[redacted]United

3,795,741

Patented Mar. 5, 1974

1

2

3,795,741

MARINE ANTIFOULANT COMPOSITIONS EMPLOYING CERTAIN ORGANOTIN COMPOUNDS

Pasquale Paul Minieri, Woodside, N.Y., assignor to Tenneco Chemicals, Inc.

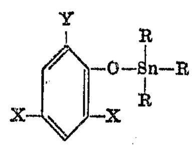
No Drawing. Continuation-in-part of application Ser. No. 3,233, Jan. 15, 1970, which is a continuation-in-part of application Ser. No. 708,782, Feb. 28, 1968, both now abandoned. This application Mar. 6, 1972, Ser. No. 232,194

Int. Cl. A01n 9/00

U.S. Cl. 424—288 14 Claims

ABSTRACT OF THE DISCLOSURE

Marine antifoulant compositions comprise an organic water-resistant film-forming vehicle and an organotin compound that has the structural formula



wherein each R represents an alkyl group having from 4 to 8 carbon atoms or a phenyl group; one of the X substituents represents phenyl or menthyl; the other X substituent represents hydrogen, halogen, nitro, or an alkyl group having from 1 to 4 carbon atoms; and Y represents hydrogen, halogen, or nitro. Particularly satisfactory results have been obtained using an acrylic ester resin as the vehicle and triphenyl (2,4-dichloro-6-phenylphenoxy)tin or triphenyl (2,4-dinitro-6-phenylphenoxy)tin as the antifouling agent.

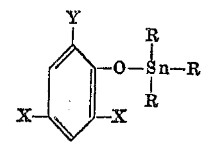
This is a continuation-in-part of my copending patent application Serial Number 3,233, which was filed on Jan. 15, 1970 which has been abandoned, and which is a continuation-in-part of my patent application Ser. No. 708,782, which was filed on Feb. 28, 1968 and which has been abandoned.

This invention relates to marine antifoulant compositions and to their use in the protection of ship and boat bottoms, wharves, docks, pilings, and the like from attack by marine organisms that have a deteriorative effect on such objects. More particularly, it relates to marine antifoulant compositions that contain as their active ingredient certain toxic organotin compounds and to the use of these compositions in the control of marine organisms, fungi, and bacteria.

In the past metal salts and metal oxides, such as copper naphthenate, copper acrylate, zinc naphthenate, mercury oxides, and the like, have been used in marine antifoulant paints and other antifouling compositions. These materials have not been entirely satisfactory in this application because they are not sufficiently active against the undesirable marine organisms, because they cause electrolytic corrosion of the substrate, because they are toxic to fish and other desirable marine life, or because they are expensive to use.

In accordance with this invention, it has been found that certain organotin compounds have unusual and valuable activity as marine antifouling agents. These compounds, which are highly effective in preventing marine fouling of a variety of surfaces, have a long-lasting antifouling effect and are toxic to a wide variety of undesirable marine organisms, but as used they have negligible toxicity to desirable marine life and to human beings.

These organotin compounds have the structure formula



wherein each R represents an alkyl group having from 4 to 8 carbon atoms or a phenyl groups; one of the X substituents represents a phenyl group or a methyl group; the other X substituent represents hydrogen, an alkyl group having from 1 to 4 carbon atoms, a halogen atom, or a nitro group; and Y represents a hydrogen atom, a halogen atom, or a nitro group. Illustrative of these compounds are the following:

tri-n-butyl(2-phenyl-4-chlorophenoxy)tin;
tri-n-butyl(2,4-dichloro-6-phenylphenoxy)tin;
tri-n-butyl(2,4-dinitro-6-phenylphenoxy)tin;
tri-n-butyl(4-methylphenoxy)tin;
tri-n-butyl(2-methyl-4-menthylphenoxy)tin;
trioctyl(2,4-dichloro-6-phenylphenoxy)tin;
triphenyl(2-phenyl-4-chlorophenoxy)tin;
triphenyl(2,4-dichloro-6-phenylphenoxy)tin;
triphenyl(2,4-dinitro-6-phenylphenoxy)tin;
triphenyl(4-menthylphenoxy)tin;
triphenyl(2-methyl-4-menthylphenoxy)tin;
triphenyl(2-bromo-6-menthylphenoxy)tin;

and the like. One of these organotin compounds or a mixture of two or more of them may be used in the marine antifouling compositions of this invention.

The organotin compounds may be prepared by any suitable and convenient procedure. For example, they may be prepared by the reaction of a substituted phenol with triphenyl tin hydroxide or a trialkyl tin hydroxide in a hydrocarbon or ketone solvent or by the reaction of an alkali metal salt of a substituted phenol with triphenyl tin chloride or a trialkyl tin chloride in a suitable solvent. The preparation and properties of these compounds are described in detail in U.S. Pat. No. 3,524,869.

