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ORGANOTIN SALTS OF MONOALKYL ALKENYLSUCCINATES

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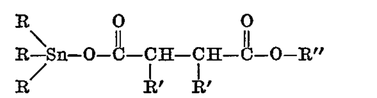
U.S. Cl. 260—429.7 7 Claims

ABSTRACT OF THE DISCLOSURE

Organotin compounds that have the structural formula



wherein each R represents phenyl or an alkyl group having from 4 to 12 carbon atoms; one R′ represents an alkenyl group having from 8 to 22 carbon atoms; the other R′ represents hydrogen; and R″ represents an alkyl group having from 1 to 16 carbon atoms are used to protect surface-coating compositions from attack by microorganisms. Among the most effective of these biocidal compounds is (tri-n-butyltin)-n-butyldodecenylsuccinate.

This invention relates to novel biocidal compounds and to their use in the control of the growth of fungi, bacteria, and other microorganisms. More particularly, it relates to organotin salts of monoalkyl alkenylsuccinates and to surface-coating compositions containing these compounds that have improved resistance to deterioration resulting from attack by microorganisms.

It is well known in the art that paints and varnishes often have inadequate resistance to the action of microorganisms. Some of these coating compositions, such as enamels and house paints, contain as their resinous binders drying oils, oleoresinous varnishes, or alkyd resins, which are subject to attack by fungi and bacteria. Others, for example, aqueous dispersions of water-insoluble synthetic linear polymers, generally contain as plasticizers and thickeners materials that have their origin in animal or vegetable sources and that render the compositions susceptible to mildew. The resulting deterioration of the surface-coating compositions seriously hinders their full scale utilization, particularly in those areas and in those applications that are conducive to such attack.

Various biocidal materials have been suggested for use in surface-coating compositions, but none have been suggested for use in surface-coating compositions, but none has proven entirely satisfactory in this application. Some do not provide the required prolonged protection against attack by microorganisms, while others undergo sulfide staining and still others hydrolyze in alkaline aqueous paint systems or separate from the applied coating by migration, volatilization, or leaching once the coating has been spread in a thin layer over the surface to be protected.

This invention relates to biocides that are of particular value in surface-coating compositions. These biocides, which are thoroughly compatible with the resinous binders that commonly are used in surface-coating compositions and which are resistant to sulfide staining, provide excellent and prolonged resistance to deterioration resulting from attack by fungi and other microorganisms without adversely affecting the color, pH, viscosity, and other physical properties of the surface-coating compositions.

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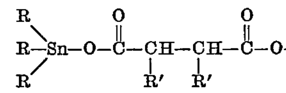
The biocidal compounds of this invention are organotin salts of monoalkyl alkenylsuccinates. These compounds may be represented by the structural formula



wherein each R represents phenyl or an alkyl group having from 4 to 12 carbon atoms; one R′ represents a straight-chain or branched-chain alkenyl group having from 8 to 22 carbon atoms; the other R′ represents hydrogen; and R″ represents an alkyl group having from 1 to 16 carbon atoms. Illustrative of these compounds are the following:

(tri-n-butyltin)-methyl-n-octenylsuccinate,
(tri-n-butyltin)-n-hexyldodecenylsuccinate,
(tri-n-hexyltin)-n-octyl-n-octadecenylsuccinate,
(tri-n-octyltin)-n-decyl-n-dodecenylsuccinate,
(tridodecyltin)-isooctyleicosenylsuccinate,
(triphenyltin)-hexadecylisododecenylsuccinate,

and the like. A single organotin salt of a monoalkyl alkenylsuccinate or a mixture of two or more of these compounds may be present in the surface-coating compositions of this invention. Particularly advantageous results have been obtained using tri-n-butyltin salts of monoalkyl alkenylsuccinates.

In addition to being useful in the preservation of surface-coating compositions, the organotin compounds of this invention can also be used as agricultural fungicides because they can be applied to plants, to plant seeds, or to the soil in which plants are growing to control the growth of a number of plant pathogens.

