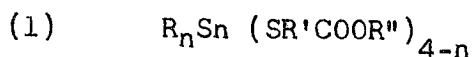


1 This invention relates to new organotin compounds and to compositions containing the same.

As heat and light stabilizers for various resins, particularly vinyl chloride resins, organotin mercapto acid esters have been used in recent years to an ever increasing extent. Such esters have the formula



wherein R represents a monovalent organic group, generally an alkyl group, preferably an alkyl group having 4-12 C atoms, such as butyl, octyl, dodecyl and the like. However, it may be also
 10 an aryl, alkaryl, aralkyl, alkenyl, oxyalkyl, oxyaryl, cycloalkyl, or any other group which, when the compound is used as stabilizer, does not adversely affect the resin.

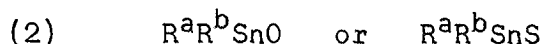
R' is an alkylene group, and R'' is the monovalent radical of an alcohol used to esterify the carboxyl group of the mercapto acid. Generally, it will be an alkyl group having not more than about 20 and preferably 4-12 C atoms. n is an integer in the range of 1-3. If n is larger than 1, R_n may contain different R groups.

20 Such organotin mercaptoesters containing the Sn-S linkage, though widely used, have still some drawbacks. One of said drawbacks is the well known objectionable smell presented by the stabilized resin during processing and also in the finished articles. Another disadvantage of the organotin mercapto acid ester stabilizers is their relatively low tin content. In order to be most effective in rigid plastic formulations, they have to be employed in such large amounts as to lower the heat distortion temperature.

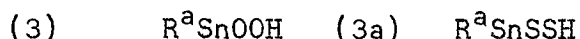
It was now found that at least one of the recited draw-
 30 backs and in many cases both can be eliminated by using, instead of the organotin mercapto acid esters, their reaction products with diorganotin oxides or sulfides, or with stannic acids, or thio-



1 stannic acids, which, although their precise structures are not always known and their degrees of hydration or polymerization may vary, may for convenience be represented by the formulae



and



wherein R^a and R^b have the same significance as R above. As used hereinafter in connection with these compounds the terms "mole" and "molar" shall be interpreted with relation to these
10 formulae.

The reaction is preferably carried out in a suitable diluent such as toluene, benzene, or another inert organic solvent, at temperatures from room temperature to about 155°C. The reaction is mostly terminated in about 30-60 minutes. In order to strip the diluent, and water if formed, reduced pressure will be generally applied. The reaction products of the diorganotin mercapto esters with diorganotin oxides or sulfides can advantageously be obtained in a single step by reacting a mercapto acid ester directly with the required amount of diorganotin oxide,
20 whereby probably the first formed diorganotin dimercapto ester reacts further in situ with the excess organotin compound; however, also in this case, of course, a preformed organotin mercapto acid ester can be reacted with the organotin compound.

Most of the resultant reaction products are clear slightly viscous liquids. When fully reacted, they are completely compatible with e.g. polyvinyl chloride, in contrast, e.g. to the organotin oxides and sulfides used as reactants. This shows that actual reaction has taken place between the organotin mercapto acid ester and the organotin oxide or sulfide.

30 In the following description, the term "organotin oxide" is used for the sake of brevity and is intended to refer not only to diorganotin oxides but equally also to diorganotin sulfides and

1 hydrocarbylstannoic acids. The compounds of this invention can be prepared directly by reaction of an organotin oxide with a mercapto acid ester HSR'COOR" in such an amount.

They can also be obtained by reacting a preformed organotin mercapto ester with the organotin oxide, so that, after formation of the Sn-S linkage, an excess, preferably at least one mole of the organotin oxide is still available.

10 In the practice of this invention a diorganotin dimercapto ester may be reacted with one or two moles of "organotin oxide"; a monoorganotin triester may be reacted with 1, 2, or 3 moles of the "organotin oxide", while a triorganotin mercapto ester may be reacted with only one mole of the "organotin oxide". Generally, if the organotin mercapto ester contains several carboxylate groups, at least one such excess mole of the "organotin oxide" should be used but not more such excess moles than correspond to the number of available carboxylate groups.

