

UNITED STATES PATENT OFFICE

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ORGANIC DERIVATIVES OF TETRAVALENT
TIN AND COMPOSITIONS CONTAINING
THE SAME

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The present invention relates to novel organic derivatives of tetravalent tin and compositions containing the same. This is a continuation-in-part of Serial No. 270,531, filed February 7, 1952.

The derivatives according to our invention are derived from tetravalent tin by having at least one valence and at the most three valences linked to the carboxyl group of an alkyl or aryl mercapto fatty acid, while the remaining valence or valences are bound to an alkyl, aryl, oxyalkyl and oxyaryl, and the furfuryl and tetrahydrofurfuryl radical.

The compounds are presented by the type formula



wherein R stands for a radical selected from the group consisting of alkyl, aryl, oxyalkyl and oxyaryl, and the furfuryl and tetrahydrofurfuryl radicals, X for the anion of a mercapto fatty acid having from 5 to 20 carbon atoms, and n for an integral number from 1 to 3.

Examples for R are alkyls, such as methyl, ethyl, butyl, octyl, dodecyl, and octadecyl; aryls, such as phenyl, tolyl, or xylol; oxyalkyl and oxyaryl, such as C_3H_7O , C_4H_9O , $C_6H_{17}O$, C_6H_5O , $C_6H_4(CH_3)O$, $C_6H_3(CH_3)_2O$; and the furfuryl and tetrahydrofurfuryl groups.

Examples for X are anions of mercapto fatty acids, such as dodecyl mercapto isobutyric acid, octyl mercapto propionic acid, benzyl mercapto isobutyric acid, and phenyl mercapto acetic acid. Taking as specific examples the dodecyl mercapto propionic acid and butyl tin compounds, the products may have the following formulas:

- (1) $C_4H_9.SN-(OOC.CH_2.CH_2.S.C_{12}H_{25})_3$
- (2) $(C_4H_9)_2SN-(OOC.CH_2.CH_2.S.C_{12}H_{25})_2$
- (3) $(C_4H_9)_3SN-(OOC.CH_2.CH_2.S.C_{12}H_{25})$

The novel tin compounds according to our invention are oily liquids of high viscosity or solids melting at low temperatures, whose composition has in each case been ascertained by analysis.

They are soluble in many organic solvents, for instance in ether, benzene, toluene, chloroform, carbontetrachloride, etc.

A general method to prepare these compounds is first to prepare the desired mercapto fatty acid and subsequently to react the acid with an organic tin oxide, or a stannonic acid containing

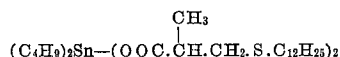
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an organic radical, or to react the alkali metal salt of the acid with an organic tin halide.

The invention will now be illustrated by a number of examples, but it should be understood that these are given by way of illustration and not of limitation and that many variations in the compounds given and the amounts indicated can be made without departing from the spirit of the invention and the scope of the appended claims.

Example 1

The preparation of dibutyl-tin di-dodecyl mercapto isobutyrate



To 800 g. n-dodecyl mercaptan are added 2 g. sodium-methylate. To this mixture 400 g. methylmethacrylate are added slowly while stirring. An exothermic reaction occurs and the temperature rises spontaneously to about 55° C. By the further addition of the methylmethacrylate, the reaction mixture is maintained at this temperature. Gradually, the viscosity of the solution increases. When the whole amount of methylmethacrylate has been added, one more gram of sodium methylate is added without causing a rise in temperature. Thereafter, the solution is heated on a boiling water bath for 1/2 hour.

After cooling down, a solution of 160 g. NaOH in 700 cc. water is slowly added with stirring, which causes a slight rise in temperature. After addition of the whole amount of NaOH, the mixture is heated to 100° C. for one hour, in order to complete hydrolysis. On cooling, the reaction mixture solidifies to a soaplike mass. This is acidified with HCl, whereby the mercapto acid separates as an oil.

60 g. dry acid
25 g. dibutyl-tin oxide, and
50 cc. benzene, to which 0.1 g. paratoluene sulfonic acid was added,

are refluxed for about 1 hour, whereby 1.7 cc. water are removed by azeotropic distillation.

The reaction mixture is filtered in order to remove slight impurities, and benzene is distilled off. In the filtrate, there remains an oily residue,

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which solidifies in the ice box and melts again at room temperature.

Analysis:

	Sn	S
calc.....	14.5	7.9
found.....	14.1	8.0

Example 2

Preparation of tributyl-tin octyl mercapto propionate



Octyl mercapto propionic acid is prepared in precisely the same way as in Example 1 from:

292 g. ethylhexyl mercaptan, and
175 g. methyl acrylate in the presence of
2 g. sodium methylate as catalyst.
22 g. of the dry acid were neutralized with
4 g. NaOH, and
32.5 g. tri butyl-tin chloride and
50 cc. benzene were added.

