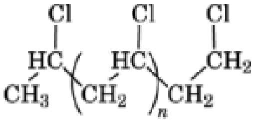
Kirk-Othmer Encyclopedia of Chemical Technology.

HEAT STABILIZERS

Heat stabilizers protect polymers from the chemical degrading effects of heat or uv irradiation. These additives include a wide variety of chemical substances, ranging from purely organic chemicals to metallic soaps to complex organometallic compounds. By far the most common polymer requiring the use of heat stabilizers is poly(vinyl chloride) (PVC). However, copolymers of PVC, chlorinated poly(vinyl chloride) (CPVC), poly(vinylidene chloride) (PVDC), and chlorinated polyethylene (CPE), also benefit from this technology. Without the use of heat stabilizers, PVC could not be the widely used polymer that it is, with worldwide production of nearly 16 million metric tons in 1991 alone (see Vinyl polymers).

The discussion centers on heat stabilizers for PVC because this polymer is the most important class of halogenated polymers requiring these chemical additives. PVC of ideal chemical structure (**1**) should be a relatively stable compound as predicted from model studies using 2,4,6-trichloroheptane [13049-21-3] (**2**) (1).



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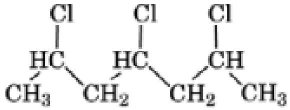
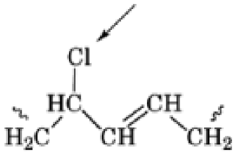


(2)

During the polymerization process the normal head-to-tail free-radical reaction of vinyl chloride deviates from the normal path and results in sites of lower chemical stability or defect sites along some of the polymer chains. These defect sites are small in number and are formed by autoxidation, chain termination, or chain-branching reactions. Heat stabilizer technology has grown from efforts to either chemically prevent or repair these defect sites. Partial structures **(3–6)** are typical of the defect sites found in PVC homopolymers (2–5).



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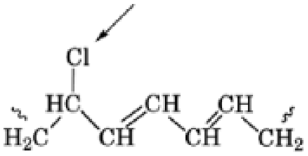

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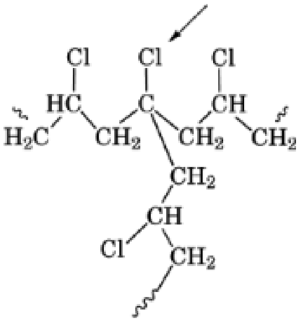

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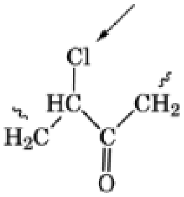


(6)

The dissociation energies for the highlighted (by pointing arrows) carbon–chloride bonds are significantly lower than that of a normal secondary C–Cl bond and can lead to thermal dehydrochlorination of the polymer backbone. In addition, the released HCl acts to catalyze further dehydrochlorination, indicating that both homolytic and ionic processes are involved. As the conjugated polyene sequences grow in length, further weakening of the carbon–chlorine bond occurs leading eventually to rapid, catastrophic dehydrochlorination, cross-linking, and chain scission resulting in loss of mechanical, electrical, and rheological properties in the final articles. A good indication of the onset of thermal degradation is the appearance of color in the polymer. When the conjugated polyenes reach a length of about seven double bonds, this chromophore begins to absorb visible light and appears yellow in color. Further degradation leads to brown and eventually black-colored products.

Some work has been conducted on the *in situ* or preventative stabilization of PVC, but these efforts have been largely unsuccessful and costly and have primarily centered on copolymerizing vinyl chloride with other vinyl monomers to block the conjugative ordering of the chlorine atoms in the polymer (6). The commercially important heat stabilizers are arrestive in nature. They chemically repair the defect sites or in some way reduce the deleterious nature of these sites during the processing and use of PVC articles. Just as important, most of the active heat stabilizers are also good HCl scavengers and reduce the catalytic effects of this deleterious by-product. PVC is so widely used because its properties are so easily manipulated by an inexhaustible variety of added components. Applications can range from rugged PVC pipes to crystal clear drinking water bottles to colorful toys to supple artificial leather depending on the choice of additives in the formulation. The needs and

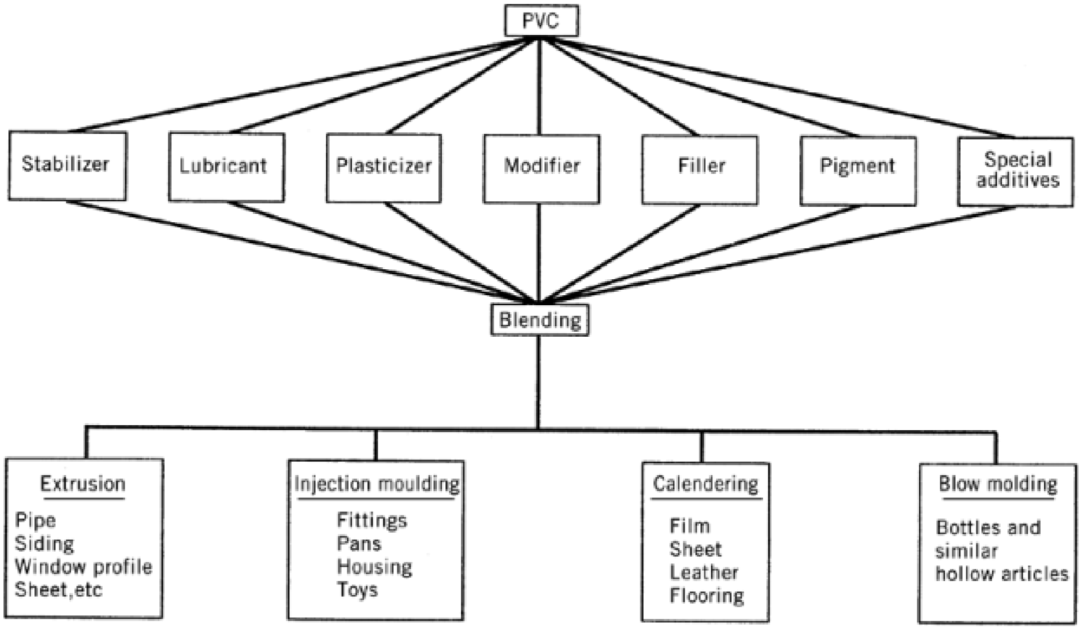


Fig. 1. PVC formulation alternatives.

choices of the heat stabilizer are dependent upon the final desired physical properties and the processes used to form the articles. Figure 1 shows the complexity of PVC formulation alternatives. Only the heat stabilizers and, normally, lubricants are essential additives to process the polymer. All of the other classes of additives are entirely discretionary.

In normal operations, PVC resin is intimately mixed with the desired ingredients under high intensity shear mixing conditions to result in a homogeneous dry powder compound. The heat stabilizers can be either liquids or powders and are added early in the blending cycle to afford stabilizing action during this operation. Preheating the resin to about the glass-transition temperature facilitates the adsorption of the liquid additives giving the final compound better powder flow properties and decreasing the bulk density. Post-compounding operations, eg, extrusion pelletizing, can increase the overall heat history of the polymer, thus necessitating slightly higher levels of heat stabilizers to compensate for this.

