

Effects of 6-Anilino-1,3,5-Triazine-2,4-Dithiol, Zinc Stearate, and Barium Stearate on the Thermal Stabilization of PVC

KUNIO MORI, ISAO KIKUCHI, and YOSHIRO NAKAMURA, *Faculty of Engineering, Iwate University, Ueda, Morioka, Japan 020*

Synopsis

Individual action and synergistic effect in the combination of 6-anilino-1,3,5-triazine-2,4-dithiol (AF), zinc stearate, and barium stearate on the color stabilization of PVC were investigated. In this system, AF selectively reacts with allylic chlorine atoms in PVC. Consequently, unstable allylic chlorine units were converted to thermally stable allylic structures, thus retarding the development of polyene sequences. Zinc stearate accelerated the reaction of AF with allylic chlorine atoms in PVC, forming the zinc salts of AF (AFZnSt, $\text{St}=\text{C}_{17}\text{H}_{35}\text{COO}-$) by reacting with AF. Barium stearate reacted with ZnCl_2 which is formed in the above reaction to give St_2Zn and BaCl_2 . Consequently, barium stearate led to the selective reaction of AF with allylic chlorine atoms in PVC and the remarkable retarding effect of discoloration of PVC.

INTRODUCTION

The discoloration mechanism for poly(vinyl chloride) (PVC) during thermal degradation has been explained by the development of conjugated double bonds formed through the zip dehydrochlorination.^{1,2} A sequence of at least five conjugated double bonds was required to obtain a colored material. The dehydrochlorination was initiated at weak sites such as allylic chlorine units, tertiary chlorine units, unsaturated chain end units, and head to head units in PVC.³⁻⁶ In these weak sites, allylic chlorine units most easily initiated dehydrochlorination.³⁻⁶ Therefore, the discoloration of PVC during thermal degradation can be moderated when the weakest sites such as allylic chlorine units are converted to a thermally stable allylic structure by means of the reaction with stabilizers.

Kennedy et al.⁷ and Gaylord et al.⁸ indicated that substitution of the labile chlorine atoms by a grafting reaction improves the thermal stability of PVC. The stabilization of PVC by organotin compounds is due to the exchange of allylic chlorine atoms in the PVC and organotin compounds.⁹ Suzuki and Nakamura⁶ investigated the thermal degradation of allylic derivatives and found that thio-phenyl ether type allylic derivatives showed higher thermal stability. Further, Starnes et al.¹⁰ found that the PVC polymer having thioether groups in side chains is also stable to dehydrochlorination during thermal degradation.

On the other hand, the authors found that the thermal stability of PVC is improved by a reactive stabilizer system such as a mixture of 6-anilino-1,3,5-triazine-2,4-dithiol (AF), zinc stearate (St_2Zn) and barium stearate (St_2Ba).¹¹⁻¹² Such a reactive stabilizer may play an important role in the conversion of unstable allylic chlorine units into stable allylic derivatives thermally. The object of this work is to elucidate these individual actions and synergistic effects in the combination of AF, St_2Zn , and St_2Ba .

EXPERIMENTAL

Preparation of PVC Sheets and Their Thermal Aging

The PVC polymer used in this work was Zeon 103EP ($\bar{P}_n = 1050$, double bond content = 2.0 units/1000 PVC monomer). The commercially available reagents of Zisnet AF (AF, Sankyokasei Co.), St_2Zn , St_2Ba , and 2-ethylhexyl phthalate (DOP) were used.

The mixture of PVC (10 g), DOP (4 g), AF (0–0.04 g), St_2Zn (0–0.1 g), St_2Ba (0–0.2 g) were milled on an open roll (2 × 5 in.) at 160°C for 5 min. The blends were pressed at 160°C for 5 min. Thus PVC sheets about 0.5 mm in thickness were obtained. PVC sheets interposed between two glass plates were aged at $170 \pm 3^\circ C$ in a gear oven. PVC sheets aged thermally were investigated by colorimetry at room temperature by using a Suga Shikenki Model AU-SCH-2 differential colorimeter.

