

3.3 Organotin Compounds as PVC Stabilizers

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3.3.1 Introduction

When poly(vinyl chloride) is fabricated, it passes between rollers (calendars) at about 200 °C, which causes elimination of some HCl at allylic defects in the polymer, as shown below (Figure 3.3.1). Furthermore, the released HCl induces further elimination, giving a polyolefin structure with a yellow coloration, which turns red, and then black, after which the polymer becomes brittle. This degeneration can be inhibited by organotin stabilizers, often organotin mercaptides that appear to have two principal functions. Firstly, they react with the HCl to give organotin chlorides, which do not catalyze the elimination process. Secondly, they substitute the chloride at the reactive sites, introducing other groups, such as mercaptide groups, which are not easily eliminated. Organotin maleates may also remove diene units by the Diels–Alder reaction.

The first generation tin mercaptide stabilizers were dialkyltin long-chain mercaptans (**1**), traditional mercaptoacetate products (**2**), and mercaptoacetic ester products, having an average tin content of 18% in the stabilizer. When a stabilizer with a high content of a monoalkyltin compound derived from a mercaptoethanol ester (**3**), was demonstrated to provide outstanding early color and color retention in white pipe, the industry quickly accepted this departure from traditional mercaptoacetate products.

Second generation products were mixed mono-/di-alkyl tin long-chain mercaptans. The stabilizer is synthesized directly from an appropriate combination of mono-*n*-butyltin trichloride and di-*n*-butyltin dichloride, which is reacted with a suitable quantity of *i*-octyl mercaptoacetate and sodium sulfide. Although the tin content in the stabilizer is increased to about 22%, these products are often used in diluted form to aid in their handling, while reducing losses.

Recently, a third generation of stabilizers has been developed, which are monoalkyltin short-chain, and/or functionalized mercaptans or sulfides. Neither dialkyltin nor monoalkyltin sulfides by themselves are particularly good stabilizers, in spite of their very high tin content. However, when the alkyltin sulfides are used in conjunction or admixture with the alkyltin mercaptides, a synergistic effect on performance is obtained. Thus, the combination of dialkyltin bis(*i*-octylmercaptoacetate) with monoalkyltin sulfide (**4**), or monoalkyltin tris(*i*-octylmercaptoacetate) with dialkyltin sulfide (**5**), affords high tin-content products with powerful stabilizing properties. Another approach to such a stabilizer composition would be a direct synthesis from an appropriate combination of mono-*n*-butyltin trichloride and di-*n*-butyltin dichloride, which is reacted with a suitable quantity of *i*-octyl mercaptoacetate and sodium sulfide. This technology has been extended to include methyltins as well as *n*-butyltins and mercaptoethanol esters as well as *i*-octyl mercaptoacetate.¹

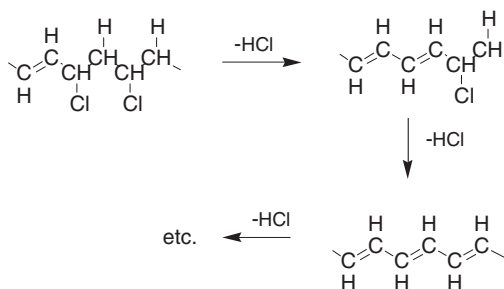


Figure 3.3.1 Dehydrochlorination of PVC

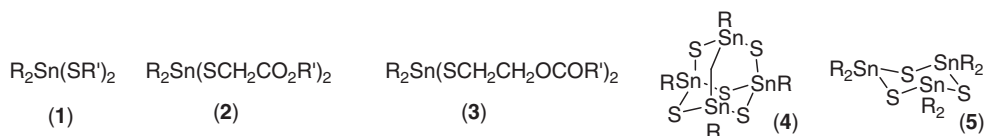


Figure 3.3.2 Formulae for sulfur containing organotin heat stabilizers

The stabilizers stated above have the following formulae (Figure 3.3.2).

This section deals with the stabilization of PVC by organotin stabilizers having different alkyl groups (methyl, ethyl, *n*-butyl, *n*-octyl, etc.) and different ligands (carboxylates, mercaptides, etc.), the mechanism of reaction and the evaluation of stability by yellowness index and conductivity.

