

PATENT APPLICATION

TITLE OF THE INVENTION

5 ALKYL-BRIDGED TIN-BASED THERMAL STABILIZERS FOR HALOGENATED
RESINS AND SYNTHESIS AND USES THEREOF

10 APPLICANT/ASSIGNEE:

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CROSS-REFERENCE TO RELATED APPLICATIONS

15 This application claims the benefit of US Provisional Patent Application, Serial No.
62/980,834, filed 24 February 2020, which is incorporated herein by reference. Priority
of US Provisional Patent Application, Serial No. 62/980,834, filed 24 February 2020 is
hereby claimed.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT

20 Not applicable

REFERENCE TO A "MICROFICHE APPENDIX"

Not applicable

BACKGROUND OF THE INVENTION

1. Field of the Invention

25 The present invention relates to stabilizer composition for halogen-containing polymer.
More particularly, the present invention relates to thermal stabilizers for halogen-containing
stabilizers, for example polyvinyl chloride or PVC.

2. General Background of the Invention

30 Processors of non-thermoset polymers have historically struggled with a balance between
the ability to process a given polymeric-based material, its properties during processing and
its final properties in a finished article. PVC specifically is a thermally unstable polymer at
traditional processing temperatures and many stabilizer systems have been developed that

attempt to address its inherent thermal instability. These multiple approaches include organic, mixed metal and tin-based stabilizers. PVC and related polymers are also blended and compounded with a variety of other ingredients including, but not limited to, pigments, fillers, lubricants, process aids and impact modifiers. These mixtures are heated during blending and processing by methods including extrusion and injection molding which can lead to the release of volatile materials. These materials may lead to unpleasant odors and/or have potential health effects on exposed workers and part of these volatiles during compounding and processing can be traced to the stabilizing system.

Examples of technologies to lower volatile materials include polymer plasticizers, post stripping the stabilizer to remove the volatile material, post adding an alkyl tin oxide to react with residual Mercaptoester, and, using higher molecular weight esters.

Existing technology of tin-based stabilizers for PVC include the use of ‘bridging sulfur’. In contrast to the alkyl-bridged stabilizers of the present invention, the bridging sulfur moieties are reactive and form part of the stabilizing action of the stabilizer containing such groups. As a result, these sulfur bridging groups are transitory in nature and do not effectively increase the molecular weight of such stabilizers and therefore have do not lower the volatility of such materials with respect to their non-sulfur bridged counterparts. The alkyl-bridged stabilizers of the present invention overcomes these problems.

BRIEF SUMMARY OF THE INVENTION

The present invention is a stabilizer composition for halogen-containing polymer. It has recently been found that tin-based thermal stabilizers with a bridging alkyl group between two tin centers are effective stabilizers while having effectively double the molecular weight of the corresponding non-alkyl bridged stabilizer. The alkyl bridged stabilizers have much lower volatility which leads to greater retention of the stabilizer in the finished article. It is expected that other bridging groups, including non-carbon-based bridging groups, would yield similar results.

The alkyl bridged materials described herein are based on tin-alkyl bonds which are not active in the stabilization process and are effective in increasing molecular weight of the stabilizing system. This approach is not limited to monomeric species containing 2 tin sites with a single bridging group and species with multiple tin sites, greater than 2, based on single or multiple tin-terminated alkyl-based bridges should also behave in similar manner.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

For a further understanding of the nature, objects, and advantages of the present invention, reference should be had to the following detailed description, read in conjunction with the following drawings, wherein like reference numerals denote like elements and wherein:

Figure 1 is a chart showing thermogravimetric analysis in °C;

Figure 2 is a chart showing TGA of Monobutyltin Trichloride (MT);

Figure 3 is a chart showing TGA of Octyl Ditin Hexachloride (BT);

Figure 4 shows preferred embodiments of the stabilizers of the present invention; and,

Figure 5 shows other possible bridging groups.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is a stabilizer composition for halogen-containing polymer. It has recently been found that tin-based thermal stabilizers with a bridging alkyl group between two tin centers are effective stabilizers while having effectively double the molecular weight of the corresponding non-alkyl bridged stabilizer. The alkyl bridged stabilizers have much lower volatility which leads to greater retention of the stabilizer in the finished article.