1. History of Stabilizer Development

Although PVC was discovered in the late nineteenth century in Germany,it was not until the discovery that certain lead soaps improved the thermal stability of the polymer in the early 1930s that commercialization of PVC began. Lead-based stabilizers have continually been used in certain applications, such as wire and cable coatings; however, because of toxicity and ecotoxicity concerns, considerable efforts are being made to eliminate all uses of lead-based heat stabilizers. In the mid-1930s, workers in the United States found that organotin carboxylates also provided good heat stability. The high activity, nonstaining nondusting characteristics, and complete compatibility, allowing total transparency, made the organotin stabilizers a good choice for rigid, flexible, and even plastisol end uses. During the 1940s, alkali and alkaline-earth metal soaps, especially those of cadmium, barium, zinc, and calcium, were discovered and commercialized as PVC heat stabilizers (see

Driers and metallic soaps). By the 1950s combinations of these metal soaps with organic costabilizers, such as phosphites and epoxides, demonstrated great processing latitude and cost effectiveness, particularly in plasticized PVC. Some of these formulations remain state-of the-art technology for certain end uses. Just as in the case for lead, considerable pressure has been exerted on the plastics industry to discontinue uses of cadmium for both stabilizers and pigments because of its high toxicity. Organotin mercaptide chemistry was introduced as a new class of PVC heat stabilizers during the 1950s and played a significant role in the development of many rigid PVC applications. The efficiency per unit dose remains unsurpassed for the organotin mercaptide-stabilized formulations for food packaging (qv), water pipes, weatherable construction panels, and molded parts. Antimony mercaptides were also discovered in the 1950s and did complete with the organotin mercaptides in rigid PVC applications for several years, but again, toxicity concerns have greatly diminished the use of this class of stabilizer.

2. Function of Stabilizers

Although great progress has been made since the 1960s to sort out the many reactions ongoing during the thermal degradation of PVC, much of the formulating and use of stabilizers remains an art in commercial practice. PVC degradation proceeds by both free-radical and ionic reactions, although the latter appears to be the more important route. Lewis acid catalysts, such as zinc chloride or hydrogen chloride, can greatly accelerate the rate of dehydrochlorination of the polymer. Heat stabilizers serve several distinct functions during PVC processing: absorption of hydrogen chloride, replacement of labile chlorines, prevention of autoxidation, and disruption of polyunsaturated sequences. An ancillary function of many heat stabilizers is provision of uv stability, leading to good weathering properties for the final articles. Good uv stability depends on having adequate heat stability because partially degraded PVC is susceptible to uv degradation regardless of the choice of uv absorber additives used.

2.1. Absorption of Hydrogen Chloride

Effective heat stabilizers have the ability to bind hydrogen chloride. Most stabilizer systems contain one or more metallic soaps or salts which readily undergo a simple acid–base reaction with the by-product hydrogen chloride as the PVC degrades:

$$\mathrm{M\,(X)}_n + \mathrm{HCl} \longrightarrow \mathrm{M\,(X)}_{n-1}\,\mathrm{Cl} + \mathrm{HX}$$

$$\mathrm{M\,(X)}_{n-1}\,\mathrm{Cl} + \mathrm{HCl} \longrightarrow \mathrm{M(X)}_{n-2}\mathrm{Cl}_2 + \mathrm{HX},\ \text{etc}$$

where M is a metal, usually Pb, Zn, Ca, Ba, or Cd, and X is a carboxylic acid, usually a weakly acidic fatty acid ligand. Typical examples of effective metal soaps and salts used as PVC stabilizers include lead stearate, dibasic lead phthalate, tribasic lead sulfate, zinc octanoate [557-09-5], barium tallate, cadmium 2-ethylhexanoate, calcium stearate, calcium nonylphenate [30977-64-1].

A new type of inorganic metal complex, called hydrotalcite has appeared (ca 1990). These synthetic minerals, functionally akin to zeolites, have layered structures of Al and Mg and function to trap hydrogen chloride between these layers (7). The hydrotalcite minerals are generally used with other stabilizers as part of a stabilizer system. A typical hydrotalcite may be represented by a formula such as $\mathrm{Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O}$. Many modifications can be made by changing the Al to Mg ratio and by including other metal salts, such as zinc oxide. Unlike most metallic salts, the hydrotalcites are compatible with PVC and can provide completely transparent PVC articles.

Many PVC stabilizer formulations also contain one or more organic costabilizers that can also absorb hydrogen chloride. Typical of these additives are epoxidized fatty acid esters and organophosphites:

$$P(OR)_3 + HCl \longrightarrow H{-}\overset{\overset{\displaystyle O}{\|}}{P}(OR)_2 + R{-}Cl$$

Organotin mercaptides can also absorb hydrogen chloride.

$$R{-\!\!-}Sn\,(SR')_3 + HCl \longrightarrow R{-\!\!-}Sn\,(SR')_2\,Cl + HSR'$$

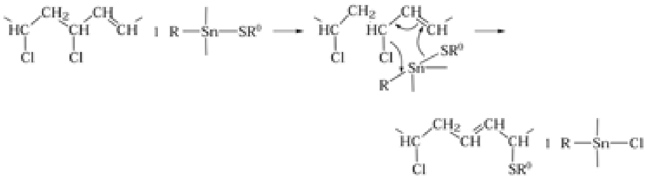
$$R{-\!\!-}Sn\,(SR')_2\,Cl + HCl \longrightarrow R{-\!\!-}Sn\,(SR')\,Cl_2 + HSR',\ \text{etc}$$

Although some of these stabilizers are added specifically to react with evolved hydrogen chloride, when the primary function of the stabilizer is to repair defect sites or disrupt autoxidation reactions, the degree that these stabilizers react with hydrogen chloride can actually detract from their primary function necessitating the use of higher levels of stabilizers in the PVC formulation.

2.2. Replacement of Labile Chlorines

When PVC is manufactured, competing reactions to the normal head-to-tail free-radical polymerization can sometimes take place. These side reactions are few in number yet their presence in the finished resin can be devastating. These abnormal structures have weakened carbon–chlorine bonds and are more susceptible to certain displacement reactions than are the normal PVC carbon–chlorine bonds. Carboxylate and mercaptide salts of certain metals, particularly organotin, zinc, cadmium, and antimony, attack these labile chlorine sites and replace them with a more thermally stable C–O or C–S bound ligand. These electrophilic metal centers can readily coordinate with the electronegative polarized chlorine atoms found at sites similar to structures **(3–6)**.

In the early 1960s, two different ^{14}C and one ^{113}Sn radio-labeled di-*n*-butyl-tin bis(isooctylthioglycolate) stabilizers were synthesized. Heat stability studies with these organotin compounds demonstrated the important replacement reactions leading to the following proposed mechanism (8). It is believed that the salts of zinc, cadmium (9), and lead (10) also undergo these reactions resulting in their respective ligands substituting on the PVC chains.



This mechanism not only accounts for the substitution of the more labile chlorine atom on the polymer chain, it also results in the elimination of a new potential initiation site by moving the double bond out of conjugation with any adjacent chlorine atoms. The newly formed C–O or C–S bonds, with $\Delta H > 484$ kJ/mol (100 kcal/mol), are significantly more thermally stable than even the normal C–Cl bonds in PVC at about 411 kJ/mol (85 kcal/mol) (11).

Ultimately, as the stabilization reactions continue, the metallic salts or soaps are depleted and the by-product metal chlorides result. These metal chlorides are potential Lewis acid catalysts and can greatly accelerate the undesired dehydrochlorination of PVC. Both zinc chloride and cadmium chloride are particularly strong Lewis acids compared to the weakly acidic organotin chlorides and lead chlorides. This significant complication is effectively dealt with in commercial practice by the co-addition of alkaline-earth soaps or salts, such as calcium stearate or barium stearate, ie, by the use of mixed metal stabilizers.

Displacement of activated chlorine atoms also proceeds with certain types of organic compounds, but only in the presence of Lewis acid catalysts. Particular examples include epoxides, polyhydric alcohols, trialkylphosphites (12), and β-aminocrotonates (13). These additives are commonly used in conjunction with metallic stabilizers to provide complete, high performance, commercial stabilizer packages.

