

## THE STABILIZATION OF PVC AGAINST HEAT AND LIGHT

H.O. Wirth and H. Andreas

CIBA-GEIGY Marienberg GmbH

Abstract - The lecture provides a survey on the actual status of the heat and light stabilization of PVC with special emphasis on the mode of action of the stabilizers. In the first part a brief treatment of the most important facts of the thermal degradation of PVC are given, followed by a discussion of some proved specific functions of heat stabilizers by using organotin mercaptide as a typical example. A general concept differentiating preventive and curative stabilizer functions is proposed which seems to be applicable to all types of thermal stabilizers. The second part of the lecture deals with the problematics of light degradation and light stabilization. Some fundamental facts of the light degradation are briefly dealt with and provisions for an enhancement of the light stability are discussed, covering also the implication of the thermal stabilizers.

### 1. INTRODUCTION

The lecture will describe the present state of our knowledge on the chemical, particular complex chemical and physical processes occurring during the stabilization of PVC against heat and light.

In the first part the mode of action of the most important heat stabilizers and stabilizer systems is discussed, mainly on the basis of published results. Although some of the details cannot be explained at this stage, it is, however, possible to interpret the mode of action of all heat stabilizers according to a rather general concept.

As far as the light stability of PVC is concerned, the empirical phase of research could not be overcome. PVC is a very complex substrate with respect to the explanation of chemical processes. Therefore, it is understandable that the photochemical processes related to the light stabilization are much more complex. Nevertheless, efforts are also made to reflect the actual state of our knowledge concerning the light stabilization.

### 2. HEAT STABILIZERS FOR PVC AND THEIR MODE OF ACTION

#### 2.1 The most important facts of heat degradation

The papers available so far on the subject of the heat degradation of PVC are almost countless. In spite of this, there are still certain controversies and ambiguities on some questions, such as the chemical nature of the initial sites and the mechanism of dehydrochlorination. In this context special attention is to be drawn to some recently appeared monographs (Ref. 1, 2, 3) and review articles [Figge and Findeiß (4), Onozuka and Asahina (5)].

For a better understanding of the following explanation it is worthwhile to summarize briefly the most important facts of the heat degradation of PVC first: The heat degradation of PVC is substantially governed by two degradation reactions, namely dehydrochlorination and autoxidation, whereby the dehydrochlorination is the dominating reaction. With respect to light degradation, dealt with in the second part of this lecture, the emphasis is reversed.

**D e h y d r o c h l o r i n a t i o n :** Due to allylic activation the dehydrochlorination occurs as a zipper reaction and at least in the advanced state, it is of ionic nature. It may be said that the final "labile" site in PVC is always an allyl chloride grouping, for which, however, different direct and indirect routes are possible (Table 1):

TABLE 1. The final "neuralgic" grouping in PVC and routes to its formation

$\cdot \cdot -CH=HC-\underset{\substack{  \\ Cl}}{CH}-CH_2-\cdot \cdot$	
1. Production of the resin	2. Processing
<ul style="list-style-type: none"> <li>- unsaturations</li> <li>- peroxides</li> <li>- structure irregularities</li> </ul>	<ul style="list-style-type: none"> <li>- thermomechanical effects</li> <li>- autoxidation reactions</li> </ul>

This grouping may already be formed directly during the polymerization, e.g. in form of end groups. Other, indirect ways are via peroxides and structure anomalies. The possibility of its formation under processing conditions should not be underestimated. These are primarily thermomechanical effects in processing machines. Hence, the opinion expressed again and again that a perfectly constituted PVC should be stable and should not require any heat stabilizer for its processing, demands a critical examination. Finally, thermal autoxidation reactions may also contribute to its formation and above all to its multiplication. A very important mode of action of a PVC stabilizer - this may be anticipated here - consists in deactivation and elimination, respectively of the allyl chloride grouping as an initial site.

The eliminated hydrogen chloride has an autocatalytical effect on the dehydrochlorination reaction, especially in the presence of oxygen, whereby CO-groups are formed, which in turn also activate chlorine atoms in the  $\alpha$ -position for an elimination. The dehydrochlorination leads to colored polyene sequences which, due to their basic nature, may form deeply colored carbonium salts [Schlimper (6)].

**A u t o x i d a t i o n :** Simultaneously to the dehydrochlorination autoxidation processes take place: The hydroperoxides formed by autoxidation may act indirectly as initial sites of dehydrochlorination, as mentioned above. Longer polyene sequences add oxygen to form cyclic peroxides, which then may further degrade to release dehydrochlorinated chains [Berlin et al. (7)]. Allylic methyl groups form hydroperoxides with oxygen which change into ketopolyenes and finally react with hydrogen chloride and form deeply-colored onium salts.

## 2.2 Organotin stabilizers

**2.2.1 Organotin mercaptides.** The most effective, and from the chemical point of view, most interesting heat stabilizers for PVC are derived from organotin mercaptides. They give excellent results with all types of PVC and with all important methods of processing (Fig. 1):

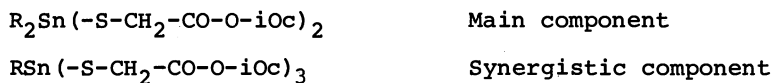


Fig. 1. Structural formula of the most important organotin mercaptide stabilizer type

R stands for a tin bonded alkyl group such as methyl, n-butyl, n-octyl or even esteralkyl.

Practically, mixtures of di- and monoorganotin compounds are often used because of synergistic effects. For this reason the monoalkyl tin compound is also designated as a synergistic component. The heat stabilizing effect mainly depends on the mercapto groups. The tin-bonded alkyl groups, however, have a greater significance with respect to processability, toxicity and volatility.

The mode of action of the organotin mercaptide stabilizers are simply explained by considering preventive and curative functions. We may differentiate between four preventive and two curative functions. The mode of action of other heat stabilizers can be similarly interpreted. The fact, that in the case of organotin mercaptide stabilizers all these functions are united in one single molecule makes it very interesting.

First of all the preventive functions: Organotin mercaptide stabilizers have an antioxidative 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. As a matter of fact, the loss of hydrogen chloride is noticeably retarded by a phenolic antioxidant (Fig. 2):

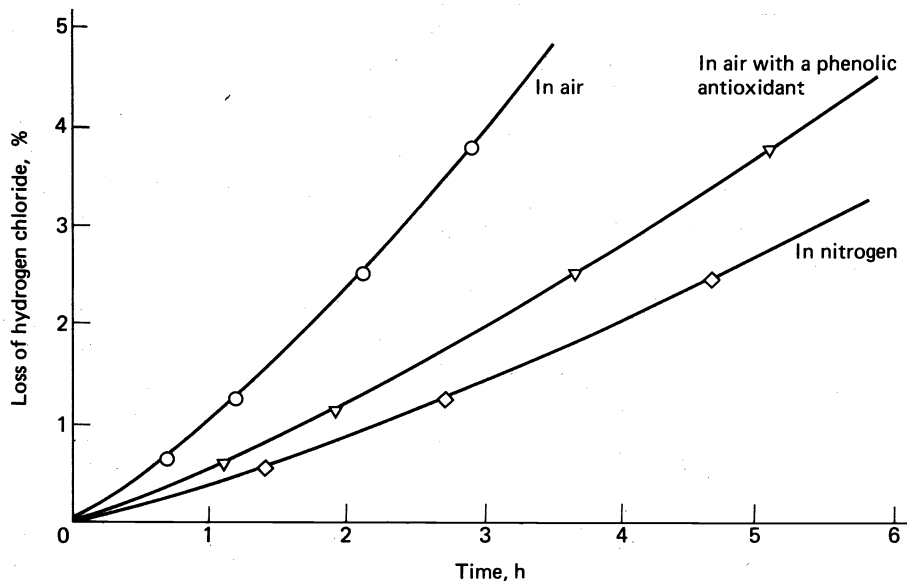


Fig. 2. Thermal dehydrochlorination curves of PVC  
 - in air, - in nitrogen  
 - in air and in presence of a phenolic antioxidant