Testing to determine weight loss of the stabilizer precursors at elevated temperatures confirms that non-bridged stabilizers have higher volatility and higher weight loss versus the alkyl-bridged stabilizers of the present invention. The focus of the testing was the halogen-based tin compounds that are the ultimate product of stabilization of a halogen-containing polymer, namely the alkyltin chlorides. This testing confirms that the non-bridged stabilizers, represented by Monobutyltin Trichloride or MT, have higher volatility and subsequently higher weight loss over the experimental period versus the bridged analogues, represented by Octyl DiTin Hexachloride or BT, see Fig. 1. It can be further noted as shown in Figs. 2 and 3, that at approximately 200°C, which is at the high end of the temperature range of PVC processing, MT was completely lost while BT has undergone less than 20% weight loss. BT can be viewed as an effective dimer of the MT species, which would result from the use of a traditional non-bridged tin stabilizers of the sort monobutyltin tris(EHMA). Both of the chlorides in Fig. 1 would be created as the ultimate stabilization product by displacement of the reactive ligands of their respective starting thermal

stabilizers. In addition to lower weight loss during processing, it is expected that bridging species will also be less susceptible to extraction during their in-use lifetimes. These species are expected to offer improved odor characteristics due to the expected lower volatility of partially substituted species from stabilization of the type $L_{3-x}Cl_xSn\text{-bridge-Sn}Cl_xL_{3-x}$, where $x=1$ or 2 , for bridging stabilizers, and L can be mercaptide ligand among others, As shown in Fig. 4.

PVC COMPOUND FORMULATION:

Test Conditions: The PVC compound was blended following standard additive addition order and temperature. The color stability of each compound was evaluated using a Brabender running operating at 190 degrees Celsius / 60 rpm with samples taken in 2-minute intervals. The colors of each chip were measured relative to a standard white tile and "L Values" and "b Values" reported in the tables 2 and 3, respectively, below.

Description of STABILIZER Preparations

Synthesis of $Cl_3Sn-C_8H_{16}-SnCl_3$ (Octyl Ditin Hexachloride). This material was synthesized according to published methods, see Organometallics, Vol 21, No. 22, 2002.

Synthesis of High Mono-Octyltin $(RE)_3$, follows Route A described below. In this case the Mercapto Sulfur ester is 2-Mercaptoethyl ester of C16 - C18 unsaturated fatty acid. These are commonly referred to as Reverse Ester PVC Stabilizers.

Synthesis of $(RE)_3Sn-C_8H_{16}-Sn(RE)_3$ follows Route B described below. In this case the Mercapto Sulfur ester is 2-Mercaptoethyl ester of C16 - C18 unsaturated fatty acid. These are commonly referred to as Reverse Ester PVC Stabilizers.

Synthesis of High Mono-Octyltin $(EHMA)_3$ follows Route A described below. In this case the Mercapto Sulfur ester is 2-Ethylhexyl Mercaptoacetate.

Synthesis of $(EHMA)_3Sn-C_8H_{16}-Sn(EHMA)_3$ follows Route B described below. In this case the Mercapto Sulfur ester is 2-Ethylhexyl Mercaptoacetate.

SYNTHESIS ROUTE A

1.02 eq of Mercapto Sulfur containing ester were reacted with a mixture of Mono-octyl Tin Trichloride (95 wt%) and Dioctyl Tin Dichloride (5 wt%) representing 1.0 equivalents of chloride using aqueous Sodium Hydroxide aqueous solution to convert the Chloride to the Mercaptide. This mixture is allowed to settle for 60 minutes to allow the organic and aqueous phases to split. The bottom aqueous layer is removed, and the remaining organic phase was dried under vacuum and heat. This was then filtered to yield a clear liquid.

SYNTHESIS ROUTE B

1.02 eq of Mercapto Sulfur containing ester were reacted with a mixture of Octyl Tin Hexachloride representing 1.0 equivalents of chloride using aqueous Sodium Hydroxide aqueous solution to convert the Chloride to the Mercaptide. This mixture is allowed to settle for 60 minutes to allow the organic and aqueous phases to split. The bottom aqueous layer is removed, and the remaining organic phase was dried under vacuum and heat. This was then filtered to yield a clear liquid.