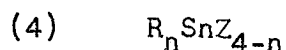
20 If the excess of "organotin oxide" over the amount required for the Sn-S linkage is less than 1 mole, the reaction product will be a mixture of conventional organotin mercapto esters with compounds of the composition discussed hereinbelow. If the amount of "organotin oxide" is in excess of the available carboxylate groups, said excess will form a component which interferes with the stabilizer action.

For the use of the new organotin mercapto compounds as stabilizer, it may be sufficient to add to the resin a mixture of an organotin mercapto ester and the "organotin oxide" in the proportions defined hereinabove. The new compound is then formed during the heat processing of the resin.

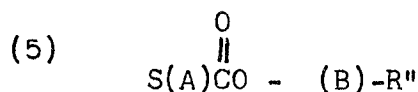
30 When, in the foregoing, reference has been had to mercapto acid ester or organotin mercapto acid esters, only such esters are included in which R' is an alkylene group of at least 2 C atoms. The reaction does not take place with the thioglycolic acid ester

1 compounds, and this is further evidence for the configuration of the new compounds. It appears that some minimum spacing between the Sn-S and the carboxylate groups is necessary and that the spacing alkylene group of the mercapto acid must have at least a length of two carbon atoms.

Assuming said reaction mechanism, the obtained reaction products would be represented by the formula

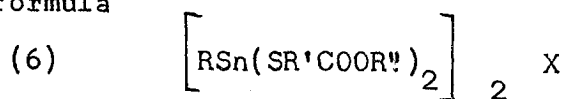


wherein R has the same significance as above, n is an integer from 1 to 3, and Z has the formula

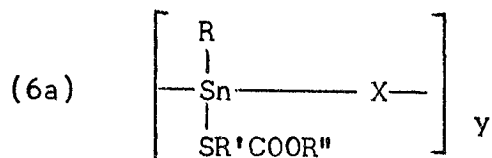


wherein R'' has again the same meaning as above, A is phenylene, or an alkylene chain of at least two methylene groups, which may be interrupted by phenylene; and B is one of the compounds (2) or (3). If the reaction product contains more than one Z group, such additional Z moieties need not contain the group B. Also, in one or more of the said methylene groups, one or more hydrogen atoms may be replaced by harmless substituents including an ester group.

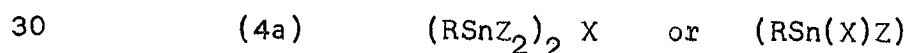
20 If, instead of the compounds of the formula (1), compounds of the formula



or



X being oxygen or sulfur, and y designating the degree of polymerization, are taken as starting materials, the reaction products will be represented by the formulae



wherein R, Z, and X have the same meaning as defined above.

Compounds of the formula (6) are obtained by reaction of

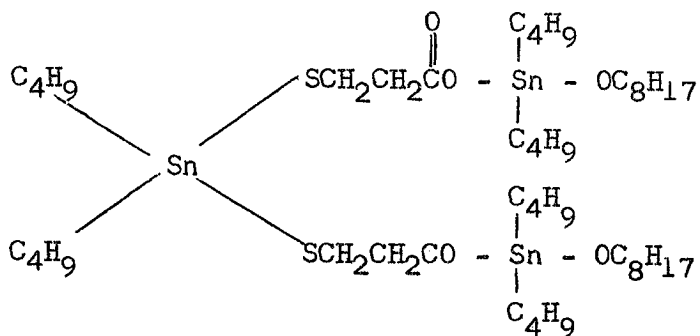
1 two moles of the mercapto acid ester with 1 mole of an organo-
stannoic acid, while those for formula (6a) require only one mole
of the mercapto acid ester. Otherwise, the reaction is carried
out in the same way as set forth above.

Though the above given formulae are consistent with all
observations made with respect to the organotin mercapto ester -
organotin oxide reaction products, it must be understood that the
formulae are not to be considered a limitation of the scope of the
invention which relates broadly to products obtained by the recited
10 reaction of organotin mercapto esters with "organotin oxides",
provided that the mercapto acid of the ester has at least two CH₂
or similar groups. Suitable mercapto acid components are, e.g.,
beta mercaptopropionic acid, β to ω mercaptolauric acids, mercapto
phenyl acetic acid, mercaptobenzoic acid, and similar acids.