The organotin compounds are usually applied to the surface that is to be protected against attack by fouling organisms as compositions that comprise an organic water-resistant film-forming vehicle and an amount of the active material that will accomplish the desired protective result. In most cases from about 1 pound to 10 pounds, and preferably 0.5 pound to 3 pounds, of the organotin compound is used per gallon of the composition. In addition the compositions may contain pigments, fillers, solvents, stabilizers, auxiliary antifouling agents, and other additives in the amounts ordinarily employed for these purposes.

Any of the organic water-resistant film-forming vehicles that are commonly used in marine coatings may be used in the marine antifoulant compositions of this invention. These include, for example, polyvinyl chloride; vinyl chloride copolymers with vinyl acetate, vinyl propionate, vinyl butyrate, styrene, methyl methacrylate, and dimethyl maleate that contain about 70 percent to 95 percent of vinyl chloride; polyvinyl acetals; polyesters; alkyl resins; chlorinated rubber; phenol-formaldehyde resins; urea-formaldehyde resins; polyurethane; acrylic ester resins and methacrylic ester resins; epoxy resins; oleoresinous varnishes; and the like. Especially satisfactory results have been obtained using the following organic water-resistant film-forming vehicles:

(a) Ethyl acrylate-methyl methacrylate copolymers having viscosities in the range of about 250 to 335 centipoises at 30° C.;
(b) Mixtures containing 50 percent to 90 percent by weight of rosin and 10 percent to 50 percent by weight of a vinyl chloride vinyl acetate copolymer containing 70 percent to 95 percent of vinyl chloride;
(c) Linseed oil-modified glyceryl phthalate alkyd resins;
(d) Polyvinyl butyral;
(e) Epoxy resins prepared by the condensation of epichlorhydrin and bis-phenols; and
(f) Styrene-butadiene polymers containing 30 percent to 70 percent of styrene.

Polymers having molecular weights in the range of about 400 to 1,000,000 can be used as the film-forming vehicle in the compositions of this invention. For each of the aforementioned types of polymers, the preferred molecular weight range is that at which its solubility, viscosity, tensile strength, flexibility, and other properties are most satisfactory for use in surface-coating compositions. The molecular weights of alkyd resins, polyesters, oleoresinous varnishes, and epoxy resins are preferably between about 400 and 5,000. For vinyl halide homopolymers and copolymers, styrene homopolymers and copolymers, acrylic and methacrylic ester resins, polyurethane, phenol-formaldehyde resins, and urea-formaldehyde resins, the preferred molecular weights are between about 20,000 and 250,000.

The organotin compounds may be incorporated into the marine antifoulant compositions by any suitable procedure. For example, a solution of the organotin compound in toluene or xylene may be added to the vehicle, or the compound per se may be added to the vehicle and other ingredients of the composition.

In another embodiment of the invention, the organotin compound is dissolved in an organic solvent that is preferably a hydrocarbon or ketone, such as toluene, xylene, acetone, methyl isobutyl ketone, or petroleum spirits, and the resulting composition is used to impregnate textiles, rope, wood, leather, paper, and the like. Materials treated in this way are resistant to attack by marine organisms, fungi, and bacteria, particularly in outdoor uses where the surfaces are exposed to a significant degree to water.

This invention is further illustrated by the examples that follow.

EXAMPLE 1

Triphenyl(2,4-dichloro-6-phenylphenoxy)tin was tested against a number of marine organisms by the procedure described by Miller in "Industrial and Engineering Chemistry Product Research and Development," 3 (3), 226–230 (1964). In this test porous carbon plates impregnated with the test compound are immersed vertically in the sea from a pier. Test specimens are removed periodically and the types of organisms attached to the test surfaces are noted. For comparative purposes, plates impregnated with tin oxide, a commercial anti-fouling agent, were included in the tests.

The data obtained are summarized in Table I.

From the data in Table I, it will be seen that some of the test plates treated with triphenyl(2,4-dichloro-6-phenyl-phenoxy)tin were not completely covered by fouling organisms after 18 months' exposure in the sea, whereas all of those treated with the commercial antifouling agent, tributyl tin oxide, had failed after 2 months' immersion.