It can be easily proved that organotin mercaptide stabilizers decompose hydroperoxides. This corresponds to a secondary antioxidant effect (Fig. 3):

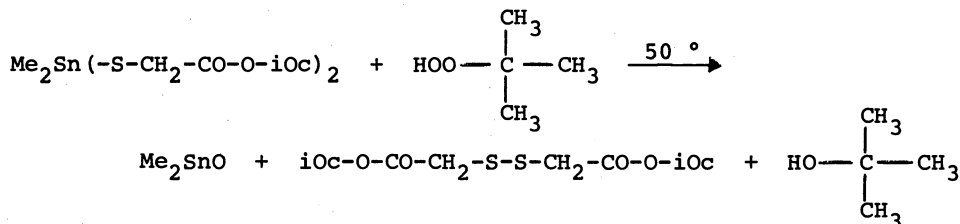


Fig. 3. Reaction of an organotin mercaptide stabilizer with t-butyl hydroperoxide

There are indications that organotin mercaptides also stop (kinetic) autoxidation chains. Thus, compounds of this type are even patented as antioxidants for other plastics.

Organotin mercaptide stabilizers are able to bind or to neutralize hydrogen chloride (Ref. 8). Hydrogen chloride - as already mentioned - has an autocatalytic effect on the dehydrochlorination, especially in presence of oxygen. Thus, binding of the thermally eliminated hydrogen chloride is also a preventive function (Fig. 4):

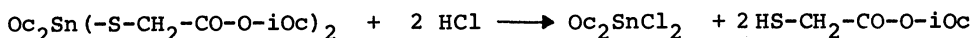


Fig. 4. Binding of hydrogen chloride by an organotin mercaptide stabilizer

The dialkyl tin dichloride, thus formed, still has a certain stabilization effect of its own; this phenomenon will be discussed later. The further fate of the mercaptocarbonic acid ester will also be treated at a later stage.

During this lecture thermal dehydrochlorination curves for the characterization of stabilizers and stabilizer conversion products will be used several times. The induction period - axial section on the time coordinate - of these curves is a common criterion of all heat stabilizers. Within this period normally the processing takes place. The length of induction period may be considered simply as a measure of the heat stability of PVC. It does not however - and this must be emphasized - allow any 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 Fig. 5 the dehydrochlorination curves for a dioctyltin mercaptide stabilizer are shown:

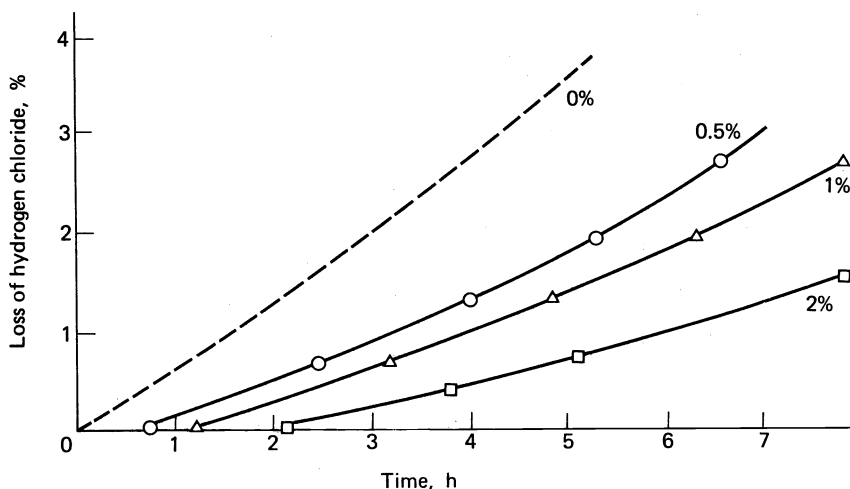


Fig. 5. Thermal dehydrochlorination curves of PVC at 175 °C in presence of different amounts of dioctyltin-bis-isooctylthioglycolate

It can be seen that the induction period increases almost linearly with the stabilizer concentration. As a very 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, it becomes apparent that the gradient of the curves decreases with increasing concentration of the stabilizer. This can be seen as an indication that the conversion products have a favourable effect on the heat stability of PVC.

The exchange of labile chlorine atoms, acting as initial sites for the dehydrochlorination, for less easily removable groups is an extremely important stabilizing function which has also preventive character. This exchange reaction has first been proposed and also proved by Frye et al. (9) (Fig. 6):

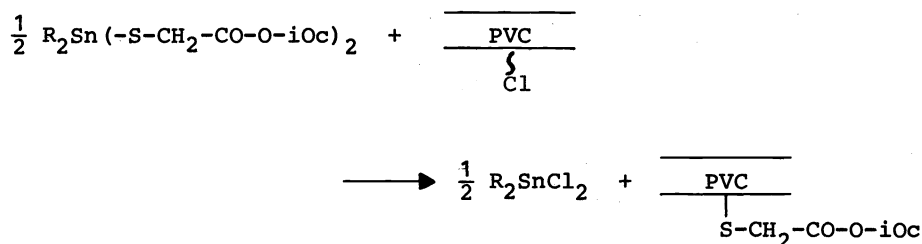


Fig. 6. Exchange of labile chlorine atoms in PVC by organotin mercaptide stabilizers (Ref. 9)

This substitution reaction is due to the special complex chemical properties of the organotin species. Under the conventional conditions of a nucleophilic substitution this reaction tends to an elimination. The substitution mechanism already proposed by Frye is shown in Fig. 7:

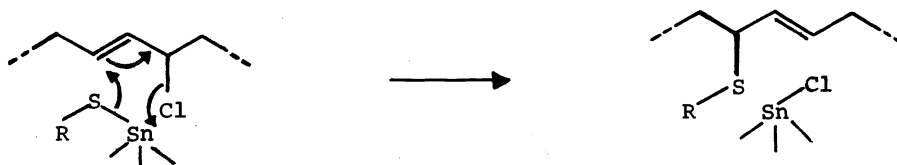


Fig. 7. Proposed mechanism of exchange of chlorine atoms in PVC by mercaptide groups of organotin stabilizers (Ref. 9)

There is a multi centre mechanism, which - as proved by Poller et al. (10) - is connected with an isomerization (allylic rearrangement). Just like the ability to bind hydrogen chloride, this exchange reaction is a general characteristic of all efficient PVC heat stabilizers and stabilizer systems.

A most essential condition of this exchange reaction is, of course, that the transferred groups - in this case the mercaptocarbonic acid ester group - have a lower tendency to be eliminated than the chlorine atom. In the investigation of Suzuki and Nakamura (11) this was proved by model substances. In this context the substitution studies using model substances by Poller et al. (10) may also be mentioned.

There are two possible reactions of organotin mercaptide stabilizers both ending at the stage of dialkyltin dichloride (Fig. 8). Thus, the formation of dialkyltin dichloride may be considered, as a first approximation, to be a measure of the total stabilizer conversion. Accordingly the diagram in Fig. 9 shows the correlation between the stabilizer conversion and the time of heat treatment at 180 °C. There are no data available on organotin stabilizer conversions although these reactions - especially those with hydrogen chloride - have been known for a long time.

**Results:** - (1) There is an increasing (relative) stabilizer conversion with increasing time of heat treatment. - (2) There is a decrease of (relative) stabilizer conversion with increasing stabilizer concentration (this can be seen more clearly on Fig. 10). - (3) Under technical processing conditions (corr. to a stabilizer concentration of ca. 1 % and an average heating time of 10 min) the (relative) stabilizer conversion is as low as 12 %.