3.3.2 Types of Organotin Stabilizers

The Alkyl Group

Most of the organotin stabilizers in general use have structures of the type $\text{R}_n\text{SnX}_{4-n}$ where R is normally an alkyl group, usually methyl, *n*-butyl, or *n*-octyl, and X is one of a large group of saturated or unsaturated carboxylates or mercaptide derivatives. The carboxylates are frequently esters or half esters of maleic acid and the thiol residues often derived from alkyl thioglycolates, HSCH_2COOR .

There are three major types of tin stabilizers (organotin stabilizers), distinguished by their respective alkyl groups: *n*-octyl, *n*-butyl, and methyl:

1. *n*-Octyltin stabilizers have either one or two octyl groups bonded to the tin atom. Some *n*-octyltin stabilizer formulations are approved for food contact applications by most regulatory agencies worldwide.
2. *n*-Butyltin stabilizers have one or two butyl groups bonded to the tin atom. *n*-Butyltins are used in rigid applications, such as siding and window profiles, and are approved for use in drinking-water pipe in the United States and Canada.
3. Methyltin stabilizers have one or two methyl groups bonded to the tin atom.²

Dialkyltin compounds of the above groups, particularly the di-*n*-butyl derivatives, are the most effective stabilizers. Their solubility in the PVC resin and in almost all plasticizers imparts a clarity to the finished product which is unmatched by any other group of stabilizers currently in use. Each particular di-*n*-butyl derivative has special properties for each method of processing. Therefore, the finished product usually contains a mixture of several stabilizers, designed for a specific product, its processing scheme, and its environmental exposure. Varying the structure of the R groups in dialkyltin compounds R_2SnX_2 has relatively little effect on the stabilizer efficiency, and the nature of X is much more important. For di-*n*-butyltin compounds, for example, the diacetate is a poor stabilizer, the dilauryl mercaptide is much better, and the di(isooctyl mercaptoacetate) is extremely good. In general, mercaptoacetates or mercaptopropionates confer good thermal properties but no photoprotection. Maleate esters on the other hand do confer a degree of photostability, in addition to the fact that they are sulfur-free, which has advantages in some applications.

The Ligands

The most effective stabilizer systems in practice are subdivided into:

1. Sulfur-containing stabilizers (organotin mercaptides and sulfides).
2. Sulfur-free stabilizers usually containing Sn-O bonds.

Sulfur-containing stabilizers can be used in mixtures with lubricants for PVC to be used in foodstuff packaging and for pipes for drinking water. In the manufacture of high-transparency foils, this stabilizer class can be used in practice only when UV absorbers are included.

Stabilizers containing Sn–S bonds may be of many types, for example organotin mercaptides, organotin mercaptoalcohols, organotin thioglycollates, and organotin polymers containing sulfur.

In contrast to sulfur-containing tin compounds, tin carboxylates have to be used with antioxidants. The advantage of the use of sulfur-free stabilizers is the good photostability and the lack of odor. These stabilizers, too, need additional lubricants, since they tend to stick to the metal parts of calendars and extruders.³

3.3.3 Tin Carboxylates

The earliest tin stabilizers, di-*n*-butyltin dilaurate and di-*n*-butyltin maleate, are typical of sulfur-free stabilizers. These products, and subsequent developments in tin carboxylates, provided clarity to PVC and a much lower order of toxicity than lead- or cadmium-containing stabilizers. One stabilizer in this group, di-*n*-octyltin maleate, is sanctioned by the United States FDA for rigid PVC food-contact applications. Tin carboxylates are used in rigid PVC–acetate copolymer applications, but do not offer the degree of stability required to process rigid PVC homopolymers. They do, however, exhibit excellent light stability properties and are sometimes used in combination with the sulfur-containing organotins to enhance the outdoor weathering capabilities of rigid PVC.

Organotin derivatives of maleic acid may have an additional stabilizer function with the Diels–Alder reaction (Figure 3.3.3) by scavenging function.⁴ Their performance is good in all types of vinyl chloride polymerization, i.e. suspension, emulsion, and bulk. Optimum results are obtained when they are combined with small amounts of phenolic antioxidants particularly in plasticized PVC, impact-modified PVC, and PVC copolymers.