TABLE I

[Triphenyl(2,4-dichloro-6-pehnylphenoxy)tin as a marine antifoulant]

Months immersed	Test compound	Amount compound in plate (grams)	Fouling on surface[1]								
			1	2	3	4	5	6	7	8	9
1	Triphenyl(2,4-dichloro-6-phenylphenoxy)tin.	0.133	0	0	0	0	0	0	0	0	0
		0.023	0	0	0	0	0	0	0	0	0
	Tributyl tin oxide	0.097	0	0	0	0	1	0	0	0	0
		0.020	0	0	2	0	10	0	0	0	0
	None		Completely fouled								
2	Triphenyl(2,4-dichloro-6-phenylphenoxy)tin.	0.133	0	0	5	0	0	0	0	0	0
		0.023	0	0	2	0	0	0	0	0	0
	Tributyl tin oxide	0.097	More than 50% fouled; test discontinued								
		0.020	More than 50% fouled; test discontinued								
3	Triphenyl(2,4-dichloro-6-phenylphenoxy)tin.	0.133	0	0	7	0	0	0	0	0	0
		0.023	0	0	5	0	2	0	0	0	0
4	do	0.133	0	0	0	0	0	0	0	0	0
		0.023	1	0	0	0	0	0	0	0	0
5	do	0.133	0	0	20	0	0	0	0	0	0
		0.023	2	0	20	0	0	0	0	0	0
6	do	0.133	0	0	70	0	0	0	0	0	0
		0.023	More than 50% fouled; test discontinued								
7	do	0.133	0	0	70	0	0	0	0	5	0
8	do	0.133	0	0	70	0	0	0	0	5	0
18	do	0.133	0	0	75	0	0	0	0	5	0

[1] Percent of surfaces covered by organisms: (1) Branacles, (2) Encrusting bryozoans, (3) Algae, (4) Bugula, (5) Hydroids, (6) Oysters, (7) Tube worms, (8) Tunicates, (9) Slime forming microorganisms.

EXAMPLE 2

Using the procedure described in Example 1, the effectiveness of a number of organotin derivatives of substituted phenols as marine antifoulants was determined. In each case the number of months that the treated carbon plates were immersed in sea water before more than 50 percent of the surfaces of the plates was covered with marine growth was noted. The compounds tested and the results of the test are summarized in Table II.

From the data in Table II it will be seen that each of the compounds of this invention was at least as effective as a marine antifouling agent as tributyl tin oxide.

TABLE II

[Evaluation of organotin derivatives of substituted phenols as marine antifoulants]

Test compound	Amount compound in plate (grams)	Immersion time (months) before 50% fouling
Triphenyl(2-phenyl-4-chlorophenoxy)tin	0.0118	2
	0.0377	5
Triphenyl(2,4-dinitro-6-phenylphenoxy)tin	0.0236	5
	0.0545	8
Triphenyl(4-menthylphenoxy)tin	0.0111	2
	0.0362	4
Triphenyl(2-methyl-4-menthylphenoxy)tin	0.0124	2
	0.0375	4
Tributyl(2,4-dichloro-6-phenylphenoxy)tin	0.020	3
	0.189	4
Tributyl(2-methyl-4-menthylphenoxy)tin	0.033	2
	0.103	2
Tributyl tin oxide	0.020	2
	0.097	2

EXAMPLE 3

To a paint prepared by mixing together the following materials:

	Pounds per gallon of paint
Titanium dioxide	1.43
Aluminum silicate	0.45
Magnesium silicate	0.98
Ethyl acrylate-methyl methacrylate copolymer (viscosity—285 cp. at 30°C.; Gardner-Holdt viscosity—L)	3.85
Ethylene glycol monoethyl ether	2.59

was added 1.00 pound per gallon of paint of triphenyl (2,4-dichloro-6-phenylphenoxy)tin. The resulting composition had a viscosity of 60 Krebs units.

The paint was applied to 8" x 10" fiberglass test panels. The fronts and backs of the panels were utilized to provide duplicate test surfaces. For comparative purposes, panels were also painted with a proprietary yacht bottom paint that contained tri-n-butyl tin oxide as its antifouling agent. The painted panels were immersed in the ocean near Miami, Fla.

The condition of the panels after 6 and 7 months' immersion is summarized in Table III.

TABLE III

[Evaluation of acrylic ester paint containing marine antifoulants]

Antifouling agent	Period of immersion	Test surface	Physical condition of paint	Percent	
				Fouling on surface	Fouling resistance [1]
Triphenyl(2,4-dichloro-6-phenylphenoxy) tin	6 months	Front	Good	None	100
		Back	do	None	100
	7 months	Front	do	[2] 7	93
		Back	do	[2] 7	93
Tributyl tin oxide	6 months	Front	do	[3] 9	91
		Back	do	[3] 12	88
	7 months	Front	do	[3] 25	75
		Back	do	[3] 28	72

[1] Ratings are determined by subtracting percent fouling on surface from 100%.
[2] Green algae.
[3] Barnacles and green algae.

From the data in Table III it will be seen that the panels containing triphenyl(2,4 - dichloro-6 - phenyl - phenoxy)tin as the antifouling agent had undergone less fouling in 7 months' immersion in the ocean than those containing tributyl tin oxide as the antifouling agent had undergone in 6 months' immersion.