Ultraviolet Spectroscopy

Ultraviolet spectra of aged PVC (A-PVC), dissolved in tetrahydrofuran (THF) were obtained by using a Shimadzu UV-310 spectrophotometer. All A-PVC solutions (2.5 g/L) were carefully prepared under an inert atmosphere. A-PVC polymers were prepared as follows. 1 g of aged PVC sheets described above was dissolved in 20 mL of THF. The solution was poured into 200 mL of 50% methanol with vigorous stirring in a high speed mixer to give a crude A-PVC. The A-PVC was purified twice by the method of methanol (200 mL)–THF (20 mL) reprecipitation, washed with methanol, and dried in a calcium chloride desiccator *in vacuo* for 24 h. To avoid oxidation of samples, THF did not contain peroxide.

Dehydrochlorination of PVC Sheets

Thermal degradation of PVC sheets was conducted in a sealed glass tube at $170 \pm 3^\circ C$. The total amount of dehydrochlorination is indicated in the sum ($A + B$) of hydrogen chloride from both evaporated (A) from PVC sheets and reacted (B) with metal stearates during the thermal degradation. The procedures were as follows.

PVC sheets (4 g) were aged at $170 \pm 3^\circ C$ in sealed glass tubes. The contents after aging were dissolved in 50 mL of 0.01 N NaOH aqueous solution and the solution was adjusted to pH 7. Chlorine anions (A) in the solution were titrated with 0.01N $HgNO_3$ aqueous solution by using diphenylcarbazone indicator. On the other hand, the aged PVC sheets (4 g) were dissolved in THF (40 mL). The solution was poured into 300 mL of 0.01 N NaOH aqueous methanol (50%) with stirring. The aqueous methanol solution, after filtering, was evaporated until methanol and THF were removed. The aqueous solution was boiled for 1 h after adding 5 mL of 30% H_2O_2 solution and adjusted to pH 7; if the solution was cloudy, it was filtered. Chlorine anions (B) in the solution were titrated in a similar manner as above.

Reaction of AF with St_2Zn

The mixtures of AF with St_2Zn were stirred at 50°C or 80°C in methanol or in a high boiling point hydrocarbon (Solveso 150). The reaction mixture was filtered at 50°C. The collected product was purified by washing thoroughly with hot methanol or Solveso 150.

Reaction of AF with 4-Chloro-2-hexene or 2-Chlorobutane (RCl)

4-Chloro-2-hexene was used as a model for allylic chlorine atoms in PVC, and 2-chlorobutane as a model for ethylene chloride units which is a normal structure for PVC. The reaction of AF with RCl in the presence of St_2Zn and St_2Ba was conducted in a sealed glass tube at 100°C for 30 min with shaking. The reaction mixture was poured into methanol (100 mL) and was neutralized with 0.01 N HCl solution. The identification and determination of the products in the solution were conducted by use of a Hitach High Liquid Chromatograph 633.

Reaction of Metal Stearates with Metal Chlorides

PVC (Zeon 121, 10 g)—DOP (7 g) pastes containing St_2Ba (0.001 mol) and $ZnCl_2$ (0.001 mol) or St_2Zn (0.001 mol) and $BaCl_2$ (0.001 mol) were prepared, and then heated at 170°C for 10 min. The gelled PVC products (2 g) were dissolved in 20 mL of THF, and the solution was poured into 200 mL of 50% aqueous methanol with vigorous stirring in a high speed mixer. After removal of the polymer and metal stearates mixture, the amount of $ZnCl_2$ and $BaCl_2$ in the solution was determined by a chelate titration method.