The organotin salts of monoalkyl alkenylsuccinates may be prepared by any suitable and convenient procedure. For example, they may be prepared by the reaction of a trialkyltin oxide with the appropriate monoalkyl ester of an alkenylsuccinic acid.

The organotin compounds of this invention can be used to impart fungal and bacterial resistance to a wide variety of surface-coating compositions including both organic solvent-based and water-based coating systems. They are particularly valuable as biocides in water-based coatings that contain as their resinous binder a water-insoluble synthetic linear addition polymer.

In a preferred embodiment of the invention, the novel organotin compounds are used in aqueous dispersions that contain about 10 percent to 60 percent by weight of a water-insoluble resinous binder that is an oleoresinous binder or a synthetic linear addition binder. Suitable oleoresinous binders include drying oils, such as linseed oil, tung oil, soybean oil, dehydrated castor oil, safflower oil, or fish oil; bodied drying oils; blends of drying oils or bodied drying oils with a resin component, such as limed rosin, an ester gum, or a phenolic resin; oleoresinous varnishes formed by heating one of the afore-mentioned resins with one or more drying oils or bodied drying oils; and alkyd resins, which are resinous products resulting from the reaction of a polyhydric alcohol, such as pentaerythritol or glycerol, with a dicarboylic acid, such as phthalic anhydride, and fatty acids.

The useful aqueous dispersions of synthetic linear addition polymers are ordinarily prepared by the emulsion polymerization of ethylenically unsaturated compounds, especially those of monoethylenically unsaturated character, although butadiene, chlorobutadiene, and isoprene may be used to some extent. Illustrative of the synthetic linear addition polymers that can be used as the resinous binder in the aqueous dispersions are polyvinyl acetate; polyvinyl butyrate; polyvinyl chloride; copolymers of vinyl acetate with vinyl chloride; copolymers of vinyl acetate with acrylonitrile; copolymers of vinyl chloride with acrylonitrile; copolymers of vinyl chloride with vinylidene chloride; polyethylene; polyisobutylene; polystyrene; copolymers of styrene with butadiene; copolymers of acrylonitrile with butadiene; copolymers of methacrylic acids esters of alcohols having 1 to 8 carbon atoms with vinyl acetate; vinyl chloride, acrylonitrile, or styrene; copolymers of acrylic acid esters of alcohols having 1 to 8 carbon atoms with vinyl acetate, vinyl chloride, acrylonitrile, or styrene; copolymers of the aforementioned acrylic acid esters, the aforementioned methacrylic acid esters, and acrylic acid; and copolymers of styrene with maleic anhydride.

In another preferred embodiment of the invention, an organotin salt of a monoalkyl alkenylsuccinate is used as the biocide in a solvent-based system that contains an oleoresinous binder as hereinbefore defined.

Only a small concentration of the organotin compound need be present in the surface-coating compositions of this invention. It has been found that as little as 0.10 percent of one or more of these compounds, based on the weight of the composition, will bring about an appreciable improvement in the resistance of the composition to attack by microorganisms. Three percent or more of the biocidal compounds can be used, but these larger amounts generally do not provide further improvement in the properties of the surface-coating compositions and for this reason are not ordinarily used. While the amount of the biocidal compound that will provide optimum protection for a surface-coating composition depends upon such factors as the choice of biocidal compound, the choice of resinous binder and other components of the surface-coating composition and the amount of each that is used, and the application for which the coating composition is intended, in most cases about 1 percent to 2 percent of the organotin compound, based on the weight of the surface-coating composition, is used.

In addition to the resinous binder and the organotin compound, the surface-coating compositions of this invention may contain various auxiliary materials, such as pigments, extenders, solvents, dyes, deforming agents, driers, emulsifiers, plasticizers, and the like in the amounts ordinarily used for these purposes.