Resins stabilized by the organotin mercapto acid ester -
"organotin oxide" reaction products are all those resins for which
the organotin mercapto esters have been used. Such resins are
particularly vinyl halide polymers and their copolymers with other
ethylenically unsaturated compounds such as vinyl acetate, vinyl-
20 dene chloride, styrene, acrylic compounds and the like. As the
new stabilizers contain a much higher tin content per unit of
weight, they are particularly useful for the stabilization of rigid
compounds. They may be used in amounts of 0.1 to 5.0, preferably
0.1 to 3.0, parts of stabilizer per 100 parts of resin.

Among the reaction products of organotin compounds contain-
ing several mercapto acid ester groups, the best stabilizing
properties are generally shown by those compounds in which only one
COOR group has reacted with an organotin oxide; though reaction
of more than one COOR group with an "organotin oxide" increases the
30 relative tin content of the compound, the increase in stabilizing
efficiency is often no longer equivalent to the increase shown by
the first inserted organotin oxide group.

1 isooctylmercaptopropionate and 746.1 g (3.0 moles) of dibutyltin oxide. The reaction product was a clear light yellow liquid analyzing for 30.89% Sn, which corresponds to the formula



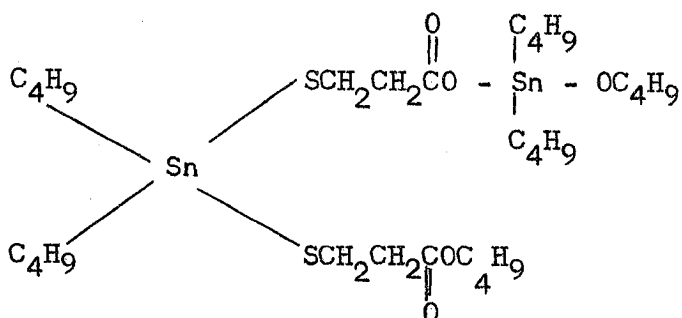
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EXAMPLE 3

162 g (1.0 mole) of butyl mercaptopropionate were heated as described in Example 1 with 248.7 g (1.0 mole) of dibutyltin oxide in 250 ml of toluene for 30 minutes first at a temperature of 120°C at a pressure of 90 mm Hg and then for 30 minutes at 155°C at a pressure of 15 mm Hg.

There were obtained 390 g of a clear colorless liquid with 28.36% Sn (29.6% Sn theory) of a compound to which I attribute the following configuration:

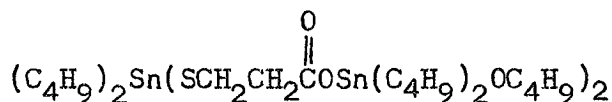
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EXAMPLE 4

30 325 g (2.0 moles) of butyl mercaptopropionate were treated with 746.1 g (3.0 moles) of dibutyltin oxide as described in the preceding example. The obtained product was a clear slightly yellow liquid analyzing for 32.35% Sn, satisfying the formula

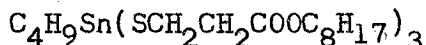
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EXAMPLE 5

While the preceding examples illustrate the one-step procedure, this example shows first the preparation of a mercapto ester and in a second step its reaction with an "organotin oxide".

208.7 g (1.0 mole) of butylstannoic acid and 250 ml of toluene were charged into a three-neck flask and dehydrated via azeotropic distillation at 120°C under atmospheric pressure.

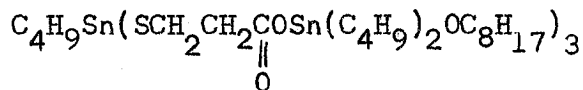
654 g (3.0 moles) of isooctyl betamercaptopropionate were added to the thus obtained product, and the mixture was stripped as set forth in the preceding examples at a temperature of 120°C and a pressure of 90 mm Hg. The filtered reaction product of the composition



was a clear slightly yellow liquid and had a tin content of 13.38% (theory 14.35%).