RESULTS AND DISCUSSION

Synergism of Combination of AF, St_2Zn , and St_2Ba

The effects of AF, St_2Zn , and St_2Ba on the discoloration of PVC sheets at 170°C are summarized Table I. Here the degree of discoloration for PVC sheets was indicated until the Hunter's color difference value reached 12%. The discoloration of PVC sheets during thermal degradation was remarkably retarded, when the three components of AF, St_2Zn , and St_2Ba were simultaneously used

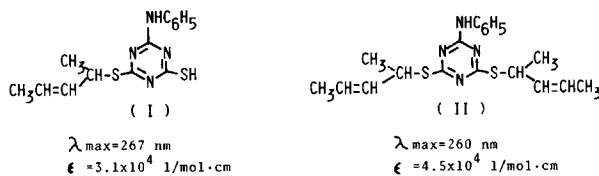
TABLE I
Effects of AF, St_2Zn , and St_2Ba on the Discoloration of PVC Sheets at 170°C

Stabilizer (phr)			Time until discoloration ($\Delta E = 12\%$) of PVC sheets (h)			
AF	St_2Zn	St_2Ba	0	1	2	3
0.2			→	→		
0.2	0.5		→	→		
0.2	0.5	1.5	→	→		
0.2		1.5	→	→		
0.2	0.5	1.5	→	→		
0.2	0.5	1.5	→	→	→	→

as a stabilizer. However, in cases in which even one or two components were lacking, these stabilizer systems had little retarding effect or none at all, indicating that the synergistic effect appears only in the combination of AF, St_2Zn , and St_2Ba .

Action of AF

On the crosslinking reaction of PVC with 6-R-1,3,5-triazine-2,4-dithiols and metal activators, the activation energy of crosslinking for AF was higher than that of the degradation of PVC, as reported previously.^{13,14} The crosslinked PVC with high network chain density by AF was very difficult to obtain even with the addition of accelerators such as polyethylene glycol derivatives. However, AF was an available compound which retards the discoloration of PVC.¹¹⁻¹³ These results, described in our previous paper, imply that it may be possible to react AF with allylic chlorine atoms in PVC easily under mild conditions; the allylic chlorine atoms are in the original PVC or form during thermal degradation. Whether AF reacts truly with a slight amount of allylic chlorine atoms during the thermal degradation of PVC sheets was investigated. The UV spectrum of A-PVC sheets is illustrated (Fig. 1), compared with those of models I and II:



The λ_{\max} of A-PVC was at 260 nm and agreed with that of 2-anilino-4,6-bis(4-hexyl-2-thio)-1,3,5-triazine (II). The reduced viscosity (η_{sp}/c) of A-PVC increased with an increase in aging time and in AF content (Fig. 2). Further, the reactions of AF with 4-chloro-2-hexene or 2-chlorobutane (RCl) in the presence

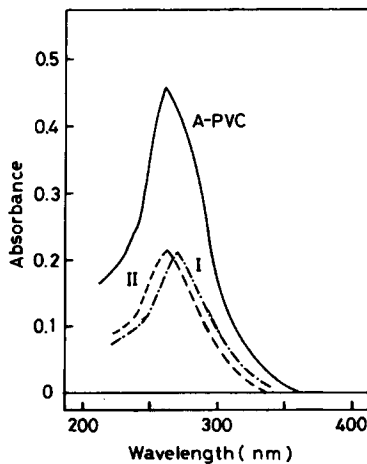


Fig. 1. UV spectra of A-PVC and model compounds I and II (see text).

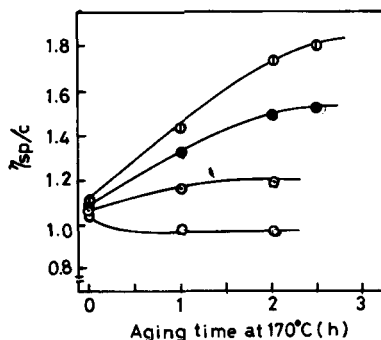
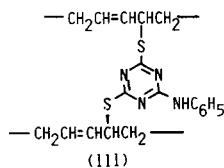


Fig. 2. Effects of aging time at 170°C and AF contents in PVC sheets on the η_{sp}/c of A-PVC. PVC sheets: PVC 100 parts, DOP 40 phr, AF 0–0.4 phr St_2Zn 0.5 phr, St_2Ba 1.5 phr. (○) AF 0 phr; (◐) AF 0.05 phr; (●) AF 0.2 phr; (◑) AF 0.4 phr.