These stabilizers were evaluated for their effect on PVC processing, in particular their impact of color developing as function of heat and time relative to their traditional non-bridged counterparts, namely high mono-octyl Sn (EHMA)₃ and high mono-octyl Sn (RE)₃. These stabilizers were compounded in the PVC formulation shown:

Table 1. Blend Compositions

Component	PHR			
	Sample1	Sample 2	Sample 3	Sample 4
Shintech SE-950 PVC resin	100.0	100.0	100	100
High mono-octyltin(EHMA) ₃	1.41			
(EHMA) ₃ Sn-C ₈ H ₁₆ -Sn(EHMA) ₃		1.39		
High mono-octyltin(RE) ₃			2.28	
(RE) ₃ Sn-C ₈ H ₁₆ -Sn(RE) ₃				2.36
Lubricant package, Advalube® B3314	2.5	2.5	2.5	2.5
Impact Modifier, Durastrength 535	5.0	5.0	5.0	5.0
Calcium Carbonate, Omya UFT	3.0	3.0	3.0	3.0

Chemours 960 TiO ₂ Pigment	10.0	10.0	10.0	10.0
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Test Conditions: The PVC compound was blended following standard additive addition order and temperature. The color stability of each compound was evaluated using a Brabender running operating at 190 degrees Celsius / 60 rpm with samples taken in 2-minute intervals. The colors of each chip were measured relative to a standard white tile and “L Values” and “b Values” reported in the tables 2 and 3, respectively, below.

Samples 1 and 2 are non-alkyl bridged and alkyl-bridged species based on octyltin centers and EHMA as ligand. At equivalent tin the alkyl-bridged species provides effectively equivalent stabilizing performance versus its non-bridged counterpart as judged by the similarity of the color development as outlined in Tables 2 and 3.

Samples 3 and 4 are non-alkyl bridged and alkyl-bridged species based on octyltin centers and RE as ligand. At equivalent tin the alkyl-bridged species provides effectively equivalent stabilizing performance versus its non-bridged counterpart as judged by the similarity of the color development as outlined in Tables 2 and 3.

Table 2. Color Values, L value data

Time (Min)	Sample 1	Sample 2	Sample 3	Sample 4
2	89.4	88.5	88.8	89.5
4	89.5	89.2	89.7	89.6
6	88.9	88.9	90.5	90.3
8	88.9	90.0	90.3	91.2
10	91.5	83.8	90.8	91.9

Table 3. Color Values, b Value data

Time (Min)	Sample 1	Sample 2	Sample 3	Sample 4
2	0.88	0.89	1.43	2.5
4	1.43	1.45	2.55	3.7
6	1.94	2.22	3.17	3.9
8	3.19	5.11	3.82	8.4
10	19.07	23.5	4.82	29.5

The stabilizer composition of the present invention for halogen-containing polymers, preferably comprises at least two tin-based centers having a bridging alkyl group between the tin-based centers. This formula can have multiple tin-based centers and corresponding multiple bridging alkyl groups. The stabilizer may be of one of the following types:

- 5 $L_3Sn-X-SnL_3$
 $L_2Sn-(X)(Y)-SnL_2$.

In these types, L is preferably a traditional ligand, such as esters of thioglycolic acid, 2-ME esters of C12-C18 fatty acids, carboxylates, maleates, sulfides, 2-ME, mercaptans, or any blends thereof. X and Y are preferably tin-terminated alkyl-based bridging groups. X and or Y can be
10 linear or branched, saturated or unsaturated, with or without heteroatoms, and/or with or without heterocycles. The alkyl bridge is preferably C1 to C80.

In other embodiments, the stabilizer composition comprises at least three repeating units of $-[SnL_2-X]_n$, where X is a tin-terminated alkyl-based bridging group and L is a traditional ligand. In these embodiments, X may be linear or branched, saturated or unsaturated, with or without
15 heteroatoms, and/or with or without heterocycles. Preferably, the alkyl bridge is C1 to C80. Preferably, L is an ester of thioglycolic acid, a 2-ME ester of C12-C18 fatty acids, a carboxylate, a maleate, a sulfide, 2-ME, a mercaptan, or any combination of two or more of an ester of thioglycolic acid, a 2-ME ester of C12-C18 fatty acids, a carboxylate, a maleate, a sulfide, 2-ME, or a mercaptan.

20 The present invention also includes the resulting PVC, CPVC, or a blend of PVC and CPVC that contains the novel stabilizer described above. Preferably, the resulting composition contains at least 0.5% by weight stabilizer.

It is expected that other bridging groups, including non-carbon-based bridging groups, would yield similar results. For example, silicones (siloxanes), silanes (silylenes), silazanes,
25 carbosilanes, and silphenylenes, as shown in Figure 5, may offer easier synthetic routes than the carbon-based bridging groups.