Because stabilizers containing maleic acid occasionally lead to eye and mucous membrane irritations, there have been many attempts to replace them with other systems, and for many years, organotin stabilizers, free of maleic acid, have been on the market. These consist of a combination of organotin carboxylates, e.g. laurates, and a small amount of an organotin mercaptide. Just as with sulfur-free organotin stabilizers, when used in suitable formulations, this combination gives rigid PVC high transparency and excellent weathering stability. In the melt, PVC stabilized with alkyltin maleates tends to stick to hot contact areas of the processing equipment, but this problem can be prevented by suitable lubricants.

The effect of dialkyltin maleates and laurates on the thermal dehydrochlorination of PVC has been compared in 1,2,4-trichlorobenzene solution by IR analysis, and showed that tin laurates are superior to tin maleates in replacing the labile chloride atoms in PVC. Attempts to trace intermediate monochlorotin derivatives in the case of maleates by polarography and Mössbauer spectroscopy were not conclusive.

Di-*n*-butyltin laurate prevents the formation of longer polyene sections, retarding the colouration of the PVC. Di-*n*-butyltin laurate cannot prevent the formation of short polyene sections. Thermal

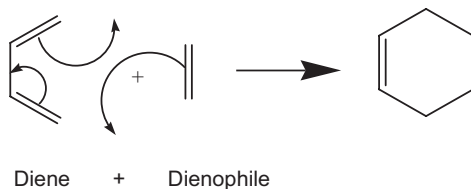


Figure 3.3.3 Diels–Alder reaction

dehydrochlorination still occurs, but its rate is decreased and longer polyenes are formed. The higher the di-*n*-butyltin laurate content, the greater the concentration of shorter polyene sequences.

3.3.4 Tin Mercaptides

The thio-organotins were introduced in the early 1950s and provided a considerable improvement in clarity and heat stability. Although they exhibited poor light stability and some odour, and were more costly than lead or barium–cadmium stabilizers, tin mercaptides soon gained acceptance in the United States for the difficult stabilization of rigid PVC, and have been the most widely used stabilizers in rigid PVC pipe and profile extrusion, injection, and blow molding up to the present time.

Tin mercaptides offer a unique set of properties for rigid PVC processing: classical vinyl stabilization and antioxidant functions combined with fusion promotion and melt viscosity reduction. Melt rheology studies have shown that in addition to excellent color stability, organotin–sulfur bonded compounds furnish a lower melt viscosity in rigid PVC than structurally equivalent organotin–oxygen bonded compounds (tin carboxylates) of similar viscosity, molecular weight, and compatibility. They also impart lower melt viscosities than Group II A and B metal carboxylates (barium–cadmium, calcium–zinc stabilizers). A possible explanation lies in the ability of sulfur to internally satisfy the secondary bonding capabilities of tin to a greater extent than oxygen, thus preventing secondary cross-linking or ‘melt stiffening’ of rigid PVC or copolymers which would otherwise occur through the coordination of the tin atom with groups on the polymer chain.⁵

3.3.5 The Mechanism of Stabilization

Organotin mercaptide stabilizers have an anti-oxidative action. This contributes to the stabilization in as much as the dehydrochlorination is much faster in the presence of air (oxygen) than in the presence of inert gas, and the loss of HCl is noticeably retarded by phenolic antioxidants.

Organotin mercaptide stabilizers decompose hydrogen peroxides, providing a secondary antioxidant effect (Figure 3.3.4).

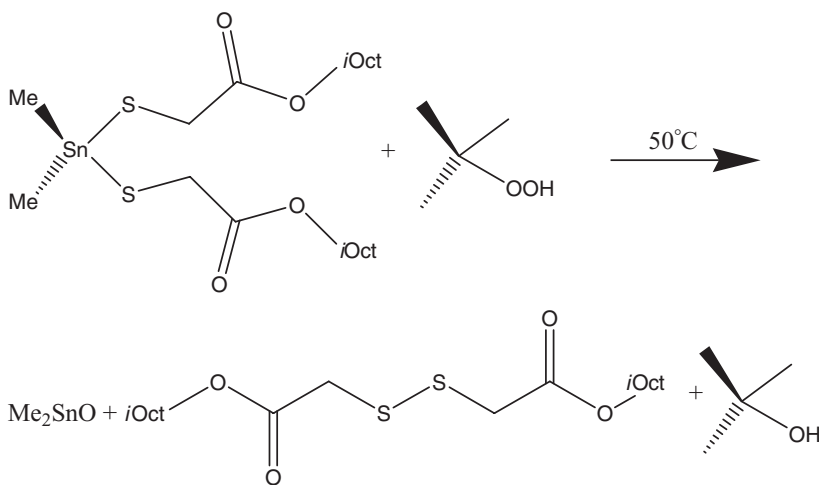
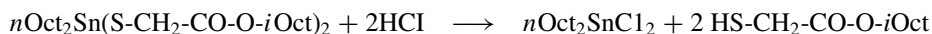