2.3. Prevention of Autoxidation

The observation that PVC thermally degrades more rapidly in air than in a nitrogen atmosphere leads to the conclusion that the prevention of oxidative reactions can improve the thermal stability of PVC (14). When phenolic antioxidants (qv) are included in the formulation, the rate of hydrogen chloride evolution, at 180°C in air, is noticeably retarded. Therefore, good stabilizers must also provide antioxidant protection. Many of the additives previously discussed, which provide HCl scavenging and labile chlorine displacements, are also fairly good antioxidants as evidenced by their activity in other nonhalogenated polymers, particularly trialkyl- and triarylphosphites, β-aminocrotonates, and organotin mercaptides. The organotin mercaptides are particularly efficient in their reduction of hydroperoxides (15):

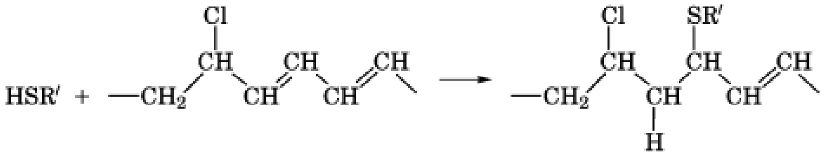
$$R_2Sn(SR')_2 + \text{—}CH_2\text{—}\underset{OOH}{\underset{|}{C}H}\text{—}CH_2\text{—} \longrightarrow [R_2SnO]_n + \text{—}CH_2\text{—}\underset{OH}{\underset{|}{C}H}\text{—}CH_2\text{—} + R'S\text{—}SR'$$

2.4. Disruption of Polyunsaturated Sequences

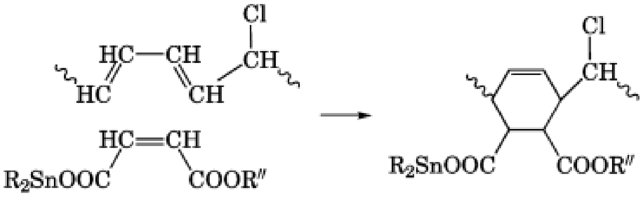
Sequential lengthening of the conjugated double bonds along a PVC molecule leads to the gradual development of color resulting from absorption of visible light (see Color). This lengthening conjugation further weakens the already weak allylic C–Cl bonds and leads to further loss of hydrogen chloride which, in turn, catalyzes further degradation. Left unchecked, the complete catastrophic degradation of the polymer is imminent.

Disruption of the conjugation of these long polyene groups can lead to color bleaching of the partially degraded PVC. Simple mercaptans effectively add to these highly reactive double bonds (16). Organotin mercaptides are also known to undergo this reaction, although it is likely that the actual reagent is the free mercaptan resulting from reaction with evolved HCl (17):

$$R_2Sn(SR')_2 + HCl \longrightarrow R_2\underset{Cl}{\underset{|}{S}}nSR' + HSR'$$



The organotin maleate and maleate half-ester derivatives also exhibit this bleaching effect reportedly by a Diels-Alder addition reaction (18). The reaction is specific to the organotin maleates; other organotin carboxylates containing normal dieneophiles fail to produce similar results (19).



3. Stabilizer Test Methods

Heat stabilizers are tested in a variety of ways to simulate their performance during PVC processing, ie, calendering, extrusion, pressing, heat curing, and molding. Because of the wide number of these applications, it is impossible to provide one or two definitive laboratory tests for all stabilizer products. In general, heat stabilizers are tested as a component in a complete formulation where each ingredient has a measured effect on the overall performance. Stabilizer performance is generally evaluated by visually inspecting the color of the test pieces as a function of heating and processing time. Static oven aging, dynamic two-roll milling, and torque rheometry are three of the most common tests used to evaluate heat stabilizers. A whole host of tests are conducted on the final products of the various processes to make judgments as to the effectiveness of any particular PVC formulation. Standard tests for stabilizer evaluation include ASTM D2115, Oven Stability of PVC Compounds; ASTM D2538, Fusion of PVC Compounds Using a Torque Rheometer; ASTM D1499, Stability of PVC to Light Exposure; and DIN 53-381F, Heat Stability of PVC Compounds by Metrastat Oven.

4. Classes of Heat Stabilizers

4.1. Organotin Compounds

Organotin-based heat stabilizers are the most efficient and universally used PVC stabilizers. Nearly 40% of the 64,000 metric tons of stabilizers used in the United States during 1992 were organotin-based products. These are all derivatives of tetravalent tin, and all have either one or two alkyl groups covalently bonded directly to the tin atom. The commercially important alkyltins are the methyltin, *n*-butyltin, and *n*-octyltin species. For about 10 years between 1980 and 1990, estertin or β-carboalkoxyethyltin derivatives were produced commercially. Aryltin and branched alkyltin derivatives are relatively poor heat stabilizers (20). The class of tri-*n*-alkyltin compounds are known to be toxic, and because they are very poor stabilizers, they are completely avoided in PVC heat stabilizer applications. The anionic ligands can be chosen from a wide variety of groupings but are normally chosen from maleate, alkylmaleate, esters of thioglycolic acid or esters of mercaptoethanol, depending on the end use application and the processing conditions for the PVC compound. Almost all organotin stabilizer products are formulated with mixtures of monoalkyltin and dialkyltin species in a ratio to maximize the stability of the resin together with all of the other microingredients in a given PVC formulation.

4.1.1. Alkyltin Intermediates

For the most part, organotin stabilizers are produced commercially from the respective alkyltin chloride intermediates. There are several processes used to manufacture these intermediates. The desired ratio of monoalkyltin trichloride to dialkyltin dichloride is generally achieved by a redistribution reaction involving a second-step reaction with stannic chloride (tin(IV) chloride). By far, the most easily synthesized alkyltin chloride intermediates are the methyltin chlorides because methyl chloride reacts directly with tin metal in the presence of a catalyst to form dimethyltin dichloride cleanly in high yields (21). Coaddition of stannic chloride to the reactor leads directly to almost any desired mixture of mono- and dimethyltin chloride intermediates:

$$\mathrm{Sn^0 + 2\ Cl_2 \longrightarrow SnCl_4}$$

$$\mathrm{Sn^0 + 2\ CH_3Cl \longrightarrow (CH_3)_2\,SnCl_2}$$

$$(y + x)\ \ \mathrm{(CH_3)_2\,SnCl_2} + x\ \mathrm{SnCl_4} \longrightarrow y\ \ \mathrm{(CH_3)_2\,SnCl_2} + 2x\ \mathrm{CH_3SnCl_3}$$

The direct reaction of other alkyl chlorides, such as butyl chloride, results in unacceptably low overall product yields along with the by-product butene resulting from dehydrochlorination. All alkyl halides having a hydrogen atom in a β- position to the chlorine atom are subject to this complication.

The other important direct alkylation processes involve reaction of electron-rich olefinic compounds with either tin metal or stannous chloride (tin(II) chloride) in the presence of stoichiometric amounts of hydrogen chloride (22). Butyl acrylate ($\mathrm{R = C_4H_9}$) was used commercially in this process to prepare the estertin or β-carboalkoxyethyltin chlorides as illustrated in the following.

$$\mathrm{Sn^0 + 2\ HCl + 2\ H_2C{=}CHCOOR \longrightarrow (ROOCCH_2CH_2)_2\,SnCl_2}$$

$$\mathrm{SnCl_2 + HCl + H_2C{=}CHCOOR \longrightarrow ROOCCH_2CH_2SnCl_3}$$

A number of activated olefinic compounds react very well in this scheme including methacrylates, crotonates, acrylonitrile, and vinyl ketones. These reactions are typically run in an etherial solvent and can be run without the complications of undesirable side reactions leading to trialkylated tin species.