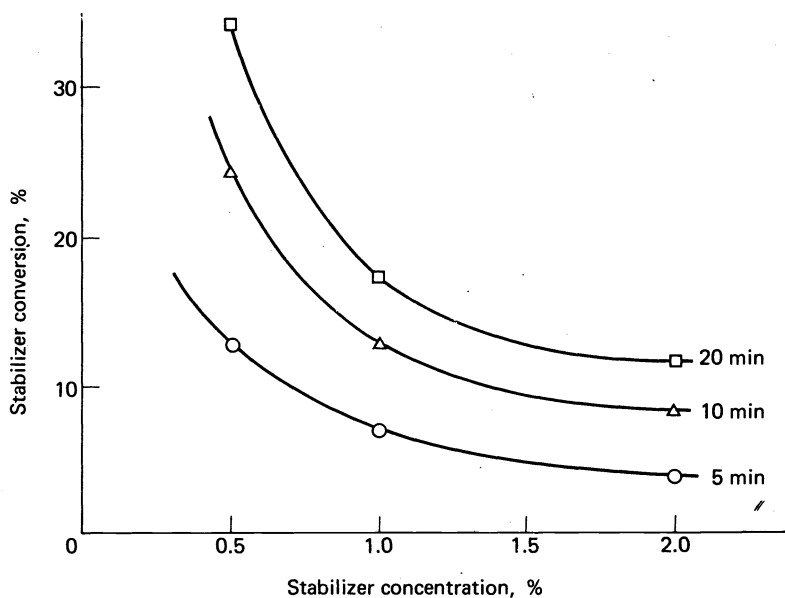


Fig. 10. Stabilizer conversion vs stabilizer concentration curves for different heating times in a continuous milling test at 180 °C (stabilizer: dioctyltin-bis-isooctylthioglycolate)

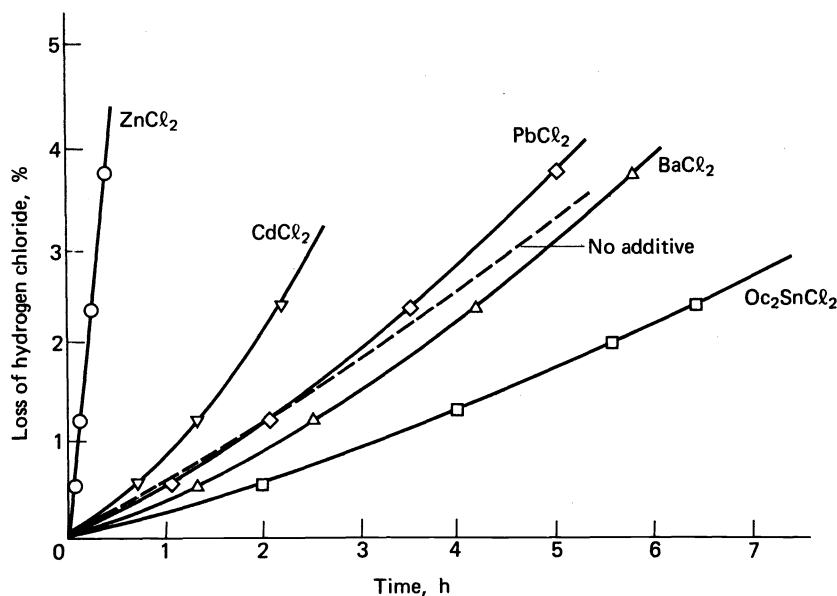


Fig. 11. Thermal dehydrochlorination curves of PVC at 175 °C in presence of different metal chlorides, formed as reaction products of the corresponding stabilizers (concentration each 5 mmol per 100 g PVC)

The cadmium chloride and especially the zinc chloride have a destabilizing effect. The lead chloride and the barium chloride behave almost neutrally. Surprisingly, however, the dioctyltin dichloride considerably retards the dehydrochlorination of PVC. This retarding effect is also attributed to other alkyltin chlorides and can be assumed to be a general property of organotin compounds (Fig. 12):

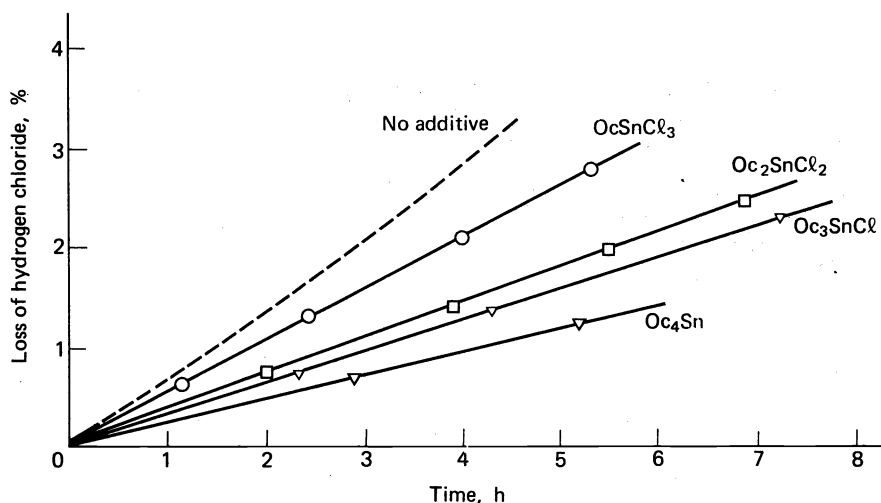


Fig. 12. Thermal dehydrochlorination curves of PVC at 175 °C in the presence of different octyltin chlorides and tetraoctyltin (concentration each 5 mmol per 100 g PVC)

There is an increase in this retarding effect on the thermal dehydrochlorination of PVC from mono-octyltin trichloride via dioctyltin dichloride to tri-octyltin chloride, and it is most pronounced with tetraoctyltin. But it is not possible to describe them as stabilizers, since these organotin derivatives do not exhibit an induction period, which is an essential condition of a heat stabilizer.

The observation that organotin chlorides as reaction products of organotin stabilizers retard the dehydrochlorination of PVC, may be related to specific complexing of allyl chloride groups in the PVC as shown in Fig. 13:

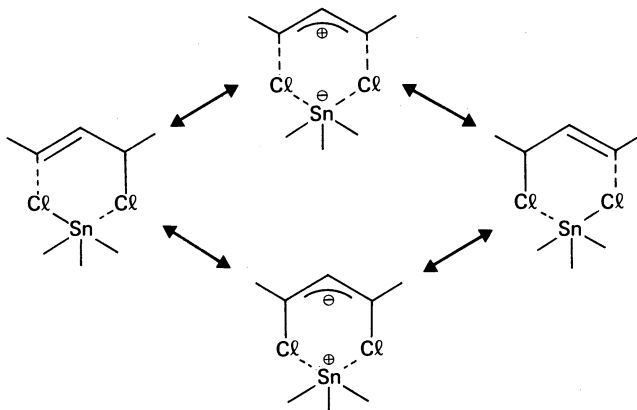


Fig. 13. Proposed explanation for the retardation effect of organotin chlorides on the thermal dehydrochlorination of PVC

In principle, this more or less organotin specific retardation effect could also be related to the organotin mercaptides themselves. That means we have to consider a fourth stabilization function of organotin mercaptide stabilizers depending on complex chemical effects (without chemical changes) emanating from both, mercaptides and chlorides. Now we can also understand why the stabilizer conversion has such a low value. Further investigations are necessary to prove this assumption.