Figure 3.3.4 Reaction of an organotin stabilizer with *t*-butyl hydroperoxide. (Reproduced from reference 6, copyright 2003, John Wiley & Sons, Ltd.)

Organotin mercaptide stabilizers also break autoxidation chains, and, compounds of this type are even patented as antioxidants for other plastics.

Organotin mercaptides are able to bind or to neutralize HCl, which – as already mentioned – has an auto-catalytic effect on dehydrochlorination, especially in presence of oxygen, thus providing a further preventive function (Scheme 3.3.1).



Scheme 3.3.1 Binding of the HCl by an organotin mercaptide stabilizer⁶

The induction period – the axial section on the time coordinate of the dehydrochlorination curve – is a common criterion of all heat stabilizers. Normally, within this period, the processing takes place. The length of the induction period may be considered simply as a measure of the heat stability of PVC. However, this does not – and this must be emphasized – allow any definitive conclusions to be drawn concerning the initial color, which is of the utmost importance from the practical standpoint. From the shape of the dehydrochlorination curve, especially from its gradient, very important conclusions can be drawn, particularly concerning the interactions of stabilizer conversion products with PVC, and also with each other.

In Figure 3.3.5, the dehydrochlorination curves for a di-*n*-octyltin mercaptide stabilizer are shown. It can be seen that the induction period increases almost linearly with the stabilizer concentration. As a first approximation, the length of the induction period may also be considered as a measure of the binding capacity of the stabilizer for hydrogen chloride. Furthermore, the gradient of the curves decreases with increasing concentration of the stabilizer, and this can be seen as an indication that the conversion products have a favorable effect on the heat stability of the PVC.

The exchange of the labile chlorine atoms (which act as initial sites for dehydrochlorination, for less easily removable thiolate groups) is an extremely important stabilizing function, which has also preventive character. This exchange reaction has first been proposed and established by Frye *et al.* (Scheme 3.3.2).

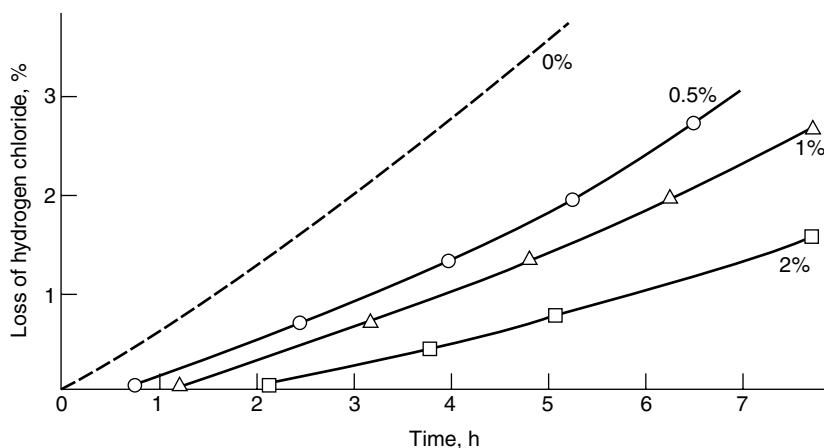
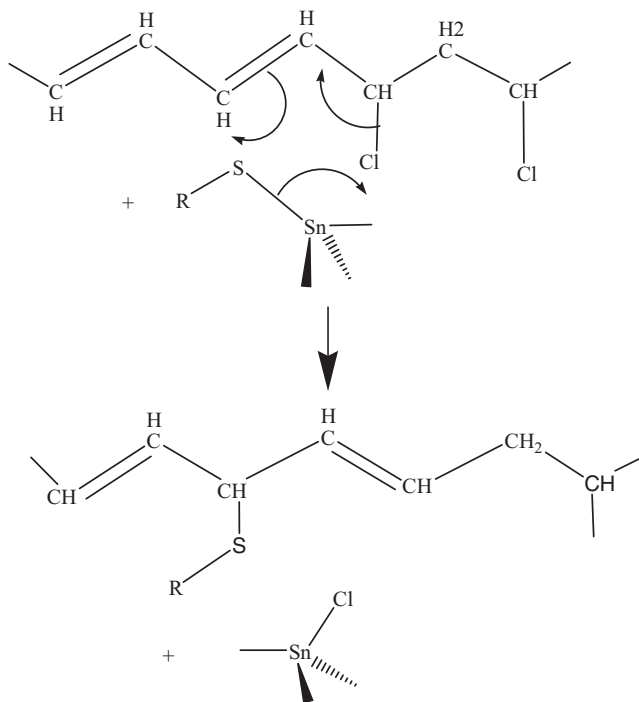