The present invention also includes a method of preparing the novel alkyl-bridged stabilizer.

The present invention also includes a method of preparing PVC, CPVC, or blends thereof containing the novel alkyl-bridged stabilizer. Preferably, these compositions are prepared
30 according to Synthesis Route A or B described above.

CLAIMS

1. A stabilizer composition for halogen-containing polymers, the stabilizer comprising:
at least two tin-based centers; and
at least one bridging alkyl group between the at least two tin-based centers.
- 5 2. The stabilizer composition of claim 1, of the type $L_3Sn-X-SnL_3$.
3. The stabilizer composition of claim 1, of the type $L_2Sn-(X)(Y)-SnL_2$.
4. The stabilizer composition of claim 3 wherein X and Y are tin-terminated alkyl-based
bridging groups.
5. The stabilizer composition of claims 1-4 wherein X and/or Y is linear or branched,
10 saturated or unsaturated, with or without heteroatoms, with or without heterocycles, where alkyl
bridge is C1 to C80.
6. The stabilizer composition of claims 1-5 wherein L is a traditional ligand.
7. A thermal stabilizer composition for halogen containing polymers, the composition
comprising at least three repeating units of $-[SnL_2-X]_n$,
15 wherein X is a tin-terminated alkyl-based bridging group; and,
wherein L is a traditional ligand.
8. The thermal stabilizer of claim 7 wherein X is linear or branched, saturated or
unsaturated, with or without heteroatoms, with or without heterocycles, where alkyl bridge is C1
to C80.
- 20 9. The thermal stabilizer of claims 6, 7 or 8 wherein L is an ester of thioglycolic acid, a 2-
ME ester of C12-C18 fatty acids, a carboxylate, a maleate, a sulfide, 2-ME, a mercaptan, or any
combination of two or more of an ester of thioglycolic acid, a 2-ME ester of C12-C18 fatty acids,
a carboxylate, a maleate, a sulfide, 2-ME, or a mercaptan.
10. A composition of PVC, CPVC or a blend thereof, the composition comprising a
25 stabilizer, the stabilizer comprising:
at least two tin-based centers; and,
at least one bridging alkyl group between the at least two tin-based centers.
11. The composition of claim 10, wherein the stabilizer is of the type $L_3Sn-X-SnL_3$.
12. The composition of claim 10, wherein the stabilizer is of the type $L_2Sn-(X)(Y)-SnL_2$.
- 30 13. The composition of claim 12 wherein X and Y are tin-terminated alkyl-based bridging
groups.
14. The composition of claims 10-13 wherein X and/or Y is linear or branched, saturated or

unsaturated, with or without heteroatoms, with or without heterocycles, where alkyl bridge is C1 to C80.

15. The composition of claims 10-15 wherein L is a traditional ligand.

16. The composition of claim 15 wherein L is an ester of thioglycolic acid, a 2-ME ester of C12-C18 fatty acids, a carboxylate, a maleate, a sulfide, 2-ME, a mercaptan, or any combination of two or more of an ester of thioglycolic acid, a 2-ME ester of C12-C18 fatty acids, a carboxylate, a maleate, a sulfide, 2-ME, or a mercaptan.

17. A composition of PVC, CPVC or a blend thereof, the composition comprising a stabilizer, the stabilizer comprising at least three repeating units of $-\text{[SnL}_2\text{-X-]}_n$,

10 wherein X is a tin-terminated alkyl-based bridging group; and,
 wherein L is a traditional ligand.

18. The composition of claim 17 wherein X is linear or branched, saturated or unsaturated, with or without heteroatoms, with or without heterocycles, where alkyl bridge is C1 to C80.

19. The composition of claims 17 or 18 wherein L is an ester of thioglycolic acid, a 2-ME ester of C12-C18 fatty acids, a carboxylate, a maleate, a sulfide, 2-ME, a mercaptan, or any combination of two or more of an ester of thioglycolic acid, a 2-ME ester of C12-C18 fatty acids, a carboxylate, a maleate, a sulfide, 2-ME, or a mercaptan.

20. The composition of claims 10 or 17 wherein the composition contains at least 0.5% by weight of the stabilizer.

20 21. A method of preparing alkyl bridged thermal stabilizers of the type $\text{L}_3\text{Sn-X-SnL}_3$.

22. The invention as shown and described herein and subject to the ongoing and planned experimentation.