EXAMPLE 4

A paint was prepared by mixing together the following materials:

	Pounds per gallon of paint
Titanium dioxide	2.00
Magnesium silicate	0.60
Vinyl chloride-vinyl acetate copolymer (91% vinyl chloride)	1.00
Rosin	1.00
Toluene	2.00
Methyl Isobutyl ketone	2.50
Antifoulant [1]	0.90

[1] Either tributyl(2,4-dichloro-6-phenylphenoxy)tin or tributyl tin oxide.

The paint was applied to 8" x 10" fiberglass test panels, and the painted panels were immersed in the ocean near Miami, Florida.

The conditions of the panels after 3 months' immersion is summarized in Table IV.

TABLE IV

[Evaluation of vinyl copolymer-rosin paints containing marine antifoulants]

Antifouling agent	Physical condition of paint	Percent	
		Fouling on surface	Fouling resistance
Tributyl(2,4-dichloro-6-phenylphenoxy) tin.	Good	19	81
Tributyl tin oxide	do	28	72

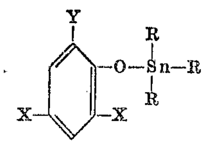
Each of the other substituted phenoxy tin compounds disclosed herein can be used in a similar way to impart

resistance to attack by marine organisms to materials susceptible to such attack.

The terms and expressions which have been employed are used as tems of description and not of limitation. There is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof; it is recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. A marine antifouling composition comprising an organic water-resistant film-forming marine-coating vehicle and an antifouling amount of from about 0.1 pound to 10 pounds per gallon of said composition of an organotin compound having the structural formula



wherein each R represents phenyl or an alkyl group having from 4 to 8 carbon atoms; one of the X substituents represents phenyl or menthyl; the other X substituent represents hydrogen, halogen, nitro, or an alkyl group having from 1 to 4 carbon atoms; and Y represents hydrogen, halogen, or nitro.

2. A marine antifouling composition as set forth in claim 1 that contains 0.5 pound to 3 pounds of the organotin compound per gallon of said composition.

3. A marine antifouling composition as set forth in claim 1 wherein the organotin compound is triphenyl-(2,4-dichloro-6-phenylphenoxy)tin.

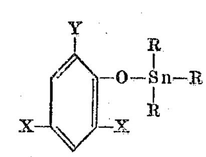
4. A marine antifouling composition as set forth in claim 1 wherein the organotin compound is triphenyl-(2,4-dinitro-6-phenylphenoxy)tin.

5. A marine antifouling composition as set forth in claim 1 wherein the organotin compound is tributyl(2,4-dichloro-6-phenylphenoxy)tin.

6. A marine antifouling composition as set forth in claim 1 wherein the organotin compound is triphenyl(4-menthyl-phenoxy)tin.

7. A marine antifouling composition as set forth in claim 1 wherein the organotin compound is triphenyl(2-methyl-4-menthylphenoxy)tin.

8. A process for inhibiting the fouling of surfaces exposed to undesirable marine organisms which comprises applying to said surfaces a biocidal composition comprising an organic water-resistant film-forming marine-coating vehicle and an antifouling amount of from about 0.1 pound to 10 pounds per gallon of said composition of an organotin compound having the structural formula



wherein each R represents phenyl or an alkyl group having from 4 to 8 carbon atoms; one of the X substituents represents phenyl or menthyl; the other X substituent represents hydrogen, halogen, nitro, or an alkyl group having from 1 to 4 carbon atoms; and Y represents hydrogen, halogen, or nitro.

9. The process of claim 8 wherein the biocidal composition contain 0.5 pound to 3 pounds of the organotin compound per gallon of said composition.

10. The process of claim 8 wherein the organotin compound is triphenyl(2,4-dichloro-6-phenylphenoxy)tin.

11. The process of claim 8 wherein the organotin compound is triphenyl(2,4-dinitro-6-phenylphenoxy)tin.

12. The process of claim 8 wherein the organotin compound is tributyl(2,4-dichloro-6-phenylphenoxy)tin.

13. The process of claim 8 wherein the organotin compound is triphenyl(2-methyl-4-menthylphenoxy)tin.

14. The process of claim 8 wherein the organotin compound is triphenyl(4-menthylphenoxy)tin.

References Cited

UNITED STATES PATENTS

3,321,365	5/1962	Menn et al.	424—288
2,970,923	2/1961	Sparmann	106—15
3,524,869	8/1970	Minieri	424—288

ALBERT T. MEYERS, Primary Examiner

V. D. TURNER, Assistant Examiner

U.S. Cl. X.R.

106—15 AF; 117—138.5; 260—429.7