Figure 3.3.5 Thermal dehydrochlorination curves of PVC at 175°C in the presence of different amounts of di-*n*-octyltin-bis-*i*-octylthioglycolate. (Reproduced from reference 6, copyright 2003, John Wiley & Sons, Ltd.)



Scheme 3.3.3 Proposed mechanism of exchange of chloride atoms in PVC by mercaptide groups of organotin stabilizers:⁶ coordination of allylic chlorine by organotin mercaptide with subsequent rearrangement to a non-allylic structure

Mono-*n*-butyltin tris(*i*-octylmercaptoacetate) combines improved early color with shortened long-term stability. This is due to its intermediate Lewis acid character between that of diisooctyl bis(*i*-octylmercaptoacetate) and tin tetra(*i*-octylmercaptoacetate). The decreased effectiveness of tri-*n*-butyltin *i*-octylmercaptoacetate may be ascribed to the increased reluctance to coordination by the tin atom, due to presence of the third alkyl (*n*-butyl) group. Additionally, the use of trialkyltin derivatives in PVC stabilization has been avoided because of their toxicity.

Whether the alkyl group attached to tin is methyl, *n*-butyl, *n*-octyl, or carboxymethylethyl would appear to have minor significance in that all four types may be satisfactorily employed in rigid PVC structures. In the United States it is the methyltin or *n*-butyltin types which predominate. Because of their high cost, octyltin derivatives are utilized only where FDA approval is required, thus severely limiting their market. The ‘estertins,’ which have been recently introduced, will be successful to the extent that they can compete with the established methyltin and *n*-butyltin stabilizers on a cost-performance basis. An estertin mercaptoethanol ester, so-called reverse estertin, has following ligand structure: S-CH₂-CH₂-O-CO-alkyl.⁸

However, differences in performance do exist, which are dependent on the alkyl substituent present and which must be taken into consideration by stabilizer manufacturers when developing new products, and by end users when formulating and processing PVC compounds with these products. In the case of dialkyltin bis(*i*-octylmercaptoacetate), as the alkyl chain length decreases from octyl to methyl, the

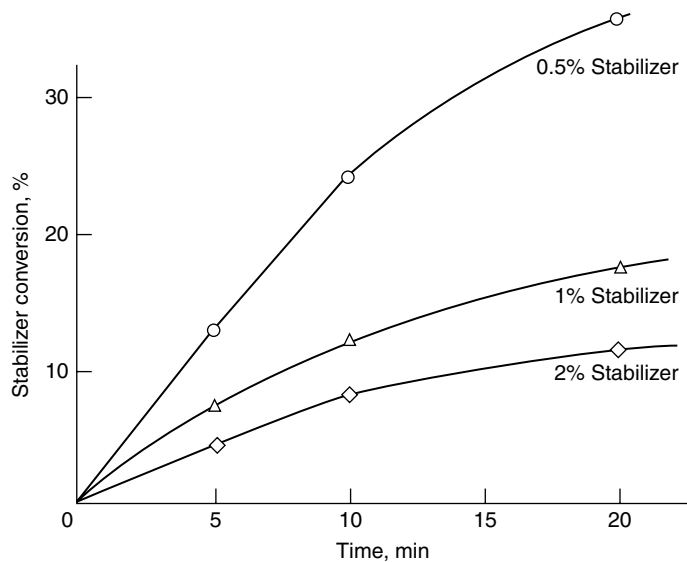


Figure 3.3.6 Stabilizer conversion in PVC versus heating time curves in a continuous milling test at 180°C (stabilizer: di-n-octyltin bis(i-octylthioglycolate). (Reproduced from reference 6, copyright 2003, John Wiley & Sons, Ltd.)