of St_2Zn and St_2Ba were tested in a sealed glass tube at 100°C for 30 min. AF reacted easily with 4-chloro-2-hexene to give only II in a quantitative yield (Table II). The reaction of 4-chloro-2-hexene in a large excess of 2-chlorobutane also gave only II in the same yield. However, even in the extreme conditions at 170°C for 1 h, AF failed to react with 2-chlorobutane. These three results show that AF is introduced as a crosslinking chain as illustrated in III,



but a portion insoluble in THF was not formed at all in the range below 0.4 phr of AF contents. Therefore, the absorbance of A-PVC at 260 nm indicates the degree of reaction of allylic chlorine atoms in PVC with AF. Figure 3 shows the effects of aging time at 170°C and AF contents in PVC sheets on the absorbance at 260 nm. The absorbance first increased with an increase in aging time and then reached a constant value up to 0.2 phr of AF contents. The value increased linearly with increasing AF contents up to 0.2 phr of AF contents.

TABLE II
Model Reactions of AF (0.8 mmol) with 2-Chlorobutane or 4-Chloro-2-hexene in the Presence of St_2Zn (0.8 mmol) and St_2Ba (0.8 mmol) at 100°C for 30 Min

No.	R-Cl (%)		Yield (%)	
	$\begin{array}{c} \text{CH}_3\text{CH}_2 \\ \\ \text{CH}-\text{Cl} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{CH}_3\text{CH}=\text{CH} \\ \\ \text{CH}-\text{Cl} \\ \\ \text{CH}_3 \end{array}$	$\begin{array}{c} \text{NHC}_6\text{H}_5 \\ \\ \text{N} \quad \text{N} \\ / \quad \backslash \\ \text{N} \quad \text{N} \\ \quad \\ \text{R}-\text{S} \quad \text{S}-\text{R} \end{array}$	$\begin{array}{c} \text{NHC}_6\text{H}_5 \\ \\ \text{N} \quad \text{N} \\ / \quad \backslash \\ \text{N} \quad \text{N} \\ \quad \\ \text{HS} \quad \text{S}-\text{R} \end{array}$
1	10	—	0	0
2	—	2	99	0
3	100	2	98	0

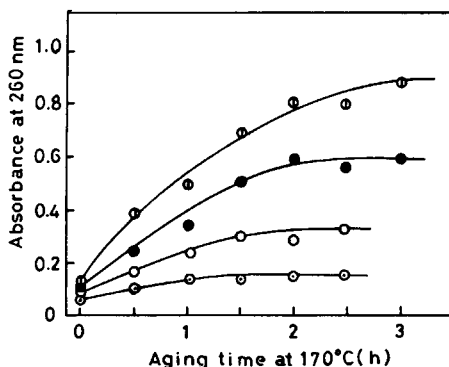


Fig. 3. Effects of aging time and AF contents in PVC sheets on the absorbance at 260 nm. PVC sheets: PVC 100 parts, DOP 40 phr, AF 0.05–0.4 phr, St_2Zn 0.5 phr, St_2Ba 1.5 phr. (○) AF 0.05 phr; (◻) AF 0.1 phr; (●) AF 0.2 phr; (◊) AF 0.4 phr.

On the other hand, the esterification of allylic chlorine atoms in PVC by St_2Zn and St_2Ca occurred easily.^{15,16} However, in this stabilizer system containing AF, such an esterification did not occur whereas only the thioetherification by AF proceeded.