Now to the *c u r a t i v e* functions: The observation that organotin mercaptide stabilizers are able to repair damaged sites of the PVC leading to discoloration, is very remarkable. In our opinion we should talk about curative functions. Thus, a significant color improvement is observed by treating a thermally discolored PVC sheeting with an organotin mercaptide stabilizer



as can be seen clearly from Fig. 14 (Ref. 12):

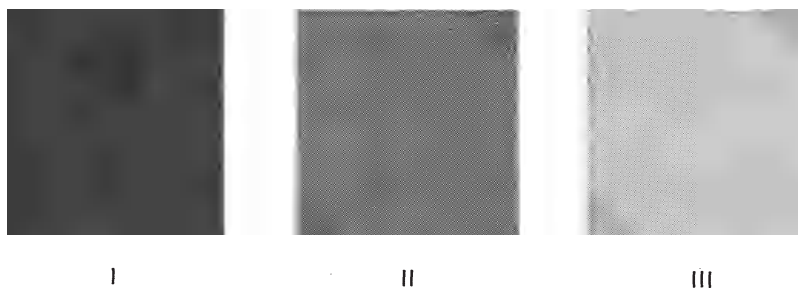


Fig. 14. PVC sheeting: (I) discolored by heat processing; discoloration improved by treatment with 2 % dibutyltin-bis-isooctylthioglycolate; (II) immediately after incorporation; (III) after 30 min subsequent processing (180 °C)

We assume that the color improvement immediately after incorporation of the stabilizer mainly depends on the destruction of onium complexes. But we are convinced that the color improvement obtained after 30 min is mainly due to the addition of mercaptans - liberated from the stabilizer by reaction with hydrogen chloride - to longer polyene sequences (Fig. 15):

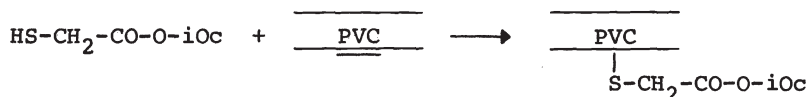


Fig. 15. Addition of isooctylthioglycolate to a double bond (schematically) in PVC

The addition of mercaptans to polyene sequences has already been considered by Jasching (13) in 1962. Further evidence in this respect can be deduced from a study of Poller et al. (14). See also Ref. (15). Indeed there is a considerable color improvement if thermally discolored PVC is treated with isooctylthioglycolate (Ref. 12).

Consequently there are two stabilizing reactions leading independently to sulphur incorporation into PVC (Fig. 16):

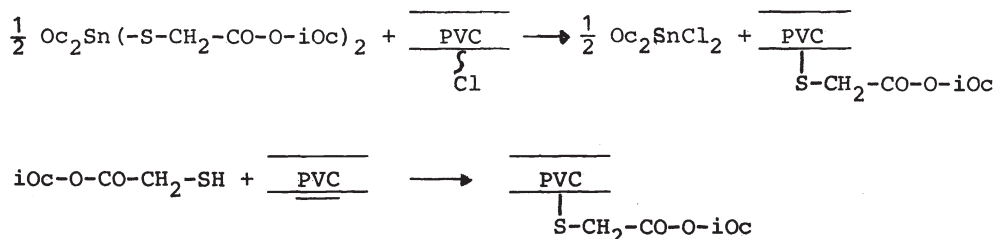


Fig. 16. The two independent stabilizing reactions responsible for the sulphur content in PVC processed with organotin mercaptide stabilizers

In this context we can also put the question, what is the amount of sulphur being transferred to PVC under processing conditions, since this also reflects an important part of the stabilization? The first more semi-quantitative measurements have been carried out by Frye et al. (8).

By using the tracer technique, Figge and Findeiß (4) have recently determined the correlation between the mercapto group transfer and the time of heat treatment. These experiments were, however, carried out under nitrogen in a static heat test (Fig. 17):

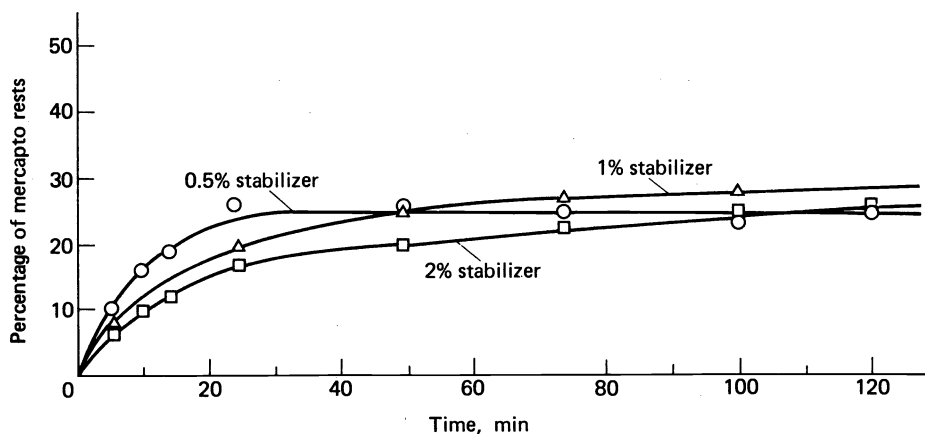


Fig. 17. Time dependence of the percentage of mercapto groups being transferred (directly or indirectly) from a dioctyltin-bis-isooctylthioglycolate ( $\approx 100\%$ ) to PVC at  $180^\circ\text{C}$  in nitrogen atmosphere (Ref. 4)

Let us initially consider the first 20 min of heating which is very important in practice. The most important result is: the lower the stabilizer concentration the higher the rate of mercapto group transfer. This is similar to the stabilizer conversion (Fig. 9). Surprisingly enough, however, it can be seen that, with increasing time of heat treatment the transfer rate becomes independent of the stabilizer concentration and approaches a threshold value of 25%. With 0.5% stabilizer this threshold value is reached in 25 min, with 3% stabilizer, however, not before 80 min. There is no simple explanation of this result and additional investigations will be necessary to clarify this complex phenomenon.

Let us now summarize the most important facts concerning the mode of action of organotin mercaptide stabilizers (Tab. 2):

TABLE 2. Differentiation of the functions of organotin mercapto stabilizers

#### I. PREVENTIVE FUNCTIONS

1. Antioxidant effect and thus reduction of forming initiation sites
2. Binding (neutralization) of hydrogen chloride and thus exclusion of its autocatalytic effect
3. Exchange of labile chlorine atoms and thus elimination of initiation sites
4. Complexchemical protective effects without chemical changes

II. CURATIVE FUNCTIONS

1. Addition of eliminated mercaptans to damaged sites (double bonds and polyene sequences, respectively)
2. Destruction of onium complexes and thus improvement of color

Hence, the mode of action of organotin mercaptide stabilizers can be explained by four preventive and two curative functions. The complex chemical protecting effects, mentioned under I.4 (Tab. 2) can be considered novel. The latter can be deduced from the retarding effect of the organotin chlorides on the dehydrochlorination of PVC.

**2.2.2. Organotin maleates.** Organotin stabilizers derived from maleic acid are slightly weaker in their thermostabilizing efficiency but excellent in their light stabilizing properties (Sec. 3.2.3.). Fig. 18 shows the two most important types.

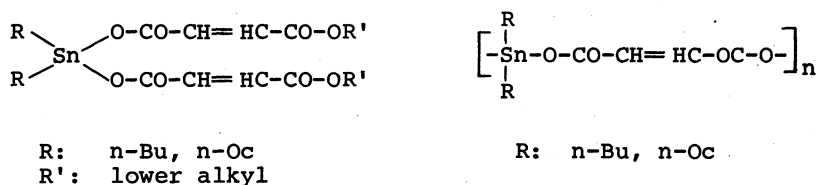


Fig.: 18. Organotin maleate stabilizers

The concept presented in Sec. 2.2.1 for organotin mercaptide stabilizers can also be applied to maleate stabilizers. Since a marked antioxidant effect is lacking, organotin maleate stabilizers can be improved by the combination with phenolic antioxidants, especially those of the sterically hindered phenol type. The superiority of organotin maleates over conventional carboxylates is most probably due to the dienophilic properties of the maleic acid. We should, therefore, speak of an additional curative function. The mentioned investigations of Frye (9) support also this explanation.