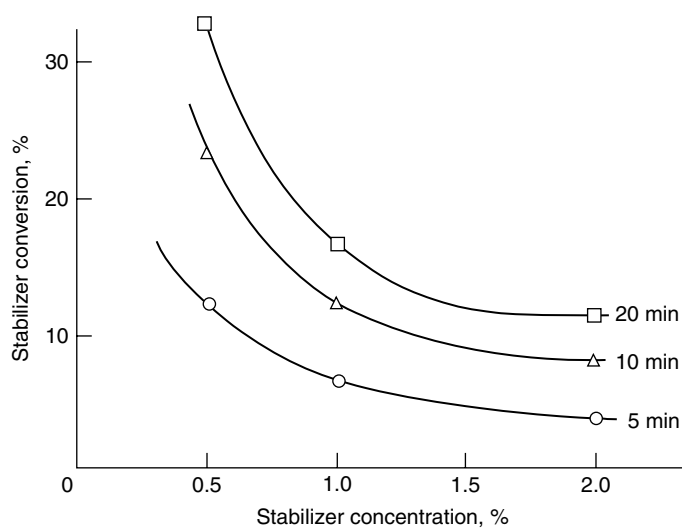


Figure 3.3.7 Stabilizer conversion versus stabilizer concentration curves for different heating times in a continuous milling test at 180°C (stabilizer: di-n-octyltin bis(i-octylthioglycolate). (Reproduced from reference 6, copyright 2003, John Wiley & Sons, Ltd.)

stabilizers become increasingly compatible with the resin, and, in fact, become better stabilizers for the resin since a greater part of the stabilizer molecule is the *i*-octyl mercaptoacetate ligand. This is manifested by lower melt viscosities, and often lubrication adjustments are required when changing stabilizers.

The estertins also demonstrate increased compatibility with PVC due to the presence of a polar ester group in the alkyl chain. Methyltin stabilizers appear to be more sensitive to the amount of monomethyl species present in the product. Put another way, less monomethyl species are required for color improvement than is the case with *n*-butyltin or *n*-octyltin compounds. This may be explained by the greater Lewis acid strength of monomethyltin trichloride and by the enhanced ability of methyltin compounds to coordinate labile chloride atoms in the PVC molecule, due to less steric hindrance offered by the smaller methyl groups compared to the bulkier *n*-butyl and *n*-octyl groups. This steric effect is most pronounced when comparing methyltin derivatives with *n*-butyltin analogs as catalysts in the production of polyurethanes. Moreover the thermal stability of dimethyltin bis(*i*-octylmercaptoacetate) itself is superior to the di-*n*-butyltin, di-*n*-octyltin, and the estertin analogs. Breakdown of the stabilizer occurs less readily in a press stability test, indicating the suitability of this methyltin stabilizer for injection molding applications.

For many years, the principal mercaptan used in organotin stabilizers was *i*-octyl mercaptoacetate. Specialty applications, where a more highly lubricating stabilizer was desirable, called for the use of dodecyl mercaptan. The linear aliphatic chain with no compatibilizing ester groups provided a greater degree of lubrication. However, the yellow color obtained with di-*n*-butyltin bis(dodecylmercaptide) precluded its use for most applications. The ability of the tin atom in di-*n*-butyltin bis(dodecylmercaptide) to coordinate labile chloride atoms in PVC is evidently inferior to that in di-*n*-butyltin bis(dodecylmercaptoacetate), with consequent poorer performance. Di-*n*-butyltin bis(*i*-octylmercaptoacetate) is an internally coordinated compound, the structure of which facilitates coordination of labile chloride atoms, while the lack of any restrained configuration in di-*n*-butyltin bis(dodecylmercaptide) results in steric hindrance to coordination by the tin atom. Sulfur coordinating with tin is exchanged with chloride, and the sulfur is bonded to the PVC C atom where chloride was bonded previously. If one compares di-*n*-butyltin bis(dodecylmercaptide) with the dimethyltin analog, one observes significantly improved color stability with the dimethyltin compound, presumably due, again, to substantially decreased steric hindrance about the tin atom. When di-*n*-butyltin compounds derived from esters of mercaptoethanol were evaluated, color stability results were obtained similar to that of isooctylmercaptoacetate.¹