The organotin compound that is used as the biocide may be incorporated into the surface-coating composition by any convenient procedure. For example, it can be combined with the pigments and other components to form a pigment phase that is mixed with the resinous binder and water or organic solvent to form the surface-coating composition. Alternatively, it can be added to a composition that contains the resinous binder, pigment, and water or organic solvent. The organotin compound can be added as such to the other components, or it can be added as a solution of the organotin compound in, for example, an alcohol, ether, or ketone.

The invention is further illustrated by the examples that follow.

EXAMPLE 1

A mixture of 13.3 grams (0.050 mole) of dodecenylsuccinic anhydride and 4.0 grams (0.054 mole) of n-butyl alcohol was heated with stirring at 100° C. for one hour. It was then heated to 100° C. under vacuum (15 mm.) for one hour. Fifteen grams of bis-(tri-n-butyltin)-oxide was added to the half ester at 50° C., and the reaction mixture was heated with stirring at 110–120° C. for two hours. The tri-n-butyltin salt of mono-n-butyldodecenylsuccinate obtained was a pale yellow oil that contained 18.5% Sn (calculated, 18.8% Sn). Its structure was confirmed by infrared analysis.

EXAMPLE 2

The following organotin compounds were prepared by the procedure described in Example 1:

(Tri-n-butyltin)-isodecyloctenylsuccinate
(Tri-n-butyltin)-isodecylcaprylenylsuccinate
(Tri-n-butyltin)-isodecyl-n-dodecenylsuccinate
(Tri-n-butyltin)-isodecyl-n-octadecenylsuccinate
(Tri-n-butyltin)-methyl dodecenylsuccinate
(Tri-n-butyltin)-ethyl isododecenylsuccinate
(Tri-n-butyltin)-n-hexyl isododecenylsuccinate

Analysis of these compounds indicated that each contained approximately the calculated amount of tin and had the indicated structure.

EXAMPLE 3

(A) A polyvinyl acetate emulsion paint was prepared by mixing together the following materials:

	Parts by weight
Water	280
Potassium pyrophosphate	3
Calcium metasilicate	135
Titanium dioxide (rutile)	220
2% aqueous solution of methylcellulose	200
Diethyl ether of diethylene glycol	37
55% aqueous solution of polyvinyl acetate	350

To samples of this paint was added either 2 percent by weight of one of the organotin compounds of this invention or 2 percent by weight of a comparative biocide.

(B) An acrylic paint was prepared by mixing together the following materials:

	Parts by weight
Water	250
Acrylic acid resin (100% solids) (Acryloid B-66)	385
Monoethyl ether of ethylene glycol	259
Titanium dioxide	143
Aluminum silicate	45
Magnesium silicate	98

To samples of this paint was added either 2 percent by weight of one of the organotin compounds of this invention or 2 percent by weight of a comparative biocide.

(C) An exterior house paint was prepared by mixing together the following materials:

	Parts by weight
Basic lead carbonate	288
Zinc oxide	232
Titanium dioxide (rutile)	149
Talc	260
Linseed oil	242
Bodied linseed oil	114
Mineral spirits	114
Antiskinning agent (Exkin 2)	2
Manganese naphthenate (6%)	2.27
Lead naphthenate (24%)	11.3

To samples of this paint was added 2 percent by weight of either one of the organotin compounds of this invention or a comparative biocide.

EXAMPLE 4

Samples of the acrylic paint, the polyvinyl acetate paint, and the oil-based paint whose preparation was described in Example 3 where evaluated by the following procedure: Pieces of drawndown paper were dipped into the paint, dried for 24 hours, and again dipped into the paint. After a 24-hour drying period, the coated paper samples were cut into 1¼ inch squares. Each of the coated paper squares was placed on a plate of malt and mycophil agar, which had been inoculated with 1 ml. of a suspension of the test organism. The plates, prepared in triplicate, were incubated at 28° C. and observed weekly. The growth was estimated according to the following key, and the results of the triplicate plates were averaged. In the tables that follow

ZO=Zone of inhibition in mm.
0=No zone of inhibition
Tr=Trace zone
1–9=Increasing amounts of growth on specimen.