### 2.3 Other metal stabilizers

**2.3.1 Barium/cadmium and calcium/zinc carboxylates.** Carboxylate stabilizers based on cadmium and zinc are not less interesting in their mode of action (Fig. 19):

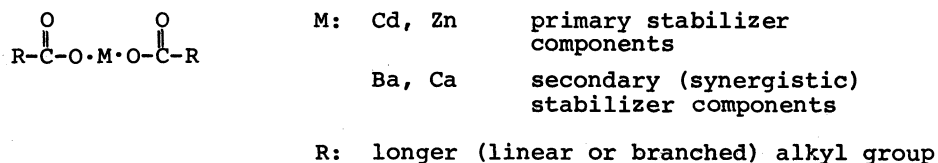


Fig. 19. Metal carboxylate stabilizers

It is well known that the carboxylates of cadmium and zinc provide PVC with a very good initial color but impart a very poor longterm stability. The behaviour of the carboxylates of barium and calcium is vice versa. These differing effects lead in combination to synergism, so that e.g. barium/cadmium stabilizers confer good initial color and also good longterm stability.

The chemical background of this synergism is now quite clear. In this context credit should be given to the very interesting investigations of Bengough and Onozuka (16), Shimura and Sakai (17), Onozuka and Asahina (5), Anderson and McKenzie (18), Braun and Hepp (19) and Hoang, Michel, Guyot (20). Special reference should be made to the fundamental research work of Frye et al. (21, 22).

Hence the mode of action of a barium/cadmium stabilizer can be described as follows (Fig. 20):

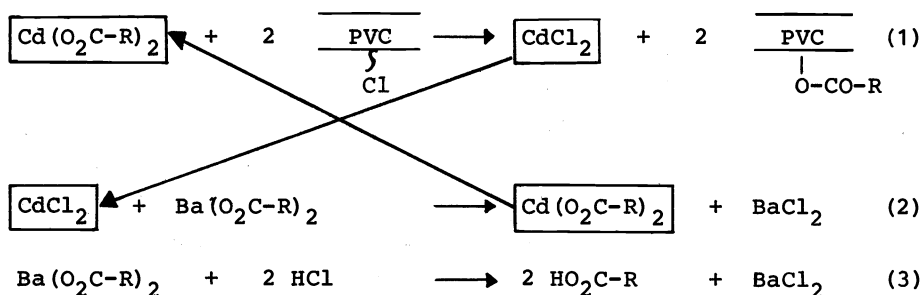


Fig. 20. The stabilizing reactions of a barium/cadmium stabilizer

- Only the cadmium carboxylate is able to exchange labile chlorine atoms (1). We can assume that this exchange occurs in a similar complex chemical way as with organotin stabilizers (Fig. 7.). - The barium carboxylate on the other hand reacts preferably with hydrogen chloride (3). - The cadmium chloride formed according to (1) is reconverted into active cadmium carboxylate according to (2). This means that the destabilizing effect of this LEWIS-acid is at least temporarily eliminated.

Very interesting and informative are the dehydrochlorination curves of cadmium stearate, barium stearate and their combination (Fig. 21.):

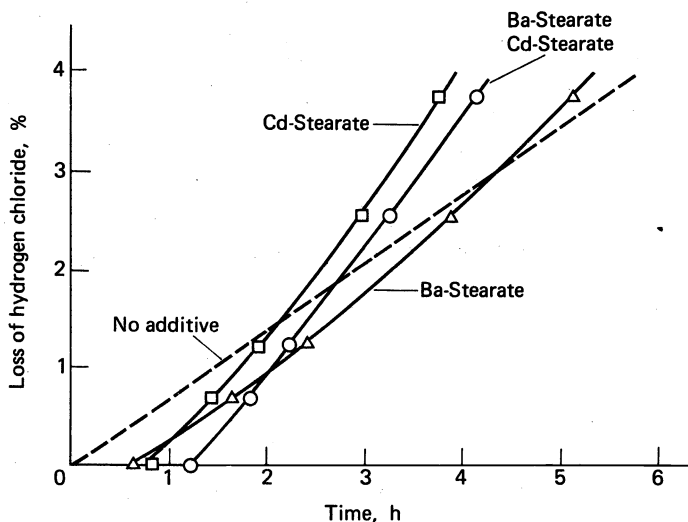


Fig. 21. Thermal dehydrochlorination curves of PVC at 175 °C in presence of cadmium stearate and barium stearate and their combination (concentration each 5 mmol per 100 g PVC also in the combination)

It can be seen that the addition of barium stearate to the cadmium stearate causes an enhancement in the induction period but does not affect the gradient of the dehydrochlorination curve. Thus, the conclusion may be drawn that apart from the exchange reaction (2) there are no deactivating interactions between cadmium and barium.

However, the addition of pentaerythritol to the cadmium stearate diminishes the gradient of the dehydrochlorination curve. This indicates that the hydroxyl groups of pentaerythritol reduce the LEWIS-acidity of the cadmium chloride and thus its destabilizing effect (Sec. 2.4.5.).

On the other hand a noticeable decrease in the gradient of the dehydrochlorination curve of the analogous zinc stearate/barium stearate combination can be seen. In this case interactions between zinc and barium have to be assumed leading to a deactivation of the zinc chloride probably in the form of BRØNSTEDT-salts.

Briggs et al. (23) have systematically examined the influence of phosphites (Sec. 2.4.3.) on the stabilizing action of cadmium and zinc laurate. It was found that phosphites have a deactivating effect on zinc chloride but not on cadmium chloride.

To sum up, it may be said that the mode of action of these complex metal carboxylate stabilizers can be described according to the same concept which has been applied to organotin stabilizers. Differences are mainly due to the fact that the chlorides formed from the carboxylates of cadmium or zinc have a destabilizing effect on PVC. This leads to the need to add further components such as epoxy compounds, polyols or phosphites. In general, the addition of phenolic antioxidants leads to an increase of effectiveness, especially if no phosphites are included in the system.

**2.3.2. Lead compounds.** Lead stabilizers belong to the very first PVC stabilizers used conferring good heat stability. They are widely used in the production of pipes, and cable insulation.

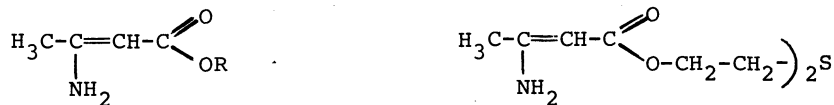
The bivalent lead possesses complex chemical properties necessary for the substitution of labile chlorine atoms and, thus, meets one of the essential requirements of a heat stabilizer. Furthermore, another advantage is, that the lead chloride formed during the stabilization process does not have a destabilizing effect on the PVC (Fig. 11).

Basic lead salts, such as basic lead carbonate, tribasic lead sulfate and dibasic lead phosphite are of special importance. A disadvantage of lead stabilizers apart from their toxicity is their hydrogen sulphide sensitivity.

As to the interpretation of the mode of action, the general concept (Sec. 2.2.1.) may also be applied to these stabilizers. The first systematic investigations on this subject were carried out by Silberman et al. (24).

#### 2.4. Organic stabilizers and co-stabilizers

**2.4.1. Aminocrotonic acid esters.** So far, heat stabilizers based on  $\beta$ -aminocrotonic acid esters are the only metal-free ones which are also suitable for suspension PVC (Fig. 22).