3.3.7 Evaluating Stability

Yellowness Index and Transparency

Films having an organotin stabilizer have a lower yellowness index than those of control films heated at different periods at 160 and 180 °C (Figure 3.3.8). The higher the organotin stabilizer concentration and heating temperature are, the higher is the yellowness index (more tin, more color). The color of the film with 2.5% organotin stabilizer has a very small yellowness index up to 30 minutes at both 160 and 180 °C, indicating that a safe induction period for dehydrochlorination is present.

While control and 2.5% organotin stabilizer containing films are transparent, films with 5% organotin stabilizer are opaque white, indicating limited solubility of organotin stabilizer in PVC.⁶

HCl Evolution from PVC and PVC with *Di-n*-Octyltin Bis(*i*-Octylthioglycollate) Stabilizer Films

Dehydrochlorination of the films at 140 and 160 °C can be determined in a Metrohm 763 PVC thermomat. In this instrument HCl evolved by heating PVC is carried by N₂ gas through a fixed amount of water. The conductivity change of water vapor versus time is measured. The conductivity is proportional to the amount of HCl evolved. Figure 3.3.9 shows HCl evolution from films of PVC, and of PVC with

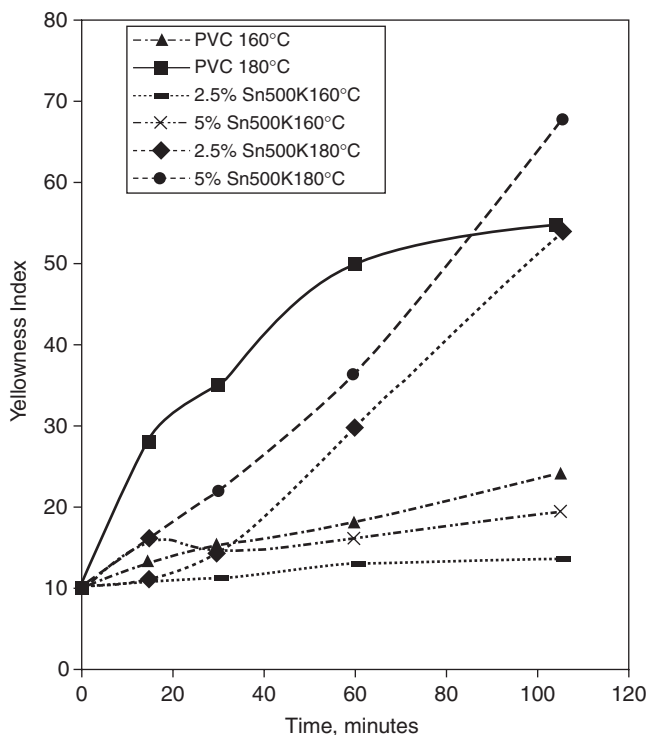


Figure 3.3.8 Yellowness index of films versus heating time. (Reproduced from reference 6, copyright 2003, Elsevier.)