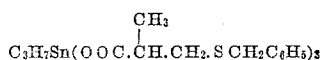
The resulting mixture was refluxed for 1 hour, and the sodium chloride formed was filtered off. The residue of the filtrate after distilling off the solvent is very similar to the product of Example 1.

Analysis:

	Sn	S
Calc.....	23.3	6.3
Found.....	22.8	6.2

Example 3

Preparation of isopropyl-tin tribenzylmercapto isobutyrate



In the same way as in Examples 1 and 2 benzyl mercapto-isobutyric acid was prepared from

248 g. benzylmercaptan, and
200 g. methylmethacrylate in the presence of
2 g. Na methylate.
63 g. dry acid and
20 g. isopropyl stannonic acid, prepared according to the literature, and
50 cc. benzene, containing 0.1 g. paratoluene-sulfonic acid,

were refluxed for 1 hour and 8.5 cc. water removed by azeotropic distillation. Slight impurities are filtered off and benzene is removed by distillation.

The residue is in appearance and properties similar to the material obtained according to Example 1.

Analysis:

	Sn	S
Calc. values.....	15.0	12.2
Found values.....	15.1	12.1

The novel compounds made according to the method described above may be used for various purposes. They are excellent stabilizers for chlorinated resins or other high molecular weight halogenated material, and may be used as antioxidants. They may also be interesting as such, or as intermediates for pharmaceuticals and

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cosmetics. As to their use for stabilizing chlorine-containing organic compositions, we wish to emphasize the superiority of these products above compounds of similar structure, such as dibutyl tin dilaurate. The presence of the sulfur in the molecule increases the compatibility with the product to be stabilized. Furthermore, the sulfur present acts as an antioxidant which improves the stabilizing effect.

The amount of the compounds to be used as stabilizers is from 0.1 to 10% by weight of the resinous composition.

In the following, examples will be given for the manufacture of plastic compositions in which the compound according to the present invention is used as a stabilizer.

Example 4

100 parts of vinylite VYNW (vinyl chloride and acetate copolymer), 50 parts of dioctyl-phthalate, and 2 parts of the product of Example 1 as stabilizer are mixed by tumbling for a period of one hour. The whole mass is then transferred to a Banbury mixer and fused for 10 min. at a temperature of approximately 300° F. It is then dropped and transferred to a warmup mill, whose roll temperature is likewise maintained at 300° F. The material is then fed as needed to a 3 or 4 roll calender. The roll temperatures of the calender range from 280°-350° F. The vinyl compound is calendered into a film at .004 inch or any other desirable gage.

Example 5

A comparison test was made in which chlorinated paraffin was heated over a period of time, without any addition on the one hand, and with addition of a stabilizer made according to the invention on the other hand.

In this test, a nitrogen current was passed through chlorinated paraffin containing 40% chlorine, at a temperature of 150° F. for 12 hours. During the test, the paraffin lost 10% chlorine.

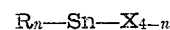
The same chlorinated paraffin, to which 3% of the product obtained in Example 3 were added, was treated in a similar manner and showed a loss of only 1.1% chlorine after 12 hours.

Example 6

The following procedure is used to advantage in making a finished solution of the resin. We use 100 parts of vinylite VYNW (vinyl chloride and acetate copolymer) along with 40 parts of tricresylphosphate. This is weighed into a dry blender; 1 part of stabilizer (made as described in Example 2) is then added. The whole mass is agitated by tumbling for 30 minutes and then transferred to a 2-roll mill whose roll temperatures are about 240° F. The mass is fluidized on the mill and then sheeted into strips which are added to a mixture consisting of 3 parts of methyl ethyl ketone and 1 part of toluene in a conventional mixer. The compound is agitated at room temperature in the mixer until complete solution results. The proportion of solvent used will vary with the concentration of solution desired, as, for instance, from 500 to 3,000 parts of solvent to 100 parts of the vinyl chloride resin used.

What we claim is:

1. As a new compound, a product corresponding to the formula



wherein R stands for a radical selected from the group consisting of alkyl, aryl, oxyalkyl and

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oxyaryl, and the furfuryl and tetrahydrofurfuryl radicals, X for the anion of a mercapto fatty acid selected from the group consisting of alkyl and aryl mercapto fatty acids having from 5 to 20 carbon atoms, and n for an integral number from 1 to 3.

2. As a new compound, dibutyl tin di-dodecyl-mercapto-isobutyrate.

3. As a new compound, tributyl tin octylmercaptopropionate.

4. As a new compound, isopropyl tin tribenzyl-mercapto-isobutyrate.

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5. A stabilized chlorine-containing resinous composition containing 0.1% to 10% by weight of the compound of claim 1.

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