(R: longer alkyl)

Fig. 22.  $\beta$ -Aminocrotonic acid ester stabilizers

Very interesting are the thermal dehydrochlorination curves of such a stabilizer type (Fig. 23):

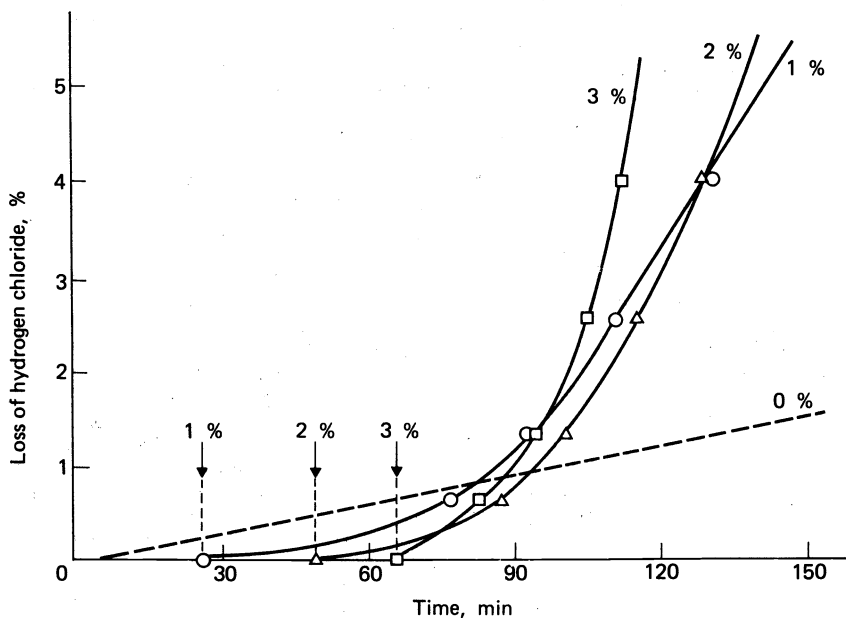


Fig. 23. Thermal dehydrochlorination curves of PVC at 175 °C in the presence of different amounts of thiodiethyleneglycol-bis-β-aminocrotonic acid ester

Here too, a marked, and for stabilizers a characteristic, induction period is observed, which increases with the concentration of the stabilizer. Unlike organotin mercaptide stabilizers (Fig. 5) the gradient of the curve rises rapidly with increasing concentrations. Obviously reaction products are formed which have a large destabilizing effect.

Model studies by Michel, Hoang and Guyot (25) provide evidence that these compounds are able to substitute labile chlorine atoms (Fig. 24):

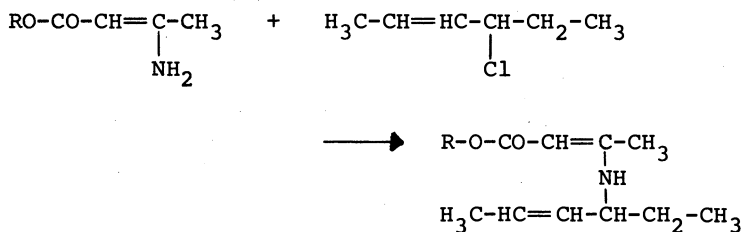


Fig. 24. Stabilizing reaction of β-aminocrotonic acid esters

Presumably the amino group in these compounds is also able to neutralize hydrogen chloride. Generally, these aminocrotonic acid esters can also be further optimized by the combination with phenolic antioxidants. A great disadvantage of the aminocrotonic acid esters is their negative influence on the light stability of the PVC (Sec. 3.2.1.). Thus their fields of application are rather limited.

On the whole it can be said that the mode of action of these aminocrotonic acid ester stabilizers may be interpreted according to the general concept (Sec. 2.2.1.). Most interesting is the fact that they exhibit also curative functions. By incorporating them in thermally discolored PVC there is a considerable color improvement.

**2.4.2. 2-Phenylindole.** 2-Phenylindole is an organic heat stabilizer for PVC which has been known for a long time. If 2-phenylindole is used alone it only

gives a satisfactory stabilizing effect to emulsion PVC. In combination with calcium/zinc carboxylates, however, it is also effective in suspension PVC.

In an interesting investigation by Hoang, Michel and Guyot (26) with 4-chlorohexene-2 as a PVC model, it has been proved that 2-phenylindole is primarily subjected to a substitution in the 3-position (Fig. 25):

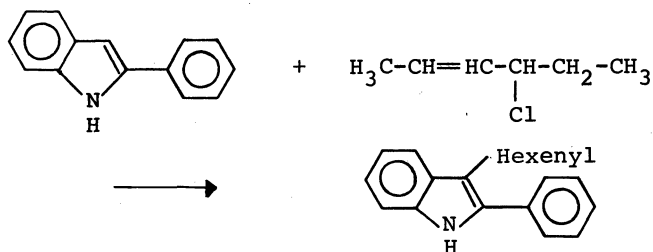


Fig. 25. Reaction of 2-phenylindole with 4-chlorohexene-2 (Ref. 26)

There is no substitution - as might be expected - at the N-atom. With regard to the PVC, here too, we can speak of an elimination or exclusion of allyl chloride groupings as initial sites.

2.4.3. Organic phosphites. Organic phosphites, especially the mixed aliphatic/aromatic triphosphites, are important costabilizers, preferably for the carboxylate stabilizers based on cadmium or zinc. According to Verizhnikov et al. (27) triphosphites per se have only a very slight heat stabilizing effect as shown in the diagramme of Fig. 26. A marked induction period is lacking.

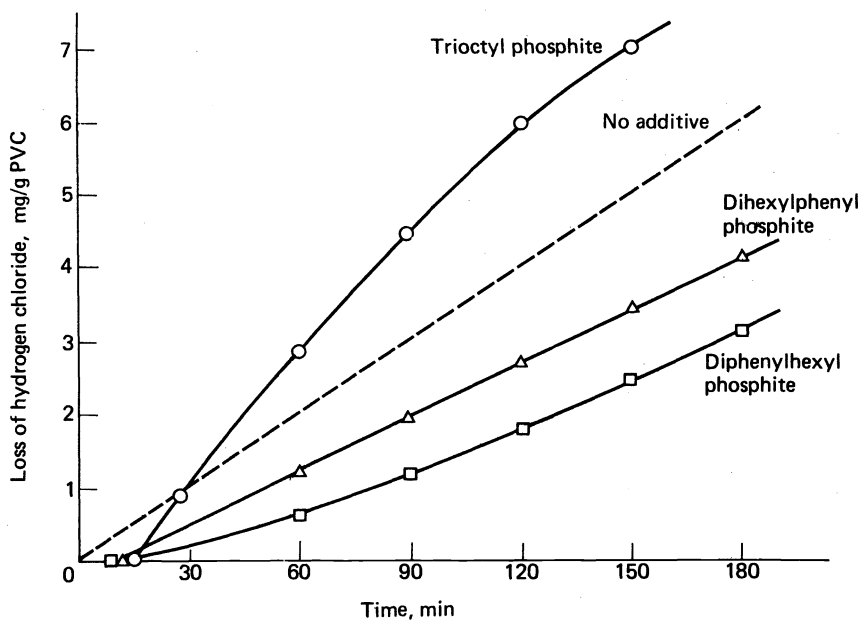


Fig. 26. Thermal dehydrochlorination curves of PVC at 175 °C in the presence of different triorganophosphites (concentration each 3 mmol per 100 g PVC) (Ref. 27)

It is clearly shown that in going from the diphenyl hexylphosphite to the trioctylphosphite, the induction period increases, and an increase in the gradient of the dehydrochlorination curves can be seen. In technical applications alkyl/aryl phosphites used as stabilizers are favoured perhaps due to an "intramolecular" synergism.

Quite a number of authors [Silberman et al. (28), Briggs and Wood (23), Anderson and McKenzie (18), Verizhnikov et al. (27), Rasuvaev et al. (29), Foss et al. (30), Hoang, Michel and Guyot (31)] have made efforts to eluci-

date the mode of action of organic phosphites as heat stabilizers and co-stabilizers, respectively. On the basis of these investigations the following functions may be attributed to them:

- Decomposition of peroxides and thus antioxidative effects (Ref. 32)
- Binding or neutralization of hydrogen chloride (especially to phosphites with aliphatic ligands)
- Substitution of labile chlorine atoms (under the catalytical effect of metal carboxylates)
- Addition to polyene sequences
- Complexing and thus deactivation of metal chlorides and furthermore improvement of transparency.