Since AF reacts with allylic chlorine atoms to give a stable allylic structure, the dehydrochlorination of PVC sheets during thermal degradation is retarded; model II, obtained by the reaction of AF with 4-chloro-2-hexene at 100°C for 30 min, was stable even at 150°C, but 4-chloro-2-hexene gradually initiated its dehydrochlorination even at 80°C.^{15,16} Figure 4 shows the effect of AF contents on the relation between the amount of dehydrochlorination of PVC sheets and aging time at 170°C. The amount of dehydrochlorination first increased gradually with an increase in aging time, then reached a constant value, and finally increased rapidly. The amount of dehydrochlorination at a first and second stage is probably due to the reaction of AF with allylic chlorine atoms in PVC; this tendency in Figure 4 is similar to that in Figure 3. The subsequent, rapid dehydrochlorination evidently is due to the degradation of PVC, implying a zipperlike reaction. Here, the dehydrochlorination under consideration is the latter. The aging time until the rapid dehydrochlorination occurs is defined as an induction period for the zip dehydrochlorination. The induction periods

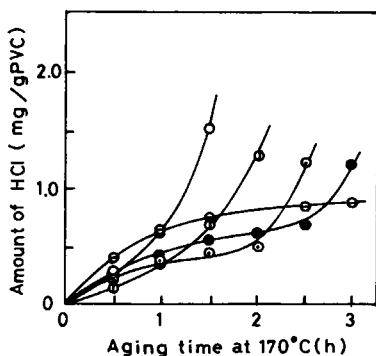


Fig. 4. Effect of AF contents on the amount of HCl by degradation of PVC sheets at 170°C. PVC sheets: PVC 100 parts, DOP 40 phr, AF 0–0.4 phr, St_2Zn 0.5 phr, St_2Ba 1.5 phr. (○) AF 0; (◻) AF 0.05 phr; (◊) AF 0.1 phr; (●) AF 0.2 phr; (◻) AF 0.4 phr.

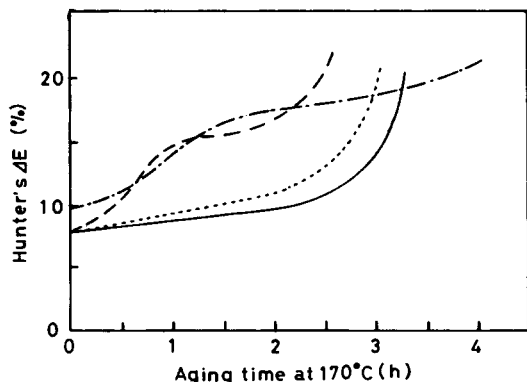


Fig. 5. Effect of AF contents on Hunter's color difference value (ΔE) of aged PVC sheets at 170°C. PVC sheets: PVC 100 parts, DOP 40 phr, AF 0–0.4 phr, St_2Zn 0.5 phr, St_2Ba 1.5 phr. (–) AF 0; (· · · · ·) AF 0.1 phr; (—) AF 0.2 phr; (– · – · –) AF 0.4 phr.

increased with an increase in AF contents in PVC sheets. The zip dehydrochlorination initiated at allylic chlorine units is, therefore, retarded by the stable AF crosslinking structure (III) in the PVC polymer.

Consequently, the color stability of PVC sheets is improved up on adding AF in the presence of St_2Zn and St_2Ba , since the development of polyene sequence is checked (Fig. 5).

Action of St_2Zn

No sufficient retarding effect of the reactive stabilizer for the discoloration of PVC sheets is recognized in the absence of St_2Zn (Table I). St_2Zn also plays an important role in the color stabilization of PVC sheets containing the three components. The influence of the amount of St_2Zn on the retarding effect of discoloration for PVC sheets is investigated (Fig. 6); AF and St_2Ba contents are

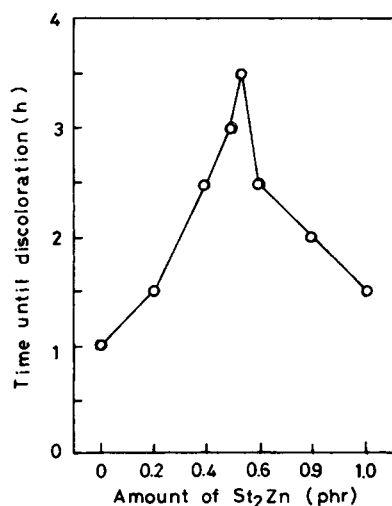


Fig. 6. Effect of the amount of St_2Zn on the time until the discoloration of PVC sheets at 170°C. PVC sheets: PVC 100 parts, DOP 40 phr, AF 0.2 phr St_2Zn 0–1.0 phr, St_2Ba 1.5 phr.