To 214 g (0.258 moles) of this compound, there were added 180.57 g (0.725 moles) of dibutyltin oxide and 100 ml of toluene. The reaction mixture was stripped at a pressure of 15 mm and a temperature of 120°C. The filtered end product was a viscous straw colored clear liquid containing 28.41% Sn.

The compound



has a theoretical Sn content of 30.0%.

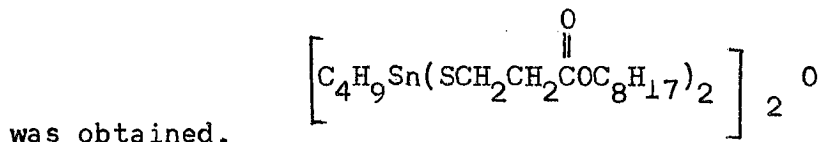
EXAMPLE 6

To 200 g of the monobutyltin tris(isooctyl mercaptopropionate), prepared as in Example 5 (.0.24 moles), there was added 128 g (0.48 moles) of dibutyltin sulfide, and 60 g (0.24 moles) of dibutyltin oxide, and 100 ml of toluene. The reaction mixture was

1 stripped at a pressure of 15 mm and a temperature of 120°C. The filtered end product, appreciably less viscous than that of Example 5, was free of the objectionable dibutyltin sulfide odor. The homogeneous liquid contained 28.5% Sn, has a theoretical Sn content of 29.55%.

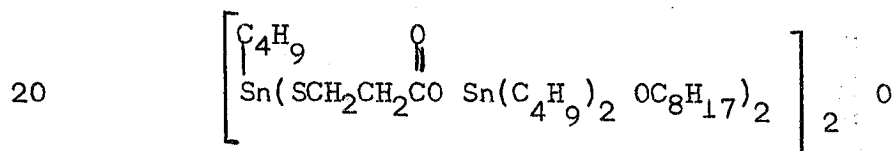
EXAMPLE 7

Example 5 was repeated with 436.8 g (2 moles) of isooctyl betamercaptopropionate, instead of the 3 moles of example 5. In this way, bis (monobutyltin diisooctyl mercapto-
10 propionate) oxide of the formula



To 1240 g (1.0 mole) of said compound, 994.8 g (4.0 moles) of dibutyltin oxide and 500 ml of toluene were added; the mixture was heated up to 120°C and stripped at a pressure of 15 mm Hg.

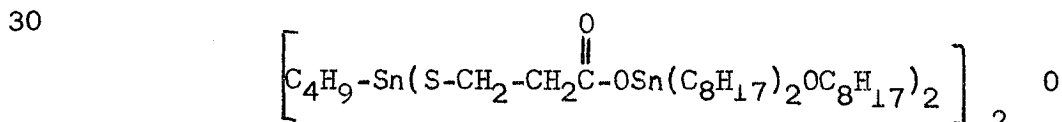
There were obtained 2150 g of a clear straw colored liquid which analyzed for 30.8% Sn, corresponding to a compound



EXAMPLE 8

620 g (0.5 moles) of the bis (monobutyltin diisooctyl mercaptopropionate) obtained as described in Example 7 were mixed with 361 g (1.0 mole) of dioctyltin oxide and 200 ml of toluene, heated up and stripped.

After filtration, 970 g of a viscous straw colored liquid were obtained containing 24.0% Sn (theory) 24.2%). The compound corresponded to the formula

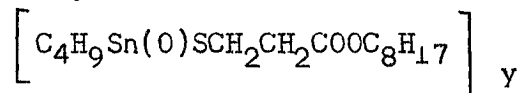


i.e. to a compound where only two of the possible reaction sites

1 had reacted.

EXAMPLE 9

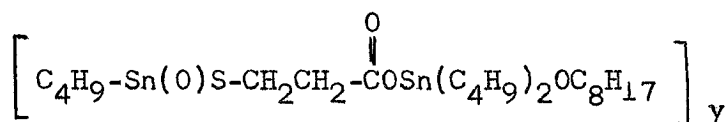
Example 5 was repeated but instead of 3 moles of the ester, only 218.4 g (1 mole) of the isooctyl beta mercaptopropionate were used. The product was a very viscous straw colored clear liquid represented by the formula



Sn found: 28.5%; theory 29.01%.