The other commercially important routes to alkyltin chloride intermediates utilize an indirect method having a tetraalkyltin intermediate. Tetraalkyltins are made by transmetallation of stannic chloride with a metal alkyl where the metal is typically magnesium or aluminum. Subsequent redistribution reactions with additional stannic chloride yield the desired mixture of monoalkyltin trichloride and dialkyltin dichloride. Both n-butyltin and n-octyltin intermediates are manufactured by one of these schemes.

$$\mathrm{2\ R_2Mg + SnCl_4 \longrightarrow R_4Sn + 2\ MgCl_2}$$

$$4\ R_3Al + 3\ SnCl_4 \longrightarrow R_4Sn + 4\ AlCl_3$$

$$R_4Sn + 2\ SnCl_4 \longrightarrow 2\ RSnCl_3 + R_2SnCl_2$$

4.1.2. Stabilizer Synthesis

The selected alkyltin chloride intermediate reacts with either a carboxylic acid or a mercaptan in the presence of an appropriate base, such as sodium hydroxide, to yield the alkyltin carboxylate or alkyltin mercaptide heat stabilizer. Alternatively, the alkyltin chloride can react with the base to yield the alkyltin oxide, which may or may not be isolated, for subsequent condensation with the selected carboxylic acid or mercaptan.

$$R_2SnCl_2 + 2\ R'SH + 2\ NaOH \longrightarrow R_2Sn\left(SR'\right)_2 + 2\ NaCl + H_2O$$

$$R_2SnCl_2 + 2\ NaOH \longrightarrow (R_2SnO)_n + 2\ NaCl + H_2O$$

$$(R_2SnO)_n + 2\ R'COOH \longrightarrow R_2Sn\left(OOCR'\right)_2 + H_2O$$

Typically, alkyltin carboxylates are prepared from isolated alkyltin oxides because this route leads to higher efficiency and purity for these products. In many of the modern alkyltin mercaptide stabilizers, sulfide sulfur ligands are also used in combination with mercaptide ligands. Usually the sulfide groups are introduced as a metal sulfide and added along with the mercaptan and base to the alkyltin chloride intermediate. The resulting stabilizer is a mixture of products having both sulfide and mercaptide groups bound to each of the alkyltin compounds.

4.1.3. Costabilizers

In most cases the alkyltin stabilizers are particularly efficient heat stabilizers for PVC without the addition of costabilizers. Many of the traditional coadditives, such as antioxidants, epoxy compounds, and phosphites, used with the mixed metal stabilizer systems, afford only minimal benefits when used with the alkyltin mercaptides. Mercaptans are quite effective costabilizers for some of the alkyltin mercaptides, particularly those based on mercaptoethyl ester technology (23). Combinations of mercaptan and alkyltin mercaptide are currently the most efficient stabilizers for PVC extrusion processes. The level of tin metal in the stabilizer composition can be reduced by up to 50% while maintaining equivalent performance. Figure 2 shows the two-roll mill performance of some methyltin stabilizers in a PVC pipe formulation as a function of the tin content and the mercaptide groups at 200°C. The test formulation contains 100 parts of PVC (Fikentscher $K = 65$), 1.2 parts of paraffin wax, 0.6 parts of calcium stearate, and 0.4 parts of methyltin-based stabilizers.

The various lubricants formulated into PVC to improve the processing can also enhance the performance of the stabilizer. In pigmented applications, calcium soaps, eg, calcium stearate, are commonly used as internal lubricants to promote PVC fusion and reduce melt viscosity. This additive is also a powerful costabilizer for the alkyltin mercaptide stabilizers at use levels of 0.2 to 0.7 phr. Calcium stearate can significantly improve the early color and increase the long-term stability at low levels; however, as the concentration increases, significant yellowing begins to occur.

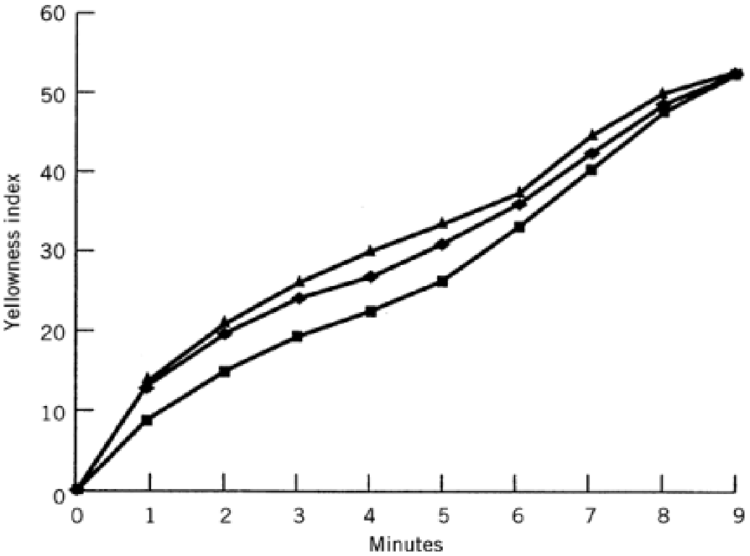


Fig. 2. Yellowness index vs two-roll mill heat stability, where the mercaptide ligands,—SCH_2COOR (▲), –SCH_2CH_2COOR' (◆), and –$SCH_2CH_2COOR'+HSCH_2CH_2COOR'$ (■), are 17, 9, and 6% Sn, respectively. $R=C_8H_{17}$; $R'=C_{18}H_{33}$.

4.1.4. Commercial Stabilizers

A wide variety of alkyltin stabilizers have been used commercially since the 1960s because no particular compound universally satisfies every requirement of PVC processing. In general, the alkyltin mercaptides exhibit the highest overall heat stability together with imparting excellent rheological properties to the polymer. The alkyltin carboxylates, on the other hand, are unsurpassed for imparting excellent weathering properties but generally give poor rheological characteristics. Table 1 lists the commercially important alkyltin stabilizer compounds. These compounds typically are formulated with several different adjuvants, both active and inert, to tailor their performance to given commercial applications. Table 2 lists the stabilizer manufacturers and the trade names associated with each.

4.1.5. Economics

The pricing of stabilizers is generally based on the PVC processing application, the type of PVC used, and the other microingredients present in the formulation. In facile extrusion operations, such as the manufacture of PVC pipes, stabilizer formulations usually contain relatively low levels of the alkyltin compounds; about 5–10% tin is usual. More difficult extrusion applications, such as window lineals, extruded sheets, and house siding, require significantly higher levels of more efficient stabilizers. Injection molding of pipe fittings and accessories also requires more efficient stabilizers. Blow molding and calendered sheet applications, particularly where glass-like clarity is required, are the most demanding processing conditions. Stabilizers for these applications are typically the highest efficiency formulations in the North American marketplace. Table 3 summarizes the typical applications of the tin stabilizers and their price range.

