulate synthetic sea water in the tank through a carbon filter. The rate of water flow and the size of the carbon filter should be selected to maintain tributyltin concentrations below 100 µg/L. Flow rates should generally be set to obtain 2 to 8 turnovers per h. The size and geometry of the tanks as well as the positioning of the inflow and outflow ports for the water circulation system should be selected to obtain a slow, relatively uniform flow of synthetic sea water past all test cylinders in the tank. Maintain the pH of the synthetic sea water between 7.8 and 8.2, and the salinity between 30 and 35 parts per thousand (ppt). The tank shall be provided with heaters to maintain the temperature between 21 and 27°C (70 and 81°F).

5.4 *Test Cylinders*—Approximately 6.4 cm (nominal 2 ½ in.) outside diameter polycarbonate pipe coated with a 10-cm band of AF paint around the exterior circumference of the test cylinder to provide 200 cm^2 of paint film that can be immersed and freely rotated in the release rate measuring container. Seal the bottom of the test cylinder with a polycarbonate disc using acetone, methylene chloride, or a polycarbonate cement so as to form a watertight joint. Do not coat the bottom 1 to 2 cm of the test cylinder. The test cylinder shall be of such height so that a rotating device can be attached to rotate the cylinder and the upper open end of the cylinder is above the level of the test container immersion liquid to prevent entry of the immersion liquid into the test cylinder.

5.5 *Test Cylinder Rotating Device*—The device shall be capable of rotating the test cylinder in the release rate measuring container at 60 ± 5 r/min. No part of the device shall be immersed in sea water.[5]

5.6 *Centrifuge Tubes,* 50-mL capacity, with screw closures[6] (or disposable bottles, culture tubes, separatory funnels, etc.) made of polycarbonate, TFE flourocarbon, or borosilicate glass.

5.7 *Mechanical Shaker,* with appropriate holders.

5.8 *Dispensers,* automatic or repeating, for reagents.

5.9 *Pipets,* with disposable polypropylene tips.

5.10 *Graphite Furnace,* atomic absorption spectrophotometer (GF-AAS) with automatic sampler.

5.11 *pH Meter,* with a mercury/mercurous chloride (Hg/Hg_2Cl_2) electrode.

5.12 *Appropriate Volumetric Flasks.*

6. Reagents and Materials

6.1 *Synthetic Sea Water*—Substitute ocean water in accordance with the Preparation of Substitute Ocean Water section of Practice D1141 or a proprietary equivalent with a salinity of 30 to 35 ppt.

6.2 *Extraction Solvent*—Toluene, spectrograde or equivalent.

6.3 *Tributyltin Standards*—Prepare standards using a stock solution of tributyltin chloride (reagent grade, minimum 96 % pure) in methanol (suggested concentration of approximately 10 mg/L). The standards are acidified with acetic acid (less than pH 4) to obtain a stable solution.

6.4 *Hydrochloric Acid* (HCl) (10 % aqueous solution).

6.5 *Hydrochloric Acid* (HCl) (0.1N).

6.6 *Nitric Acid* (HNO_3) (10 % aqueous solution) can be used in place of HCl to clean labware.

6.7 *Sodium Hydroxide* (NaOH) (3 % aqueous solution).

6.8 *Sodium Hydroxide* (NaOH) (0.1N).

6.9 All reagents and cleaning agents used must be tin-free.

7. Hazards

7.1 **Warning**—Antifouling paints contain toxic materials that could cause skin and eye irritation on contact and adverse physiological effects if ingested or inhaled. In the preparation of test specimens and the application of various types of paints, the use of appropriate protective clothing and equipment is required consistent with local, state, and federal government regulations, and recognized industrial and technical standards. Do not flush spills, overspray, and unused material down the drain, but should be dispose of as hazardous waste.

7.2 See antifouling paint supplier's Material Safety Data Sheet.

8. Calibration and Standardization

8.1 Prepare three standards throughout the range of the quantification limit to 100 µg of tin per litre by dilution in toluene of a stock solution of tributyltin chloride (96 % pure) in methanol. Include one standard with a concentration of approximately 50 µg of tin per litre. An alternate range of concentrations may be used when appropriate.

8.2 Prepare synthetic sea water spiked with three concentrations of TBT in the range of 10 to 50 µg of tin per litre by spiking with stock solution of tributyltin chloride in methanol. When the concentration of tin extracted in toluene exceeds 100 µg/L appropriate dilution should be employed to keep it within the limits of the calibration curve (0 to 100 µ g/L).

[4] Boekel Water Baths, Models 148003 and 148004 available from Boekel Industries Inc., 509-T Vine St., Philadelphia, PA 19106, or equivalent, have been found satisfactory for this purpose.

[5] A six-paddle stirrer, Model 300, manufactured by Whitaker Medical Mfg. Co., Phipps and Bird Div., 8741 Landmark Rd., Richmond, VA 23228, or equivalent, has been found satisfactory for this purpose.

[6] Oak Ridge Tubes, available from Cole-Parmer, or equivalent, have been found satisfactory for this purpose.