TABLE III
 Reaction Products of AF with St₂Zn

No.	AF (mol)	St ₂ Zn (mol)	Condition			Yield (%)	Product		
			Solvent (50 mL)	Temp (°C)	Time (min)		N (%)	S (%)	
1	0.02	0.01	methanol	50	30	89	AFZnAF	20.2 (20.9)	12.4 (12.20)
2	0.01	0.01	methanol	50	30	98	Mixture of AFZnAF and AFZnSt	8.8	10.9
3	0.01	0.01	Solves ^b 150	80	30	85	AFZnSt	9.7 (9.59)	11.6 (11.19)
4 ^a	0.01	0.01	Solves ^b 150	80	30	82	AFZnSt	9.6 (9.59)	11.4 (11.19)

^a The reaction was carried out in the presence of St₂Ba (0.025 mol).

^b Aliphatic hydrocarbon.

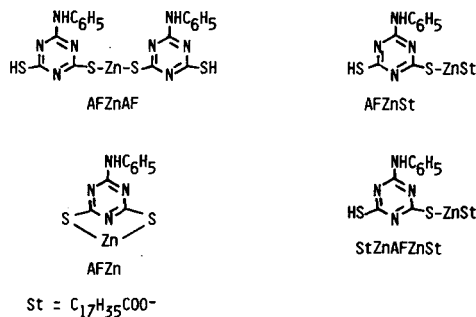
TABLE IV
Effects of AFZnSt and AFZnAF on the Discoloration and the Transmittance of PVC Sheets

No.	Stabilizer ^a (phr)	Time until dis- coloration (min)	Transmittance at 600 nm (%)
1	AFZnAF (0.23)	180	5
2	Mixture of AFZnAF and AFZnSt (0.48)	210	20
3	AFZnSt (0.5)	240	85
4	AF (0.2), St ₂ Zn (0.5)	210	83

^a PVC sheets: PVC 100 parts, DOP 40 phr, stabilizer 0.85 mmol as AF content, St₂Ba 1.5 phr.

constant. The maximum retarding effect was obtained at 0.53 phr (0.85 mmol) of St₂Zn content. In this case, the molar content of St₂Zn agreed with the AF (0.2 phr = 0.85 mmol). The highest synergistic effect is dependent on the molar ratio between AF and St₂Zn. Considering the low stabilizing effects of AF and St₂Zn independently (even in the presence of St₂Ba), the synergistic effect suggests the formation of a novel compound or a complex between both stabilizers.

On the other hand, in the crosslinking of PVC with 6-dibutylamino-1,3,5-triazine-2,4-dithiol (DB) and MgO, DB reacted with PVC polymer after forming the Mg salt of DB, as described in our previous paper.^{13,14} In the same manner in the reaction of AF with allylic chlorine atoms in PVC, AF will react after forming the Zn salts of AF. The Zn salts of AF compounds may be speculated as follows:



However, the reaction products, which are prepared by close examination of many synthetic conditions, were only the two salts of AFZnSt and AFZnAF (Table III); even in the presence of St₂Ba in Solveso 150 at 80°C, AFZnSt could be obtained by the reaction of AF with St₂Zn. In the reaction of AF with zinc isoocylate in Solveso 150, the similar type salt, AFZnOt(Ot=C₇H₁₄COO—) as well as AFZnAF, was also obtained; but only AFZnAF was obtained on the reaction of AF with zinc acetate. On the other hand, in the reaction of 6-R-1,3,5-triazine-2,4-dithiols with zinc carboxylates, the Zn salts of AFZnSt type were obtained when the 6-substituted groups are represented at an RNH group such as AF. But only AFZnAF was obtained in the case of (R)₂N—, and RO— groups, where R groups are alkyl, phenyl, etc.