The biocidal compounds tested and the results obtained are set forth in Tables I, II, and III.

resistance to attack by fungi and bacteria without adversely affecting the pH, color, viscosity, or heat aging characteristics of the paints. Unlike those containing bis-(phenylmercury)-dodecenylsuccinate as the biocide, the surface-coating compositions of this invention do not undergo gray or black staining when they are exposed to hydrogen sulfide.

While the comparative biocide 2,3,5,6-tetrachloro-4-(methylsulfonyl)-pyridine exhibited biocidal activity, it is not a satisfactory paint biocide because it hydrolyzes under

TABLE I.—RESISTANCE OF ACRYLIC PAINT FILMS TO ATTACK BY MICROORGANISMS

Biocide	pH	Effect on paint color	Bacteria: *Bacillus subtilis*	Bacteria: *Aerobacter aerogenes*	Bacteria: *Pseudomonas aeruginosa*	Fungi: *Pullularia pullulans*	Fungi: *Penicillium crustosum*	Fungi: *Aspergillus niger*
(Tri-n-butyltin)-isodecyl-n-octenylsuccinate	9.4	None	ZO–5	0	0	0	0	0
(Tri-n-butyltin)-isodecylcaprylenylsuccinate	9.3	do	ZO–5	0	0	0	0	0
(Tri-n-butyltin)-isodecyl-n-dodecenylsuccinate	9.4	do	ZO–1	0	0	0	0	0
(Tri-n-butyltin)-isodecyl-n-octadecenylsuccinate	9.3	do	ZO–5	0	0	0	0	0
(Tri-n-butyltin)-methyldodecenylsuccinate	9.1	do	ZO–1	0	0	ZO–2	0	ZO–1
(Tri-n-butyltin)-ethyl-isododecenylsuccinate	9.2	do	ZO–1	0	0	ZO–1	0	Tr
(Tri-n-butyltin)-n-butyldodecenylsuccinate	9.2	do	ZO–3	0	0	ZO–1	0	ZO–1
(Tri-n-butyltin(-n-hexyl-isododecenylsuccinate	9.2	do	ZO–3	0	Tr	0	0	0
Comparative biocides:								
Bis-(phenylmercury)-dodecenylsuccinate (Super Ad-it).	9.4	do	ZO–9	ZO–7	ZO–8	ZO–10	ZO–1	ZO–11
2,3,5,6-tertachloro-4-(methylsulfonyl)-pyridine (Dow 1013).	9.4	do	ZO–9	0	0	ZO–10	ZO–9	ZO–7

TABLE II.—RESISTANCE OF POLYVINYL ACETATE PAINT FILMS TO ATTACK BY MICROORGANISMS

Biocide	pH	Paint on paint color	Bacteria: *B. subtillis*	Bacteria: *A. aerogenes*	Bacteria: *P. aeruginosa*	Fungi: *P. pullulans*	Fungi: *P. crustosum*	Fungi: *A. niger*
(Tri-n-butyltin)-isodecyl-n-octenylsuccinate	7.2	None	ZO–3	0	0	Tr	0	0
(Tri-n-butyltin)-isodecylcaprylenylsuccinate	7.3	do	ZO–3	0	0	ZO–1	0	Tr
(Tri-n-butyltin)-isodecyl-n-dodecenylsuccinate	7.2	do	ZO–1	0	0	0	0	0
(Tri-n-butyltin)-isodecyl-n-octadecenylsuccinate	7.4	do	ZO–7	0	0	0	0	0
(Tri-n-butyltin)-ethyl-isododecenylsuccinate	7.2	do	Tr	0	0	Tr	0	Tr
(Tri-n-butyltin)-n-butyldodecenylsuccinate	7.3	do	ZO–5	0	0	ZO–2	0	ZO–2
(Tri-n-butyltin)-n-hexyl-isodedocenylsuccinate	7.3	do	ZO–5	0	0	ZO–1	0	ZO–2
Comparative biocides:								
Bis-(phenylmercury)-dodecenylsuccinate (Super Ad-it).	7.1	do	ZO–11	ZO–9	ZO–10	ZO–12	ZO–10	ZO–8
2,3,5,6-tetrachloro-4-(methylsulfonyl)-pyridine (Dow 1013).	7.4	do	ZO–9	0	0	ZO–12	ZO–7	ZO–8