10 To 409.2 g of said compound (1 mole), 248.9 g (1 mole) of dibutyltin oxide were added, and the mixture was reacted in the same manner as in the preceding examples.

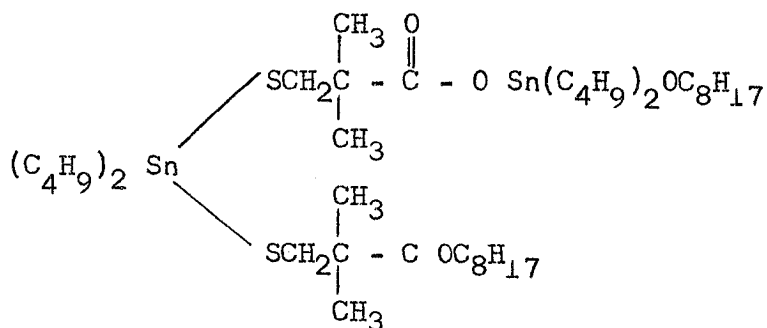
The dibutyltin oxide dissolved, and there was obtained a very viscous clear straw colored liquid containing 35.0% tin (theoretical, 36.1% tin as metal), having the following structure



EXAMPLE 10

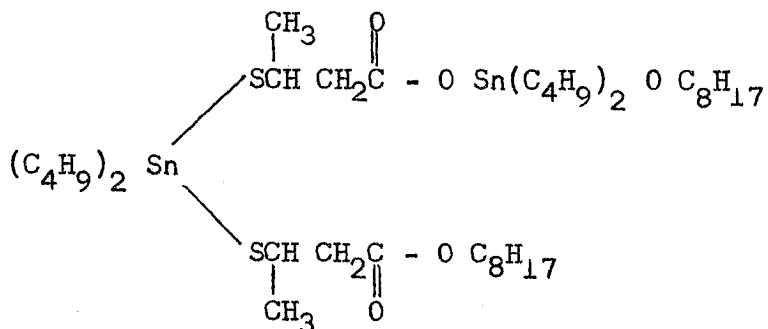
20 Dibutyltin bis(isooctyl mercaptopivalate) was prepared by reacting 49.2 g of isooctyl mercaptopivalate, 24.9 g of dibutyltin oxide, and removing the reaction water at 65°C and 15 mm Hg. The temperature was raised to 90°C and maintained for 20 minutes to ensure complete dehydration. The reaction product was filtered and analyzed for metal content (16.4% Sn).

30 Mono insertion of dibutyltin oxide was accomplished by reacting 18.7 g of the above dibutyltin bis(isooctyl mercaptopivalate) with 6.22 g of dibutyltin oxide in an open beaker. All the dibutyltin oxide dissolved at 200°C and the final product was a clear white liquid analyzing for 24.4% Sn, viscosity (G-H at 77°F), L. It had the formula

EXAMPLE 11

Dibutyltin bis(isooctyl-3-mercaptoputyrate) was prepared by reacting 46.2 g of isooctyl-3-mercaptoputyrate, 24.9 g of dibutyltin oxide, and removing the condensation water at 65°C under reduced pressure (15 mm Hg). The temperature was raised to 90°C for 20 minutes, as above. The reaction product was filtered and analyzed for 17.3% Sn as metal.

17.3 g of this reaction product were reacted in an open beaker with 6.25 g of dibutyltin oxide, all of which dissolved at 185°C. The final product was a water white clear liquid analyzing for 25.5% Sn as metal, Gardner-Holdt viscosity at 77°F of J. It corresponded to the formula

EXAMPLE 12

To 166.7 g of dibutyltin bis(isooctyl mercaptopropionate) (0.25 moles) obtained as described in Example 1 were added 52.2 g (0.25 moles) of butylstannoic acid, and the mixture was heated to 170°C. The reaction mixture was cooled to 100°C and filtered, very slowly, to give a very viscous clear liquid product

1 analyzing for 27.0% Sn.

