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Stabilization of PVC to Light and Heat*

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The actual status of the heat and light stabilization of PVC is reviewed with emphasis on the stabilizers and their mode of action.

A brief treatment of the most important facts of the thermal degradation of PVC were given, followed by a discussion of some proved individual functions of the heat stabilizers by using organotin mercaptides as a specific example. The antioxidant effect, binding of hydrogen chloride, and exchange of allylic (labile) chlorine atoms have to be considered preventive functions. The addition of mercaptans—liberated from organotin mercaptides by direct reaction with hydrogen chloride—to longer polyene sequences, and destruction of strongly chromophoric onium complexes represent stabilizer functions of curative nature.

The mode of action of metal carboxylate stabilizers like cadmium and zinc soaps can also be explained on the same basis.

The combination with barium and/or calcium carboxylates (termed "synergists"), or with "chelators" such as polyols or organic phosphites serves primarily to deactivate the degrading chlorides of cadmium or zinc.

In the case of organic stabilizers such as 2-phenylindole, epoxy compounds, aminocrotonic acid esters, and organic phosphites, the elimination of labile sites in PVC has also to be considered. Evidence for such action follows from low molecular model reactions.

*The full text of this lecture will be published in *Pure and Applied Chemistry*.

Light stabilization of PVC is also discussed. Autoxidation and simultaneous dehydrochlorination account for the most important photo degradation reactions.

Some heat stabilizers also confer excellent light stability at the same time. Apart from the conventional barium/cadmium systems the organotin maleinates deserve special mention. The light-stabilizing effect of these systems can be considerably enhanced by using UV absorbers, especially of the hydroxyphenylbenzotriazole type. A more specific explanation of the mode of action of these light stabilizing systems is given.

DISCUSSION

Prof. I. N. Einhorn (University of Utah, Salt Lake City, Utah, USA): First, may I add my compliments to the very extensive review given by Dr. Wirth. However, I note that in his review, he discussed the temperature regime of processing between 170 and 180°C. Later in this symposium we will be discussing ranges from 400 to 1500°C, and I wonder whether there are any contributions by stabilizers to vinyl chlorides at these higher temperature regimes?

Dr. Wirth: The processing of PVC is usually carried out at about 200°C, but by going down to 175°C, it is possible to see the differences in efficiency of additives much better. That is why we did so.

Prof. Einhorn: Yes, I understand that—but my comment was to ask whether the stabilizers add any stability to the degradations that would be seen at very high temperatures?

Dr. Wirth: I do not think so. Above 250°C the stabilizers themselves decompose, and the decomposition products may even catalyze the degradation.

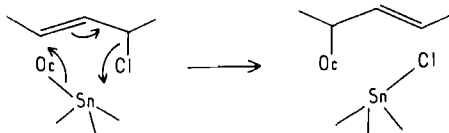
Prof. J. P. Kennedy (University of Akron, Akron, Ohio, USA): I would be careful in accepting Dr. Wirth's explanation in connection with the Lewis acids and the thermal stability of PVC. I refer to a series of slides shown by Dr. Wirth, showing the effect of zinc, calcium, lead, and barium chlorides and dioctyltin dichloride. He expressed amazement that the dioctyltin dichloride was something of a stabilizer whereas the other compounds were not. That was followed by a series of slides demonstrating the fact that the number of octyl groups on tin increased the heat stability of PVC.

Dr. Wirth: The retardation effect is not a full stabilization effect but a contributive effect.

Prof. Kennedy: It is a retardation effect of these compounds. In explanation of all that, an intermediate was proposed. This consisted in a negative allyl ion and a positive tin moiety. In my opinion, the explanation could be formulated rather differently by saying simply that the compounds looked at, including the dioctyltin compounds, are Lewis acids, so that it is a sequence of Lewis acids which are being seen.

Dr. Wirth: Yes, that may be right.

Prof. Kennedy: The stabilizing action would thus be a transfer of the octyl group from the tin onto the PVC. Thus the PVC is alkylated with the octyl group. However, with the other Lewis acids, there is a removal of the chloride to the metal. If this does occur, the intermediate must be not the negative allyl ion but the positive allyl ion. The metal is not the positive moiety, but the negative one.



I would be extremely interested to learn how this explanation would fit with Dr. Wirth's.

Dr. Wirth: We have discussed thoroughly the question of whether a positive or a negative tin moiety is involved. Since the dialkyl tin species is amphoteric in nature we could assume both possibilities. It has been proved that there is actually no transfer of octyl groups from the stabilizer to the PVC. We must, therefore, find another explanation, and I should like to refer once again to the proposed explanation given in my lecture.