In order to identify the reaction products of AF with St₂Zn in PVC sheets during thermal degradation, the effects of the AFZnSt—St₂Ba system, the

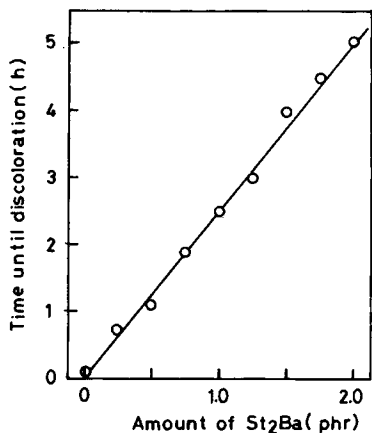


Fig. 7. Effect of the amount of St₂Ba on the time until the discoloration of PVC sheets at 170°C. PVC sheets: PVC 100 phr, DOP 40 phr, AF 0.2 phr, St₂Zn 0.53 phr, St₂Ba 0–2.0 phr.

AFZnAF—St₂Ba system, and the AF—St₂Zn—St₂Ba system on the discoloration and the transmittance of PVC sheets were investigated. The AFZnSt—St₂Ba system, as well as the AF—St₂Zn—St₂Ba system, gave very high retarding effect for the discoloration of PVC sheets and high transmittance (Table IV). The AFZnAF—St₂Ba system was inferior to both systems. AFZnAF in particular lowers the transmittance of PVC sheets noticeably, even in the case which is slightly contained. AFZnSt is also formed by the reaction of equimolar AF with St₂Zn in PVC sheets (Fig. 6).

Therefore, St₂Zn reacts with AF to form AFZnSt, and, consequently, plays an important role in the reaction of AF with allylic chlorine atoms in PVC [schemes (1) and (2)]:

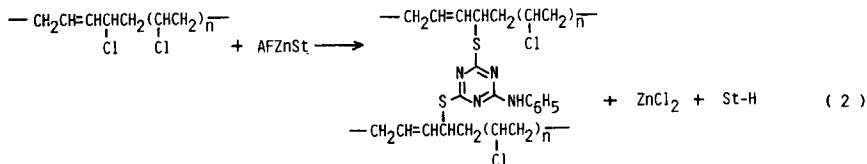
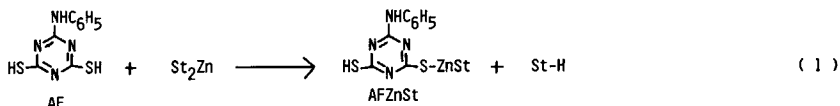


TABLE V
Reaction of Metal Chlorides with Metal Stearates

Stearate ^a	Reactant		Product	
	Chloride ^a		Metal chloride (mol)	
			Zn ⁺⁺	Ba ⁺⁺
St ₂ Ba	ZnCl ₂		0	0.97 × 10 ⁻²
St ₂ Zn	BaCl ₂		0	0.98 × 10 ⁻²

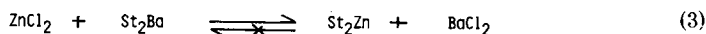
^a [Stearate] = [chloride] = 1 × 10⁻³ mol/10 g PVC

TABLE VI
Effect of St₂Ba on Reactions of 2-Chlorobutane or 4-Chloro-2-hexene (R-Cl) with Stabilizers at 100°C for 30 min

No.	AF	AFZnSt	Stabilizer (mmol)			ZnCl ₂	C ₂ H ₅ CH-Cl CH ₃	R-Cl (mmol) CH ₃ CH=CH CH-Cl CH ₃	R- (%) NHC ₆ H ₅	CH ₃ CH ₂ (CH ₃)CH-	CH ₃ CH=CH(CH ₃)CH-
			St ₂ Zn	St ₂ Ba	St ₂						
1	0.8	-	-	2	-	-	-	0	-	-	
2	-	0.8	-	2	-	-	10	5	-	-	
3	-	0.8	-	-	-	-	10	33	-	-	
4	0.8	-	0.8	-	-	-	10	34	-	-	
5	-	0.8	-	-	0.8	-	10	94	-	-	
6	0.8	-	-	2	-	-	-	-	2	66	
7	-	0.8	-	2	-	-	-	-	2	100	
8	-	0.8	-	-	-	-	-	-	2	50	
9	-	0.8	-	-	0.8	-	-	-	2	5	
10	-	0.8	-	2	-	-	100	-	2	100	