4.1.6. Health and Safety Aspects

Many of the alkyltin stabilizers are considered safe to use in almost every conceivable end use for PVC (24). Particularly, the U.S. FDA, German BGA, and Japanese JHPA have sanctioned the use of mixtures of dimethyltin and monomethyltin isooctyl thioglycolate (25), mixtures of di-*n*-octyltin isooctyl thioglycolate and mono-*n*-octyltin isooctyl thioglycolate (26), and poly(di-*n*-octyltin maleate) as the primary heat stabilizers for

Table 1. Commercially Important Alkyltin Compounds

Name	CAS Registry Number	Structure
poly(dibutyltin maleate)	[32076-99-6]	$\left[(C_4H_9)_2SnOOCCH{=}CHCOO \right]_n$
poly(dioctyltin maleate)	[32077-00-2]	$\left[(C_8H_{17})_2SnOOCCH{=}CHCOO \right]_n$
dibutyltin bis(butyl maleate)	[17209-76-6]	$(C_4H_9)_2Sn(OOCCH{=}CHCOOC_4H_9)_2$
dimethyltin bis(2-ethylhexyl thioglycolate)	[26636-01-1]	$(CH_3)_2Sn(SCH_2COOC_8H_{17})_2$
dibutyltin bis(2-ethylhexyl thioglycolate)	[25168-24-5]	$(C_4H_9)_2Sn(SCH_2COOC_8H_{17})_2$
dioctyltin bis(2-ethylhexyl thioglycolate)	[26401-97-8]	$(C_8H_{17})_2Sn(SCH_2COOC_8H_{17})_2$
dibutyltin sulfide	[4253-22-9]	$[(C_4H_9)_2SnS]_3$
methyltin tris(2-ethylhexyl thioglycolate)	[54849-38-6]	$CH_3Sn(SCH_2COOC_8H_{17})_3$
butyltin tris(2-ethylhexyl thioglycolate)	[25852-70-4]	$C_4H_9Sn(SCH_2COOC_8H_{17})_3$
octyltin tris(2-ethylhexyl thioglycolate)	[26401-86-8]	$C_8H_{17}Sn(SCH_2COOC_8H_{17})_3$
methyltin tris(2-mercaptoethyl oleate)	[59118-79-5]	$CH_3Sn(SCH_2CH_2OCOC_{17}H_{33})_3$
methyltin (2-mercaptoethyl oleate)sulfide	[68442-12-6]	$CH_3Sn(SCH_2CH_2OCOC_{17}H_{33})(S)$

Table 2. U.S. Producers and Trade Names of Alkyltin Stabilizers and Mixed Metal Stabilizers

Producers	Alkyltin trade names	Mixed metal trade names
Akcros Chemicals Inc., Dobbs Ferry, N.Y.	Stanclear	Interstab
Atochem North America, Philadelphia, Pa.	Thermolite	
Cardinal Stabilizers, Columbia, S.C.	Cardinal Clear	
Morton International, Cincinnati, Ohio	Advastab	
Polymer Additives Group, Witco Inc., New York, N.Y.	Mark	Mark
Ferro Corp., Bedford, Ohio		Therm-Chek
M-R-S Chemicals, Inc., Maryland Heights, Mo.		MiRaStab
Synthetic Products Co., Cleveland, Ohio		Synpro/Synpron

Table 3. Typical Uses And Prices For Alkyltin Stabilizers

Application	Stabilizer type	Use level[a]	Tin, %	Price,[b] $/kg
	Extrusion			
PVC pipe	mercaptide/mercaptan	0.3–0.6	5–10	2.75–4.50
window profile/siding	mercaptide	1.3–1.7	14–19	7.00–10.00
siding substrate	mercaptide/mercaptan	0.7–1.2	9–14	4.00–8.50
weatherable clear	carboxylate	2.5–3.5	14–20	9.00–14.00
	Molding			
pipe fittings	mercaptide	1.3–2.0	16–19	8.00–10.00
	mercaptide/mercaptan	1.3–2.0	11–16	4.50–8.50
food bottles	methyl/octyltin mercaptides	0.8–1.4	16–19	8.00–11.00
	Calendered sheet			
food packaging film	methyl/octyl tin mercaptides	0.8–1.4	16–19	8.00–11.00
general-purpose film	mercaptides	1.0–2.0	16–19	8.00–10.00

[a] Parts per hundred parts of PVC resin.
[b] 1992.

PVC used for food packaging purposes. These same *n*-octyltin products are also approved for use in pharmaceutical applications such as pill containers and PVC tubings (27). Since the migration into water of the alkyltin mercaptide-based products from PVC is found to be extremely low, most of these stabilizers are suitable for pipes carrying drinking water according to NSF International (28), a private industry supported regulatory agency complying with all current U.S. EPA guidelines. Tin-stabilized formulations for drinking water pipes have been in use since the late 1960s throughout North America. A risk analysis on the use of these stabilizers in PVC has been compiled (29) which emphasizes the low toxicity and ecotoxicity of this class of PVC stabilizers. The key to the safety and low toxicity for the alkyltin stabilizers lies in the fact that modern manufacturing practices eliminate the production of any significant amounts of the more toxic trialkyltin species from all stabilizers.

Several studies have chosen to focus on the volatility of the alkyltin stabilizers and their by-products of PVC stabilization, alkyltin chlorides, during the calendering operation because this process presents a worst case scenerio for PVC processing: relatively high stabilizer levels, very high exposed surface area of hot PVC melt, and high processing temperatures. In two of these studies conducted by the NATEC Institute in Germany, extremely low levels of volatilized alkyltin compounds were observed (30). Similar studies conducted by Morton International confirmed these results (31). All of these studies demonstrate that the level of volatile tin compounds in the air during PVC processing operations are significantly below the TLV of 0.1 mg/m^3 for tin compounds established for the United States workplace.

4.2. Mixed Metal Stabilizers

The second most widely used class of stabilizers, with nearly 24,000 metric tons sold in the United States in 1992, are the mixed metal combinations. These products predominate in the flexible PVC applications in the United States; however, they find competition from the lead-based products in Europe. The only noteworthy flexible PVC application where the mixed metal products do not dominate is for electrical wire and cable coatings where the lead products are preferred, although alternative mixed metal stabilizers are continually being sought to replace the leads in this application, as well. In Europe, mixed metal stabilizers are preferred for the extruded rigid building profiles because they provide good weathering and physical properties to the PVC in this use.

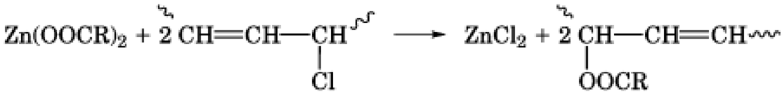
The commercially important alkali and alkaline-earth metals used in these stabilizer systems are based on the salts and soaps of calcium, zinc, magnesium, barium, and cadmium. These metal salts and soaps are combined to make a stabilizer system; there is synergy between these compounds during PVC processing. Because the chloride salts of both zinc and cadmium are easily formed during PVC processing and are strong Lewis acids, it is not surprising that short stability times and catastrophic degradation are observed when either zinc or cadmium soaps are used alone. In fact, zinc carboxylates, by themselves, are worthless as PVC stabilizers. When zinc and cadmium salts are combined with other compounds, which prevent or delay the formation of the respective Lewis acids, good PVC stability can be obtained. Particularly, the salts of calcium and barium serve this purpose. Other organic compounds, such as phosphites, epoxides, polyols, and β-diketones, can also be added to enhance the performance further.

The most popular commercial products are combinations including calcium–zinc, barium–calcium–zinc, barium–zinc, and barium–cadmium. Barium–cadmium combinations were, at one time, the most widely used mixtures, but as of the early 1990s their use has decreased considerably due to toxicity and ecotoxicity concerns surrounding cadmium compounds. Modern calcium–zinc, barium–zinc, and barium–calcium–zinc mixtures are touted as effective replacements for many of these barium–cadmium formulations. The safety of these newer products are unquestioned and certain calcium–zinc mixtures are widely used to stabilize PVC food packaging, mineral water bottles, and pharmaceutical containers throughout the world. In many applications, particularly in plasticized PVC, the mixed metal products effectively offer the right combination of processibility, heat and light stability, low odor, and nonsulfur staining characteristics to be the best choice of stabilizer.