Fig. 27 clearly shows that the addition of a phosphite increases the heat stabilizing effect of cadmium octoate and at the same time improves the transparency:



Fig. 27. Improvement in transparency of a cadmium octoate stabilized PVC sheeting (left) through use of phosphite as co-stabilizer (right)

2.4.4. Epoxy compounds. Epoxy compounds based on epoxidized fatty acid esters are very valuable co-stabilizers (Fig. 28):

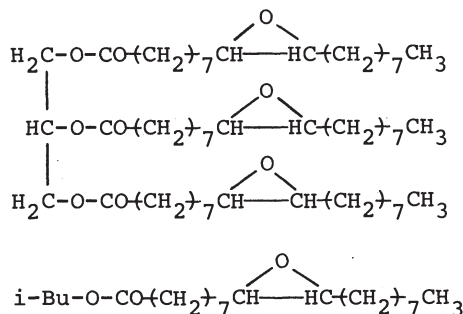


Fig. 28. Structural formula of epoxidized fatty acid esters

The primary stabilization effect of these substances - occasionally called epoxy plasticizers - is weak as shown by the dehydrochlorination curve (Fig. 29).

The importance of these epoxy compounds is due to their co-stabilizing effect in combination with almost all stabilizer systems, but especially in combination with metal carboxylate stabilizers. Furthermore, these substances also have a lubricating action.

Anderson and McKenzie (33) have investigated the combined effect of an epoxy compound and metal carboxylates in model reactions. With regard to PVC, it can be said that epoxy compounds contribute to the heat stabilization in the form of two reactions (Fig. 30).

This is supported by two further investigations of Foss et al. (30) as well as of Hoang, Michel and Guyot (34).

In metal carboxylate stabilizers based on zinc, these epoxy compounds might also act as "chelators" similar to polyols and phosphites.



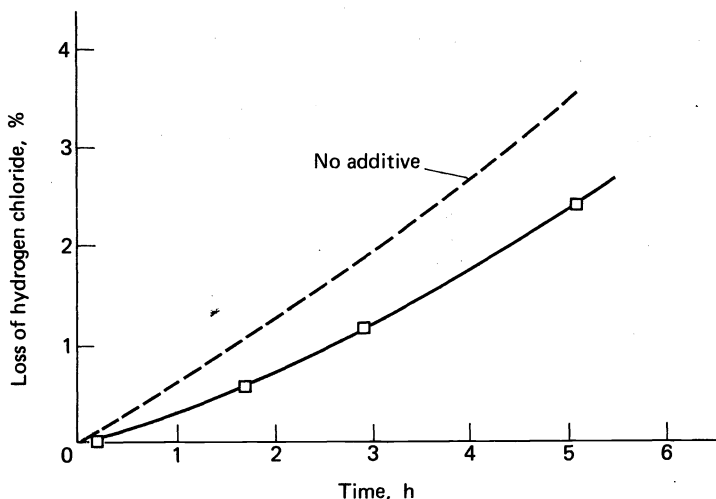
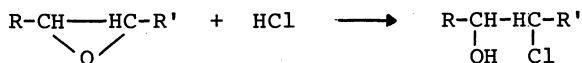


Fig. 29. Thermal dehydrochlorination curves of PVC at 175 °C in presence of 2 % epoxidized soya bean oil

Neutralization of hydrogen chloride



Substitution of labile chlorine atoms

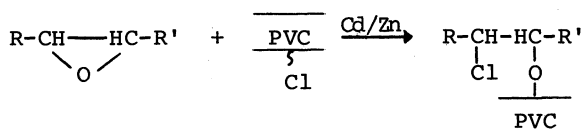


Fig. 30. Stabilizing reactions of epoxy compounds

2.4.5. **Polyols.** Polyols based on polyvalent alcohols such as pentaerythritol, trimethylolpropane, sorbitol and others are also co-stabilizers for metal carboxylates based on zinc or cadmium (Sec. 2.3.1.).

It is generally agreed upon that their effectiveness is due to complex formation and thus deactivation of the zinc and cadmium chlorides [Briggs (23)]. These systems are also called "chelators".

### 3. LIGHT STABILIZATION OF PVC

#### 3.1 The problems of the light degradation of PVC

The short wavelength range of the sun's spectrum reaching the surface of earth begins at about 300 to 310 nm. With regard to the constitution of PVC in this spectral range - that means above 300 nm - no absorption should take place (Ref. 35). According to the first law of photochemistry: "no absorption, no photochemistry", so there should be no light degradation. The experience shows, however, that the sun light is detrimental to PVC and, as a consequence, it cannot be used in outdoor application without protection against light. Hence, absorbing species must be present in PVC which are responsible for the light absorption and, therefore, also for the light degradation.

Carbonyl groups or shorter polyene sequences are considered as absorbing sites. Both can be formed during the thermal processing of PVC. Furthermore, impurities, e.g. residues from polymerization catalysts absorbing in the range between 310 to 350 nm may act as sensitizers. The latter may also be

true for certain thermostabilizers and their conversion products.

The phenomena of the light degradation are, of course, extremely complex and even today, only clarified to a very small extent. In this connection mention may be made to some publications of Gibb and MacCallum (36, 37, 38, 39), Owen et al. (40, 41, 42, 43) Kamal et al. (44), and to the monograph of Ranby and Rabek. Special credit should be given to a recent paper of Braun and Wolf (46) which deals with some very important fundamental aspects of the photodegradation of PVC. There are even two contributed papers covering these problems (Ref. 47, 48).

In a more phenomenological approach we can say that the light degradation of PVC is determined by the processes of: photolysis, photo-oxidation and dehydrochlorination. Sensitisation phenomena, energy transfer processes and singlet oxygen may also play an important part. Discoloration and loss of mechanical properties are the indications of this degradation phenomenon. We cannot go more deeply into the details within the scope of this lecture.

### 3.2 Measures for the light stabilization of PVC

3.2.1 Light stability providing thermal stabilizers. In order to impart good light stability to PVC provision should be made for processing to be carried out with a good thermal stabilizer. There are several reasons for this:

- A good thermal stabilizer prevents the formation of CO-groups and polyene sequences which are responsible for the absorption of UV-light and, therefore also for the light degradation.
- The light degradation of PVC is always accompanied by dehydrochlorination. The hydrogen chloride formed leads to a discoloration caused e.g. by onium salts. A thermal stabilizer is able to bind the hydrogen chloride formed so that a certain light protection effect is achieved.
- Effective thermal stabilizers or stabilizer systems always have antioxidative properties. This factor leads to a favourable effect on the light stability of PVC (Ref. (49)).

Hence, effective thermostabilizers influence, in general, the light stability of PVC positively. But there are considerable differences in the light stabilizing efficiency of the individual thermostabilizers. Table 3 shows a sequence of activity of the most important thermostabilizers and stabilizer systems, with regard to their light stability.

TABLE 3. Sequence of PVC thermal stabilizers providing different light stability

good	Organotin maleates
	Barium/cadmium carboxylates
	Basic lead phosphite
	Organotin mercaptides
	Calcium/zinc carboxylates
poor	$\beta$ -Aminocrotonic acid esters

Surprisingly, but well known, is the fact that organotin mercaptides which have an excellent thermostabilizing efficiency and exhibit, of course, antioxidative properties, do not impart good light stability. Most probably sensitizing effects originating from the mercapto groups are responsible for this.

On the other hand organotin maleate stabilizers provide very good light stability. However, the reasons for this are not fully understood.  $\beta$ -Aminocrotonic acid esters are situated at the end of the sequence, since the latter possess long wavelength absorption bands, they may act as sensitizers for the light degradation.