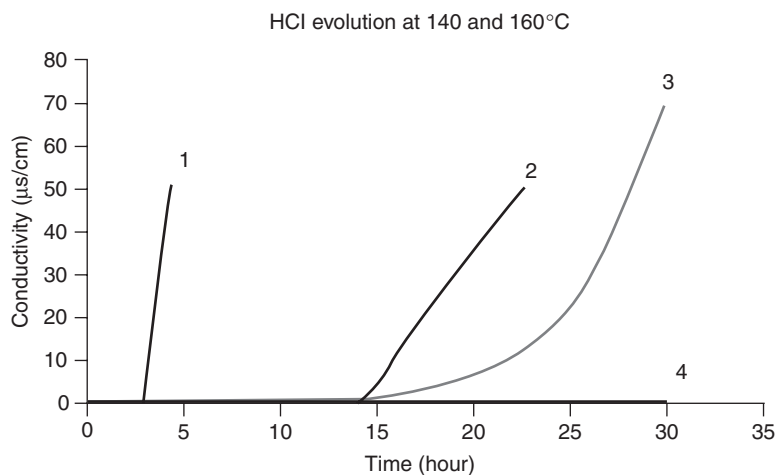


Figure 3.3.9 HCl Evolution from films heated at 140 °C and 160 °C: (1) PVC without di-n-octyltin bis(isooctylthioglycollate) at 160 °C, (2) PVC without di-n-octyltin bis(isooctylthioglycollate) at 140 °C, (3) PVC with di-n-octyltin bis(isooctylthioglycollate) at 160 °C, (4) PVC with di-n-octyltin bis(isooctylthioglycollate) at 140 °C. (Reproduced from reference 9, with permission from Elsevier.)

di-*n*-octyltin bis(*i*-octylthioglycollate) stabilizer, at 140 and 160 °C respectively. This shows that HCl evolution from a PVC film without the di-*n*-octyltin bis(*i*-octylthioglycollate) stabilizer starts after a short induction period. HCl evolution from the PVC with di-*n*-octyltin bis(*i*-octylthioglycollate) stabilizer showed longer induction periods, and at 140 °C, no HCl was evolved from the film over the time of the experiment. HCl evolution increased with temperature, being more rapid at 160 °C than at 140 °C. The onset times for HCl evolution were 14.3 and 2.5 h at 140 and 160°C, respectively, for PVC film without di-*n*-octyltin bis(*i*-octylthioglycollate) stabilizer. On the other hand, the film with di-*n*-octyltin bis(isooctylthioglycollate) stabilizer did not evolve HCl in 30.3 h at 140 °C. HCl started to evolve from the films with di-*n*-octyltin bis(isooctylthioglycollate) stabilizer in 14.3 h at 160 °C.⁹

3.3.8 Conclusion

The choice of a stabilizer depends on:

1. The requirements for processing.
2. The properties for the end-use.
3. Cost constraints within which (1) and (2) must be constrained.
4. Other formulation components which may interact with the stabilizer.

The basic type of stabilizer system selected is often dictated by end-use or regulatory constraints (NSF – National Science Foundations, PPI – Plastics Pipe Institute, United States FDA, and German BGA). Subsequent choice of a specific stabilizer should be made with the major objective of achieving optimum cost-performance – how much processing stability is available per dollar of stabilizer cost? Or conversely, what will be the lowest cost choice to furnish the required processing stability for a particular process – including all safety factors, such as regrind extrusion, power failures, and end-use stability needs? A level of stability much beyond the ‘necessary’ level can translate to significant unnecessary costs. There are laboratory tests for PVC: the yellowness index of samples treated with shear and heat is measured in a Brabender plastograph or a roller mill, and with heat only, in a static test oven as a function of time, to test thermal stability. These laboratory tests (Brabender, mill stability, and heat stability) can furnish an indication of comparative cost-performance, but the final decision really should be based on production extrusion runs and subsequent evaluation of either residual stability, or regrind extrusion, which is also conveniently done with the heat stability testing oven.

Within the organotin mercaptide group of stabilizers, the most recent ‘reverse ester’ methyltin stabilizers have demonstrated a unique ability to impart extremely good initial color stability, and to hold that color even during 100% regrind extrusion to a much greater degree and at lower costs than were previously possible. In other words, the useful processing stability of rigid PVC – to the point of product rejection – is extended. Conversely, as the stabilizer level is reduced, the decrease in stability time (seen as color development) is much less with these new methyltin stabilizers than with *n*-butyltin or mixed-metal tin stabilizers. This means that a given level of stability (necessary to run an extrusion plant, including a regrind safety factor) can be achieved with less stabilizer in the compound. Typical use levels for twin screw pipe extrusion are in the 0.3–0.4 phr (stabilizer parts per hundred parts of PVC resin) range, and 0.7–1.2 phr for single screw pipe extrusion. The stabilizing efficiency furnished by such methyltins, especially at lower use levels, is significant, when comparing actual performance data and a schematic comparison of methyltin and lead-stabilized pipe compounds at various equivalent cost levels. In this case, a level of stability much above the ‘necessary’ level would add unnecessary cost to the formulation and return no real benefits.⁵

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