4.2.1. Stabilization Mechanism

Zinc and cadmium salts react with defect sites on PVC to displace the labile chloride atoms (32). This reaction ultimately leads to the formation of the respective chloride salts which can be very damaging to the polymer. The role of the calcium and/or barium carboxylate is to react with the newly formed zinc–chlorine or cadmium–chlorine bonds by exchanging ligands (33). In effect, this regenerates the active zinc or cadmium stabilizer and delays the formation of significant concentrations of strong Lewis acids.

Reaction with defect site



$$\mathrm{Zn(OOCR)_2 + 2\,{\sim}CH{=}CH{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{\sim} \longrightarrow ZnCl_2 + 2\,{\sim}\underset{\displaystyle OOCR}{\underset{|}{CH}}{-}CH{=}CH{\sim}}$$

Regeneration of stabilizer

$$\mathrm{ZnCl_2 + Ca\left(OOCR'\right)_2 \longrightarrow Zn\left(OOCR'\right)_2 + CaCl_2}$$

The chloride salts of calcium and barium are weak Lewis acids and do not tend to promote PVC degradation. By carefully choosing the ratio of zinc or cadmium salt to calcium and/or barium soap, the overall stabilizing effects can be tuned to an optimum level for a given application or process. The typical mixed metal products usually contain between a 2:1 to 1:2 ratio of the metal salts. Ultimately, though, these delaying tactics are spent and the zinc or cadmium chlorides form resulting in rapid hydrogen chloride evolution and cross-linking reactions leading to a brittle, black, crumbling product of no value. Although it is not completely understood, the maximum level of stability for these mixtures is reached at a concentration of stabilizer of about 4–5% of the polymer. Adding higher amounts of stabilizer has little effect on the overall stability of the PVC; this same phenomenon is also observed for the alkyltin stabilizers.

4.2.2. Mixed Metal Stabilizer Synthesis

The mixed metal salts and soaps are generally prepared by reaction of commercially available metal oxides or hydroxides with the desired C_8–C_{18} carboxylic acids. The liquid stabilizer products sometimes employ metal alkylphenates and over-based metal alkylphenates, particularly calcium or barium alkylphenates, in place of the metal carboxylates. The desired ratio of metal salts can be achieved by coprecipitation from the appropriate ratio of metal oxides or, more often, from isolated metal salts by blending to give the correct ratios. During the blending process, a variety of other coadditives or secondary stabilizers, such as phosphites, polyols, epoxides, β-diketones, or antioxidants, can be added to complete the stabilizer package. Modern stabilizers are provided as either liquids or nondusting powders which are easily handled in totally automated compounding operations.

4.2.3. Commercial Stabilizers

There is a great variety of commercial formulations utilizing the mixture of the alkali and alkaline-earth metal salts and soaps. In many cases, products are custom formulated to meet the needs of a particular application or customer. The acidic ligands used in these products vary widely and have dramatic effects on the physical properties of the PVC formulations. The choice of ligands can affect the heat stability, rheology, lubricity, plate-out tendency, clarity, heat sealability, and electrical and mechanical properties of the final products. No single representative formulation can cover the variety of PVC applications where these stabilizers are used.

Typically, solid stabilizers utilize natural saturated fatty acid ligands with chain lengths of C_8–C_{18}. Zinc stearate [557-05-1], zinc neodecanoate [27253-29-8], calcium stearate [1592-23-0], barium stearate [6865-35-6], and cadmium laurate [2605-44-9] are some examples. To complete the package, the solid products also contain

Table 4. Formulations of Mixed Metal Stabilizers, %

Liquid formula	Solid formula	Paste formula
barium tallate overbase, 30	barium stearate, 25	zinc stearate, 15
barium bis(nonylphenate), 20	cadmium laurate, 50	calcium stearate, 15
zinc 2-ethylhexanoate, 15	bisphenol A, 5	tris(nonylphenyl) phosphite, 30
diphenyl decylphosphite, 30	pentaerythritol, 20	
dibenzoylmethane, 5		epoxidized soya oil, 40

other solid additives such as polyols, antioxidants, and lubricants. Liquid stabilizers can make use of metal soaps of oleic acid, tall oil acids, 2-ethyl-hexanoic acid, octylphenol, and nonylphenol. Barium bis(nonylphenate) [41157-58-8], zinc 2-ethylhexanoate [136-53-8], cadmium 2-ethylhexanoate [2420-98-6], and overbased barium tallate [68855-79-8] are normally used in the liquid formulations along with solubilizers such as plasticizers, phosphites, and/or epoxidized oils. The majority of the liquid barium–cadmium formulations rely on barium nonylphenate as the source of that metal. There are even some mixed metal stabilizers supplied as pastes. The U.S. FDA approved calcium–zinc stabilizers are good examples because they contain a mixture of calcium stearate and zinc stearate suspended in epoxidized soya oil. Table 4 shows examples of typical mixed metal stabilizers.

4.2.4. Costabilizers

The variety of known costabilizers for the mixed metal stabilizers is a very long listing. There are, however, a relatively small number of commercially used costabilizers. Some of these additives can also be added by the PVC compounder or processor in addition to the stabilizer package to further enhance the desired performance characteristics. The epoxy compounds and phenolic antioxidants are among the most commonly used costabilizers with the mixed metal stabilizers.

4.2.4.1. Epoxy Compounds. Epoxidized soya oil (ESO) is the most widely used epoxy-type additive and is found in most mixed metal stabilized PVC formulations at 1.0–3.0 phr due to its versatility and cost effectiveness. Other useful epoxy compounds are epoxidized glycerol monooleate, epoxidized linseed oil, and alkyl esters of epoxidized tall oil fatty acid.

4.2.4.2. Antioxidants. Phenolic antioxidants, added at about 0.1–0.5 phr, are usually chosen from among butylated hydroxytoluene [128-37-0] (BHT), and *p*-nonylphenol [104-40-5] for liquid stabilizer formulations and bisphenol A [80-05-7] (2,2-bis-(*p*-hydroxyphenyl)propane) for the solid systems. Low melting thioesters, dilauryl thiodipropionate [123-28-4] (DLTDP) or distearyl thiodipropionate [693-36-7] (DSTDP) are commonly added along with the phenolics to enhance their antioxidant performance. Usually a 3:1 ratio of thiodipropionate to phenolic antioxidant provides the desired protection. Most mixed metal stabilizer products contain the antioxidant ingredient.

4.2.4.3. Polyols. Polyols, such as pentaerythritol [115-77-5], dipentaerythritol [126-58-9], and sorbitol [50-70-4], most likely chelate the active metal centers to reduce their activity toward the undesired dehydrochlorination reaction. These additives are generally included in the stabilizer formulation, used in the range of 0.2 to 0.7 phr.

4.2.4.4. Phosphites. Tertiary phosphites are also commonly used and are particularly effective in most mixed metal stabilizers at a use level of 0.25–1.0 phr. They can take part in a number of different reactions during PVC processing: they can react with HCl, displace activated chlorine atoms on the polymer, provide antioxidant functionality, and coordinate with the metals to alter the Lewis acidity of the chloride salts. Typical examples of phosphites are triphenyl phosphite [101-02-0], diphenyl decyl phosphite [3287-06-7], tridecyl phosphite [2929-86-4], and polyphosphites made by reaction of PCl_3 with polyols and capping alcohols. The phosphites are often included in commercial stabilizer packages.

4.2.4.5. β-Diketones. A new class of costabilizer has emerged that is effective with the mixed metal systems. The β-diketones can significantly enhance the performance of the calcium–zinc and barium–calcium–zinc systems when used at 0.1 to about 0.7 phr. Although relatively expensive, the β-diketones greatly improve early color stability and rheological performance while benefitting the weather-ability of the final PVC articles. Typical of these additives are dibenzoylmethane [2929-86-4] and stearoyl benzoyl methane [58446-52-9]. These additives are generally formulated as part of the mixed metal stabilizer package.