Action of St₂Ba

In the absence of St₂Ba, the discoloration of PVC sheets was not retarded (Table I). The dehydrochlorination of PVC is vigorously accelerated by ZnCl₂,^{15,17} which is formed in the reaction in schemes (1) and (2); ZnCl₂ activated not only allylic chlorine units, but also remarkably normal ethylene chloride units. Therefore, in order to obtain the high retarding effect for the discoloration, it is necessary to deactivate¹⁵ ZnCl₂ by the addition of a deactivator such as St₂Ba. The discoloration of PVC sheets is retarded with an increase in the amount of St₂Ba when AF and St₂Zn are constant (Fig. 7). Further, in the AF—St₂Zn—St₂Ba system, St₂Ba reacts easily with ZnCl₂ to give St₂Zn and BaCl₂, which are inactive for the dehydrochlorination of PVC (Table V). St₂Ba consequently acts an acid acceptor, as shown in scheme (3) (Fig. 7 and Table V):



In addition [schemes (1), (2), and (3)], St₂Zn acts as a catalyzer in the reaction of AF with allylic chlorine atoms in PVC.

ZnCl₂ has a significant effect not only on the dehydrochlorination of PVC sheets, but also on the reaction of AF with allylic chlorine atoms in PVC from the model reactions (Table VI). In the reaction systems (nos. 3, 4, 5, 8, and 9), where ZnCl₂ is formed, the reaction of AF with 4-chloro-2-hexene was retarded, although that of AF with 2-chlorobutane was accelerated; ZnCl₂ activates the chlorides as a catalyst of the Friedel–Crafts type. In the presence of St₂Ba, this result was not obtained since ZnCl₂ is converted to BaCl₂ and St₂Zn. Further, AF selectively reacted with 4-chloro-2-hexene even in the presence of a large excess of 2-chlorobutane. Consequently, St₂Ba plays an important role in selective reaction of AF with allylic chlorine atoms in PVC during thermal degradation.

References

1. A. J. Arlman, *J. Polym. Sci.*, **12**, 547 (1954).
2. M. G. Geddes, *Rubber Chem. Techn.*, **40**, 177 (1969).
3. M. Asahina and M. Onozuka, *J. Polym. Sci., Part A*, **2**, 3505, 3515 (1954).
4. K. B. Abba, *J. Polym. Sci.*, **13**, 2813 (1975).
5. K. B. Abba and E. M. Soroik, *J. Polym. Sci.*, **20**, 2395 (1976).
6. T. Suzuki and T. Nakamura, *Vinyl Polym.*, **10**(1), 21 (1968).
7. J. P. Kennedy et al., *J. Polym. Sci., Part A-1*, **10**, 2501 (1972).
8. N. G. Gaylord et al., *J. Polym. Sci., Part B*, **8**, 361 (1970).
9. G. Agrey, R. C. Poller and I. H. Siddiqui, *J. Polym. Sci., Part A-1*, **10**, 725 (1972).
10. W. H. Starnes et al., *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **19**, 623 (1978).
11. Y. Nakamura and K. Mori, *J. Macromol. Sci.*, **A12**, 2, 209 (1978).
12. K. Mori and Y. Nakamura, *Kobunshi Ronbunshu*, **37**, 103 (1980).
13. K. Mori and Y. Nakamura, *J. Polym. Sci.*, **16**, 1982 (1980).
14. K. Mori and Y. Nakamura, *J. Polym. Sci.*, **16**, 2055 (1980).

15. M. Onozuka, *J. Polym. Sci., Part A-1*, **5**, 2229 (1967).
16. A. Michel, *J. Macromol. Sci. Chem.*, **A12**, 361 (1978).
17. A. H. Frey and R. W. Horst, *J. Polym. Sci.*, **40**, 419 (1959).

Received January 19, 1981

Accepted September 24, 1981