3.2.2 Pigmentation. Pigmentation of PVC is a simple but very efficient and in practice well approved measure for the enhancement of the light stability of PVC. But only those pigments may be considered that do not possess sensitizing properties. A well known, white pigment is the rutile modification of titanium dioxide.

Fig. 31 shows that the light stability of PVC processed with an organotin mercaptide stabilizer, can be considerably improved by increasing amounts of rutile:

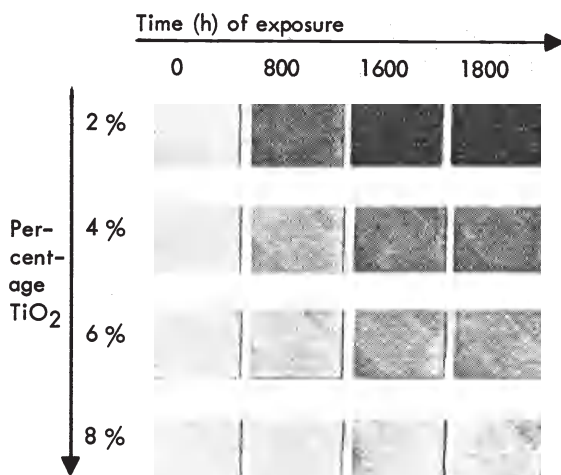


Fig. 31. Weathering stability of PVC, processed with 2 % dibutyltin-bis-isooctylthioglycolate, containing increasing amounts of TiO<sub>2</sub> (rutile)

There are also light stable and, therefore, light stability providing, color pigments available (Ref. 50). The light protection effect of these pigments is based mainly on filter effects, similar to that of the UV-absorbers.

**3.2.3 UV-Absorbers.** In case of transparent formulations the light stability can be greatly enhanced by using UV-absorbers. These are systems with a very strong absorption band at the margin of the visible to the ultraviolet region of the spectrum covering the near ultraviolet region till down to 300 nm. Figure 32 shows the structural formula of three industrial UV-absorbers:

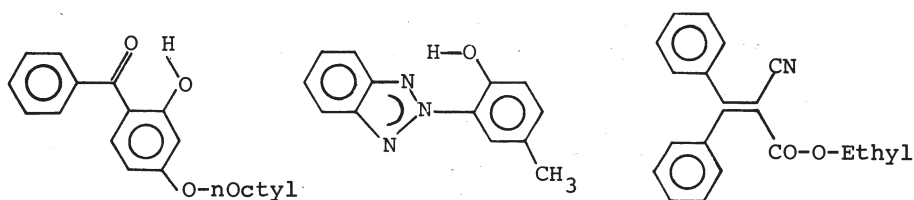


Fig. 32. UV-absorbers in technical use

The hydroxyphenyl benzotriazole derivative (the middle one) and all related structural types are designated by a very steep absorption band at the boundary of the visible range of the spectrum. The latter leads to an especially strong filter effect without showing its own color.

A photo-enolization is assumed by Burgess (51) to explain the mode of action of UV-absorbers with a chelate structure (Fig. 33):

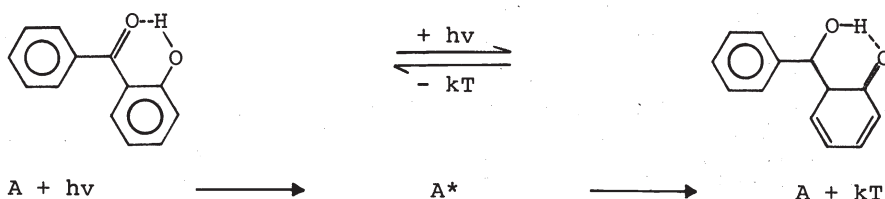


Fig. 33. Mode of action of UV-absorbers of hydroxybenzophenone type (Ref. 51)

This enolized excitation state undergoes immediate radiationless degradation, which means it is transformed to the ground state by release of heat. Also an intramolecular quenching mechanism of these systems could be considered. But there are also reasons for the assumption that these UV-absorbers are able to quench foreign excitation states. Thus, they can interfere with energy transfer processes in liquid organic scintillators.

Using such UV-absorbers, especially those of the hydroxyphenylbenzotriazole type, in all transparent PVC-formulations good to very good light protection effects can be obtained. In general it is a question of how much UV-absorber is used. Even the light stability of a PVC processed with an organotin mercaptide stabilizer can be improved for use in certain outdoor applications (Fig. 34):

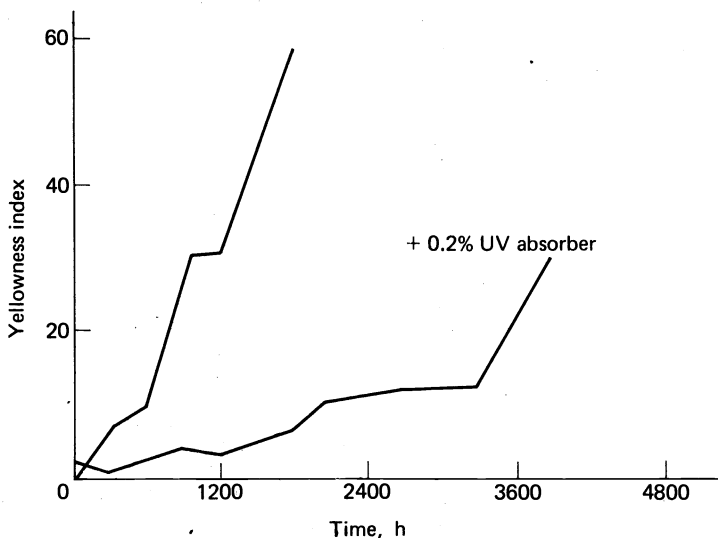


Fig. 34. Improvement of the light stability of PVC processed with 2 % of a dibutyltin-bis-isooctylthioglycolate stabilizer by adding 0,2 % of the hydroxyphenyl benzotriazole derivative (Xenotest)

Another Xenotest result is shown on Fig. 35:

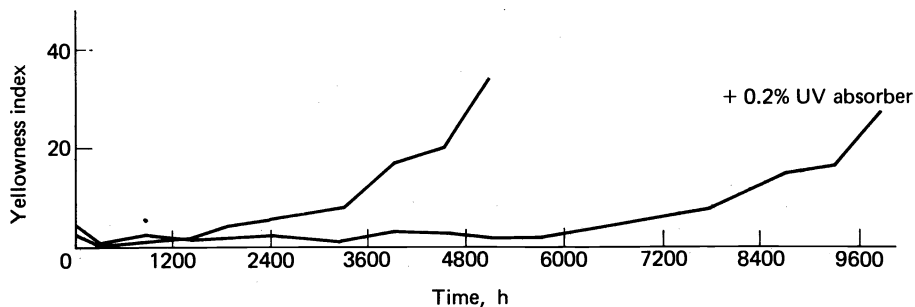


Fig. 35. Improvement of the stability of PVC processed with 2 % of dibutyltin-bis-isobutylmaleate stabilizer by adding 0,2 % of a hydroxyphenyl benzotriazole derivative (Xenotest)

It can be clearly seen that PVC processed with an organotin maleate stabilizer exhibits per se considerable light stability. The combination, however, with an UV-absorber leads to a substantial enhancement of the light stability. Such a PVC fulfills the tough requirements of outdoor application.

In a series of papers e.g. by Baum (52), Büssing (53), Oki and Mori (54) Weisfeld, Thacker and Nass (55), Szabo and Lally (56) more detailed results with UV-absorbers are reported.

The authors wish to express their thanks to Dr. Abeler, Dr. H. Müller and Dr. Wehner but especially to Dr. Büssing for many stimulating discussions.

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