4.2.4.6. Specialty Amines. Some substituted nitrogenous compounds can provide similar benefits. Esters of 2-aminocrotonate and bis-2-aminocrotonate, and appropriately substituted dihydropyridines, eg, 3,5-bis-lauryloxycarboxy-2,6-dimethyl-1,4-dihydropyridine [37044-66-7] and 3,5-bis-ethoxycarboxy-2,6-dimethyl-1,4-dihydropyridine [1149-23-1], are examples of these costabilizers. These relatively expensive costabilizers are used at 0.1–0.7 phr and are particularly effective when added to the calcium–zinc stabilizers.

4.2.4.7. Hydrotalcite. Synthetic hydrotalcite minerals are gaining commercial acceptance for their ability to costabilize PVC in the presence of other primary stabilizers (see Table 2). The performance of the mixed metal stabilizers are particularly boosted when an equal part level, about 2–3 phr, of hydrotalcite is added to the PVC formulation. These minerals function by trapping HCl within the layered lattice arrangement of atoms. The formula, $Mg_4Al_2(OH)_{12}CO_3{\cdot}3H_2O$, is commonly written; however, these minerals are generally nonstoichiometric by nature and can include some amounts of alternative elements in their compositions. They function similarly to the zeolites but exist in layered structures and have a different trapping mechanism. In addition to their performance enhancement, the hydrotalcite minerals are compatible with PVC and can be used effectively in clear PVC applications as well as the pigmented formulations.

4.2.5. Economics

As with the alkyltin stabilizers, the market pricing of the mixed metal stabilizers tend to be directed by the particular application. The calcium–zinc and barium–cadmium packages are typically used at 2.0–4.0 parts per hundred of PVC resin (phr) in the formulation. These completely formulated products are sold for $2.50–$4.40/kg for the liquid products and $3.20–$6.50/kg for the solids and pastes. The higher efficiency products aimed at rigid applications tend toward the higher end of the cost range.

The basic metal salts and soaps tend to be less costly than the alkyltin stabilizers; for example, in the United States, the market price in 1993 for calcium stearate was about $1.30–$1.60, zinc stearate was $1.70–$2.00, and barium stearate was $2.40–$2.80/kg. Not all of the coadditives are necessary in every PVC compound. Typically, commercial mixed metal stabilizers contain most of the necessary coadditives and usually an epoxy compound and a phosphite are the only additional products that may be added by the processor. The required costabilizers, however, significantly add to the stabilization costs. Typical phosphites, used in most flexible PVC formulations, are sold for $4.00–$7.50/kg. Typical antioxidants are bisphenol A, selling at $2.00/kg; *p*-nonylphenol at $1.25/kg; and BHT at $3.50/kg, respectively. Pricing for ESO is about $2.00–$2.50/kg. Polyols, such as pentaerythritol, used with the barium–cadmium systems, sells at $2.00, whereas the derivative dipentaerythritol costs over three times as much. The β-diketones and specialized dihydropyridines, which are powerful costabilizers for calcium–zinc and barium–zinc systems, are very costly. These additives are $10.00 and $20.00/kg, respectively, contributing significantly to the overall stabilizer costs. Hydrotalcites are sold for about $5.00–$7.00/kg.

4.2.6. Health and Safety Aspects

Overall, the mixed metal stabilizer industry is undergoing significant change during the early 1990s due to the increasing restrictions on cadmium compounds. Most of the research effort has focused on new products to replace the traditional barium–cadmium formulations with technical and cost-effective products. In some regions, cadmium is allowed only in applications where there are no effective replacement technologies. The replacement products generally contain salts of barium, zinc, calcium, and/or potassium; all these compositions are considered safe in the many flexible PVC end uses.

Calcium–zinc soaps are used in many PVC food container applications because these heat stabilizers are universally accepted as safe by the U.S. FDA, German BGA, Japanese JHPA, and other government regulatory groups.

4.3. Lead Stabilizers

In use since the 1940s, the lead-based stabilizers have played an extremely important role in the development of PVC as a high performance polymer. The myriad of toxicological and ecotoxicological problems surrounding the use of any lead chemicals has restricted lead stabilizers to uses in flexible PVC wire and cable coatings in the United States with consumption in 1992 estimated at 15,000 metric tons. In Europe and Asia, the lead stabilizers predominate for wire and cable uses and are also widely used to stabilize PVC pipe and weatherable building profiles. These are solid products and are supplied as powders, flakes, or strands, usually in special packaging to control dusting.

The commonly used commercial lead-based PVC stabilizers rely on one or more lead(II) oxide groups bound to the primary bivalent lead salt. These over-based lead compounds have higher levels of lead and are more basic, thus reacting more readily with evolved hydrogen chloride during PVC processing. It is typical to find combinations of mono-, di-, and tribasic lead compounds as the primary heat stabilizers because these often work together to provide a good balance of both early and long-term stability. The choice of anion also effects the performance by reducing the reactivity of the lead oxide toward other ingredients in the formulation as well as the polymer. The stabilization by-product, lead dichloride, is nearly inert, ie, it is white in color, nonionic, insoluble in water, and has low Lewis acidity. It is these properties that give lead-stabilized PVC such a low conductivity in electrical applications. Commercially, most lead stabilizers are combinations containing lead stearates which also provide good lubrication to PVC compounds. Additional lubricants often are not necessary for thermally processing these PVC formulations.

Their high toxicity has greatly limited the applications for lead stabilizers in North America and is now spreading around the world. Environmental agencies such as The World Health Organization (WHO) and the U.S. EPA are continually lowering recommended human exposures to lead compounds. Another limitation is that lead products have a high refractive index and as a result can only be used in opaque applications. Overbased lead salts have a high degree of reactivity and tend to interact, many times disfavorably, with other ingredients in the formulation. Also, they have a very high specific gravity compared to other stabilizers, resulting in higher density PVC products. Lastly, the lead stabilizers can react with almost any source of sulfur to form black lead sulfide, the so-called lead stain phenomenon. Despite these drawbacks, they remain highly effective PVC heat stabilizers.

4.3.1. Stabilization Mechanism

Traditionally, lead salts were thought to perform only as acid scavengers during PVC stabilization; it is likely that this activity leads to good long-term stability. Bivalent lead compounds can readily form complexes, and recently workers have proposed that these products also displace labile chlorines on the polymer in a fashion similar to the mixed metal stabilizers. A free-radical mechanism is proposed for this displacement which improves the early color hold of the PVC (10). Because the lead chloride is such a weak Lewis acid, costabilizers used in the mixed metal systems are generally ineffective and unnecessary. Increasing stabilizer concentration in the polymer generally leads to increased stability times.

4.3.2. Lead Stabilizer Synthesis

Most commercial stabilizers are produced by reaction of a water slurry of lead oxide with the appropriate acid while heating, yielding a solid product with a particle size of about 1 μm. This condensation proceeds leaving

Table 5. Principal Lead Stabilizers

Stabilizer	CAS Registry Number	Formula	PbO, %	Specific gravity
tribasic lead sulfate	[12202-17-4]	$PbSO_4\cdot 3PbO\cdot H_2O$	89	6.9
dibasic lead phosphite	[12141-20-7]	$PbHPO_3\cdot 2PbO\cdot \frac{1}{2}H_2O$	90	6.1
dibasic lead phthalate	[17976-43-1]	$C_4H_4(COO)_2Pb\cdot 2PbO$	80	4.2
basic lead carbonate	[1319-46-6]	$2PbCO_3\cdot Pb(OH)_2$	87	6.7
dibasic lead stearate	[56189-09-4]	$Pb(OOCC_{17}H_{35})_2\cdot 2PbO$	55	2.0
lead stearate	[1092-35-7]	$Pb(OOCC_{17}H_{35})_2$	29	1.4

the desired level of overbasing in the final product. Most often, the lead product is treated with a coating agent to reduce dusting and improve dispersability in the PVC. The stabilizer is then filtered, dried, and packaged. During the drying and coating step, other coadditives such as pigments, lubricants, and fillers can be blended into the mixture to make a total package formulation.