EXAMPLE 13

The procedure of Example 12 was repeated but instead of 0.25 moles, 0.50 moles (104.5 g) of butylstannoic acid were used. The reaction product was an extremely viscous slow filtering product containing 32.0% Sn.

EXAMPLE 14

10 The compounds of Examples 1 and 2 were compared with dibutyltin bis(isooctylacetomercaptide) with respect to heat stabilizing efficacy for vinylchloride resins on a part per part and on a per cent tin per percent tin basis. The formulation consisted of 100 phr of PVC homopolymer and 0.25 phr of mineral oil. 2.00 phr of each of the three organotin compounds were milled into this master batch for 3 minutes at 320°F, then strips of stock were oven aged at 350°F, removing samples every ten minutes. In addition, 1.50 phr of the organotin compound of example 1 and 1.15 phr of the organotin compound of example 2 were milled into the above master batch and these samples were treated analogously. The time to darkening of stock was noted, and also the ability
20 to maintain good early color.

T A B L E

Stabilizer	parts per 100 parts of resin	Time to Darkening
dibutyltinbis(isooctyl- acetomercaptide)	2.00	90'
from Example 1	2.00	110'
from Example 2	2.00	greater than 120'
from Example 1	1.50	100'
from Example 2	1.15	100'

30

In all cases, also better early color was maintained with

1 the products of examples 1 and 2, and the resins stabilized with the new stabilizers presented much less the mercaptan smell of the conventional organotin mercapto stabilizers.

When instead of the compound of Example 2, an equal amount of a compound of a similar overall chemical composition but obtained according to Patent No. 726,779 by the reaction of a polymeric dibutyltin methoxide with isooctylmercaptopropionate was used, practically no improvement over the stabilizing effect of the dibutyltin bis(isooctylmercaptopropionate) could be observed. This is further proof for the specific nature and stabilizing efficiency of the insertion compounds of the invention.

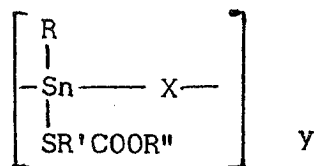
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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. As a new composition of matter, the reaction product of an organotin mercapto acid derivative selected from the group consisting of $R_n\text{Sn}(\text{SR}'\text{COOR}'')_{4-n}$, $[\text{RSn}(\text{SR}'\text{COOR}'')_2]_2$ X, and



wherein R and R'' are monovalent hydrocarbon radicals, R' is an alkylene group of at least 2 methylene groups, X is a member of the group consisting of oxygen and sulfur, n is an integer from 1 to 3, and y designates the degree of polymerization, with an organotin compound selected from the group consisting of organotin oxides, organotin sulfides, and hydrocarbyl stannic acids and esters, said organotin compound being applied in a molar amount not exceeding the number of COOR'' groups of said organotin mercapto acid derivative.

2. The reaction product as claimed in claim 1 wherein R and R'' are alkyl having 4-12 carbon atoms.

3. The reaction product as claimed in claim 1 wherein R' is an alkylene group of at least two methylene groups, which may be interrupted by a phenylene group, or may be phenylene group, or in which one or more of the methylene groups may be substituted by other harmless functional groups in place of the hydrogens.

4. A heat and light stable resin composition including as a major constituent a halogen containing resin and as a stabilizer 0.1 to 10 per cent, calculated on said resin, of the compound of claim 1.

5. A process of preparing diorganotin dimercapto ester derivatives having a high tin content comprising reacting one mole of a mercapto acid ester of the formula $\text{HSR}'\text{COOR}$, wherein R is a hydrocarbon group and R' is an alkylene radical of at least two methylene groups, with a diorganotin oxide, in an amount exceeding half a mole but not exceeding $1\frac{1}{2}$ moles.

6. The process as claimed in claim 5 wherein said mercapto acid ester is an alkyl ester of beta mercapto propionic acid.

7. The compound obtained by the process of claim 5.

8. A heat and light stable resin composition including as a major constituent a halogen containing resin and as a stabilizer 0.1 to 10 per cent, calculated on said resin, of the compound of claim 5.

*