TABLE III.—RESISTANCE OF OIL-BASED PAINT FILM TO ATTACK BY MICROORGANISMS

Biocide	Effect on paint color	Microorganisms: *P. pullulans*	Microorganisms: *P. crustosum*	Microorganisms: *A. niger*
(Tri-n-butyltin)-isodecyl-n-octenylsuccinate.	None	0	0	0
(Tri-n-butyltin)-isodecyl-caprylenylsuccinate.	do	0	0	0
(Tri-n-butyltin)-isodecyl-n-dodecenylsuccinate.	do	0	0	0
(Tri-n-butyltin)-isodecyl-n-octadecenylsuccinate.	do	0	0	0
(Tri-n-butyltin)-methyl-dodecenylsuccinate.	do	0	0	0
(Tri-n-butyltin)-ethyl-isododecenylsuccinate.	do	0	0	0
(Tri-n-butyltin)-n-butyl-dodecenylsuccinate.	do	Tr	Tr	ZO–5
(Tri-n-butyltin)-n-hexyl-isododecenylsuccinate.	do	0	0	0
Comparative biocides:				
Bis-(phenylmercury)-dodecenylsuccinate.	do	ZO–10	ZO–7	ZO–13
2,3,5,6-tetrachloro-4-(methylsulfonyl)-pyridine.	do	ZO–11	ZO–10	ZO–9

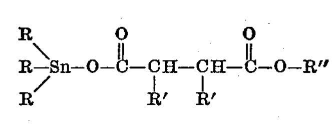
From the data in Tables I–III it will be seen that the organotin compounds of this invention are effective biocides for paint systems, and particularly for acrylic and polyvinyl acetate paint systems. They impart to the paints

alkaline conditions and loses its effectiveness on aging in acrylic paint systems and other alkaline paint systems.

The terms and expressions which have been employed are used as terms 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, but it is recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. An organotin compound having the structural formula



wherein each R represents phenyl or an alkyl group having from 4 to 12 carbon atoms; one R′ represents an alkenyl group having from 8 to 22 carbon atoms; the other R′ represents hydrogen; and R″ represents an alkyl group having from 1 to 16 carbon atoms.

2. An organotin compound as set forth in claim 1 wherein each R represents n-butyl.

3. The organotin compound as set forth in claim 1 that is (tri-n-butyltin)-n-butyl-dodecenylsuccinate.

4. The organotin compound as set forth in claim 1 that is (tri-n-butyltin)-methyl-dodecenylsuccinate.

5. The organotin compound as set forth in claim 1 that is (tri-n-butyltin)-isodecyl-dodecenylsuccinate.

6. The organotin compound as set forth in claim 1 that is (tri-n-butyltin)-isodecyl-n-octenylsuccinate.

7. The organotin compound as set forth in claim 1 that is (tri-n-butyltin)-isodecyl-n-octadecenylsuccinate.

References Cited

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JAMES E. POER, Primary Examiner

W. F. W. BELLAMY, Assistant Examiner

U.S. Cl. X.R.

260—537; 424—288

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,651,107 Dated March 21, 1972

Inventor(s) Robert J. Stanaback and Thomas E. Maggio

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 4, change "Stanback" to -- Stanaback --.

Column 1, lines 53 and 54, delete "have been suggested for use in surface-coating compositions, but none".

Column 2, line 8, in the structural formula change -R'' to -R"

Column 3, line 45, change "deforming" to -- defoaming --.

Column 4, line 66, change "where" to -- were --.

Column 5, last item in Table I, change "-tertachloro-" to -- -tetrachloro- --.

Signed and sealed this 25th day of July 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.	ROBERT GOTTSCHALK
Attesting Officer	Commissioner of Patents

FORM PO-1050 (10-69)

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