4.3.3. Commercial Stabilizers

There are six lead salts and soaps that typically are used in the commercial PVC stabilizers. The lead stearate soaps are often combined with the lead salts to provide lubrication and added stabilizer activity. The key to the high activity of these stabilizers is the very high lead content. Table 5 describes six commonly used lead stabilizers.

By far the most common lead salt used for PVC stabilization is tribasic lead sulfate. It can be found either alone or combined with another lead salt in almost every lead-stabilized PVC formulation. Many of the combinations are actually coprecipitated hybrid products, ie, basic lead sulfophthalates. Dibasic lead stearate and lead stearate are generally used as costabilizers combined with other primary lead salts, particularly in rigid PVC formulations where they contribute lubrication properties; dibasic lead stearate provides internal lubrication and lead stearate is a good external lubricant. Basic lead carbonate is slowly being replaced by tribasic lead sulfate in most applications due the relatively low heat stability of the carbonate salt which releases CO_2 at about 180°C during PVC processing.

4.3.4. Flexible Applications

The mainstay of the lead stabilizers in the United States is in flexible wire and cable coating applications. The nonconductive nature of lead stabilizers is unsurpassed by other classes of stabilizers. Rather high levels of stabilizers are necessary for these uses because of the required heat aging specifications for most insulating materials. Typically 5–8 phr of lead stabilizer is needed in most insulation compounds. Careful consideration must be given to the choice of lead stabilizer due to the high reactivity of the basic lead oxide groups with other ingredients in the formulation. This is particularly true of the plasticizer choice. The more demanding, high temperature applications require stabilizers rich in dibasic lead phthalate to provide high levels of heat aging stability; the less demanding applications, jacketing and low temperature insulation, usually rely on tribasic lead sulfate as the primary stabilizer. Under high temperature aging conditions, tribasic lead sulfate tends to react with the ester-type plasticizers to increase volatility and reduce the resilience of the PVC insulation.

4.3.5. Rigid Applications

The use of the lead stabilizers is very limited in the United States; but, they are still used in several rigid PVC applications in Europe and Asia. The highest use of lead stabilizers in rigid PVC is for pipe and conduit applications. Tribasic lead sulfate is the primary heat stabilizer with lead stearates included to provide lubrication. The lead products are typically fully formulated, usually including lubricants and pigments for pipe extrusion applications. These lead one-packs, when used at about 1.8–2.5 phr, provide all of the stabilizer and lubrication needed to process the polymer. A lead one-pack contains tribasic lead sulfate, dibasic lead stearate calcium stearate, polyethylene wax, paraffin wax, ester wax, and pigments.

Dibasic lead phosphite is used in rigid building profile applications because the PVC weathering properties are found to be very good. Normally, the titanium dioxide pigment loading is increased to about 5 phr in these formulations. In less critical uses, ie, interior profiles, tribasic lead sulfate remains the standard. There are three U.S. producers of note of lead stabilizers: Anzon (Philadelphia), a division of Synthetic Products Co. (Cleveland), with trade names Tribase, Dythal Dyphos, Lectro, and Leadstar; Eagle-Picher Ind. (Cincinnati) markets Epistatic; and Hammond Lead Co. (Hammond, Indiana) sells Halstab, Halbase, Halphal, and Halphos.

4.3.6. Economics

The lead-based stabilizers tend to be priced relatively low, with 1992 prices ranging from \$1.40 to \$3.60/kg in the United States. The lead phthalates tend toward the higher end of this range, whereas the pipe one-pack products fall into the low end.

4.3.7. Health and Safety Aspects

Worldwide, there is continuing pressure by environmental and human toxicologists to reduce the use of heavy metals such as lead in every application. In the United States, the EPA and Occupational Safety and Health Administration (OSHA) provide regulations over the producers and users of lead stabilizers. The permissible exposure level (PEL) of workers is regulated at 50 μg/m^3 of airborne lead per 8-h workday. Further, workers are not allowed to be exposed to greater than 30 μg/m^3 for more than 30 days per year (34). The state of California increased the safety factor further in 1990 by regulating exposure to less than 5 μg/m^3 for any exposure. Warning labels describing the toxic effects of lead compounds must be applied to all lead stabilizer packaging. In some states, ie, New Jersey and California, any product containing more than 0.1% lead must be labeled as containing lead.

Lead stabilizers have not been used to manufacture drinking water pipes in the United States since 1970 due to the migration levels of lead found in the water from the stabilizers. In 1991 the U.S. EPA further reduced the allowable level of lead in drinking water to zero (action level of only 15 parts per billion (ppb) lead). In 1993, The World Health Organization provided new guidelines targeting the level of lead in drinking water to less than 10 ppb. All uses of lead in PVC pipes are under scrutiny and the stabilizer industry is responding with nontoxic tin-based and calcium–zinc-based technologies. Significant efforts are underway to reduce the uses of lead stabilizers in flexible wire and cable applications as well. New mixed metal formulations are now being touted as providing the needed high levels of both heat stability and nonconducting electrical properties.

4.4. Antimony Mercaptide Stabilizers

In the mid-1950s antimony mercaptides were first proposed as PVC heat stabilizers (35). Antimony tris(laurylmercaptide) [6939-83-9] and antimony tris(isooctyl thioglycolate) [27288-44-4] are typical of this class of heat stabilizers. These compounds were used mainly in rigid PVC applications, particularly pipes, competing with the alkyltin mercaptides. Their use has greatly diminished during the late 1980s and early 1990s for a variety of reasons. Particularly, questions raising doubts about the toxicological safety of antimony compounds have arisen. The performance of the antimony products has also reduced their uses in many processes. For example, they are less compatible with PVC which leads to a cloudy appearance in clear applications; they react with sulfur sources to form Sb_2S_3, an orange-colored by-product; and they detract from the weatherability of PVC formulations. Further, because the cost of tin metal decreased significantly during the 1980s, antimony pricing has continued to rise, making these products less economically attractive than they once had been.

4.5. Commercial Stabilizers

The performance of the antimony stabilizers is significantly enhanced by adding polyhydroxybenzene compounds, eg, catechol, to the PVC (36). In commercial practice, about 5–10% catechol is formulated with the antimony mercaptide stabilizer products. The antimony mercaptides are normally prepared by heating antimony oxide with the appropriate mercaptan, normally isooctyl thioglycolate, under conditions to remove water.

$$\mathrm{Sb_2O_3 + 6\ HSCH_2COOR' \longrightarrow 2\ Sb\left(SCH_2COOR'\right)_3 + 3\ H_2O}$$

The liquid antimony tris(isooctyl thioglycolate) is then treated with the required additives to prepare the commercial products.

Current manufacturers of these products are the Polymer Additives Group of Witco Corp. (New York), with the trade name Mark, and Synthetic Products Co. (Cleveland), with the trade name Synpron. The antimony-based stabilizers are typically used for rigid PVC extrusion applications at about 0.4 to about 0.8 phr, priced at about $3.80–$4.50/kg.

4.6. Health and Safety Aspects

The U.S. EPA has significantly reduced the allowed levels of antimony compounds in drinking water causing a toxicity cloud over the viability of this class of stabilizers. Presently, antimony products are no longer allowed for use as potable water pipe stabilizers pending completion of NSF International's review (28). For these reasons, the future of this stabilizer technology appears limited.

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