

# Kinetic Study of Action of Additives in Poly(Vinyl Chloride)

## Stabilizer Systems

### III. Stobadine Dipalmitate

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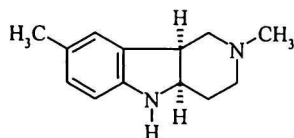
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Possibility to use Stobadine dipalmitate, the antioxidant effect of which was found in search of antiarrhythmic drugs, for poly(vinyl chloride) stabilization has been studied using seventeen film samples. Degradation in real atmosphere at 180°C was followed potentiometrically and action of Stobadine dipalmitate has been evaluated. Stobadine dipalmitate in small amount (0.125 %) is able to slow down the rate of degradation in the presence of Irganox 1010, but in combination with Ca/Zn stabilizer system it was impossible to use Stobadine dipalmitate for polymer stabilization.

Stobadine, (-)-*cis*-2,8-dimethyl-2,3,4,4a,5,9b-hexahydro-1*H*-pyrido[4,3-*b*]indole,  $M_r = 202.30$ , m.p. = 82–83 °C (dipalmitate m.p. = 55–56°C, dichloride m.p. = 270–274°C) [1] has been synthesized in search of new antiarrhythmic drugs. Stobadine is a potential drug for treatment of tissue injuries caused by oxidative processes [2, 3]. The drug belongs to a group of compounds that are able to quench singlet oxygen  $^1\text{O}_2$ . Overall  $^1\text{O}_2$  quenching rate constant value is  $1.3 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , this value is comparable to the rate constants for tocopherol homologues ( $10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ). Stobadine was also found to be a scavenger of hydroxyl radicals  $\text{HO}^\bullet$  (approximate rate constant  $1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) and alkoxyl radicals  $\text{RO}^\bullet$ . Stobadine is probably able to form the radical on the indole nitrogen [1].

Species like singlet oxygen, hydroxyl radicals, and alkoxyl radicals play significant role in oxidative processes by the thermal degradation of synthetic polymers [4]. These facts are the reason, why we have tried to utilize possible antioxidant action of Stobadine for protection of poly(vinyl chloride) (PVC) [5].



Stobadine

#### EXPERIMENTAL

Seventeen PVC mixtures with Stobadine dipalmitate as sole antioxidant or as one part of composite stabilizer system were prepared. Eight mixtures were prepared as model specimens for evaluation of the rate

constants of additives and nine mixtures were proposed on the basis of compounds used in our best stabilizer systems – CaO, zinc stearate (ZnSt), ethyl acetoacetate, and antioxidant Irganox 1010 (sterically hindered phenolic antioxidant) [5]. Later as CaO alternatives were used calcium stearate (CaSt) and magnesium stearate (MgSt). The specimens contained suspension PVC Sloviny S-622 and the additives given in Table 1. The powdered mixtures were mixed for 2 min to obtain maximum possible homogeneity. Mixtures calendering and pressing, to get 0.1 mm thick films, was very problematic. The standard procedure – calendering for 3 min at processing temperature 180°C could not be used. The mixtures did not stick on calender cylinders and were not homogenized. Increased calendering temperature 190°C and especially longer calendering time (10–15 min) caused mixtures degradation and discoloration, in some mixtures to an unacceptable level (samples 4–6). Since Stobadine dipalmitate melting point is 55–56°C we tried to change sample preparation procedure. Stobadine dipalmitate was added and mixed with PVC powder at increased temperature, at about 70°C. This change did not improve significantly preparation of the films. Stobadine dipalmitate manifested a strong lubricant effect, therefore mixtures 10–17 were prepared without Wax E (lubricant). The use of pure Stobadine did not improve preparation of films and the stability of the polymer.

Since HCl is the only degradation product at temperature 180°C, the degradation was followed by detection of the evolved HCl. It was absorbed in  $\text{AgNO}_3$  solution and the decrease of the  $\text{Ag}^+$  concentration was monitored with electrode system – silver working electrode *vs.* reference saturated calomel electrode.

Table 1. Composition of Samples

Sample	$m_{\text{PVC}}/\text{g}$	$m_{\text{Wax E}}/\text{g}$	$m_{\text{CaO}}/\text{g}$	$m_{\text{ZnSt}}/\text{g}$	$m_{\text{ethyl acetoacetate}}/\text{g}$	$m_{\text{Stobadine dipalmitate}}/\text{g}$
1	50	0.125	—	—	—	0.125
2	50	0.125	—	—	—	0.250
3	50	0.125	—	—	—	0.375
4	50	0.125	—	—	—	0.500
5	50	0.125	—	—	—	0.625
6	50	0.125	0.500	—	—	0.250
7	50	0.125	0.500	0.250	0.500	0.125
8	50	0.125	0.500	0.250	0.500	0.250
9	50	0.125	0.500	0.250	0.500	0.500

Sample	$m_{\text{PVC}}/\text{g}$	$m_{\text{CaO}}/\text{g}$	$m_{\text{ZnSt}}/\text{g}$	$m_{\text{CaSt}}/\text{g}$	$m_{\text{Irganox}}/\text{g}$	$m_{\text{Stobadine dipalmitate}}/\text{g}$
10	50	—	—	—	0.125	0.0625
11	50	—	—	—	0.250	0.0625
12	50	—	—	—	0.500	0.0625
13	50	0.250	0.250	—	0.250	0.0625
14	50	0.250	0.250	—	0.250	0.250
15	50	—	—	0.250	—	0.0625

Sample	$m_{\text{PVC}}/\text{g}$	$m_{\text{MgSt}}/\text{g}$	$m_{\text{Irganox}}/\text{g}$	$m_{\text{Stobadine dipalmitate}}/\text{g}$
16	50	0.250	—	0.0625
17	50	0.125	0.250	0.0625

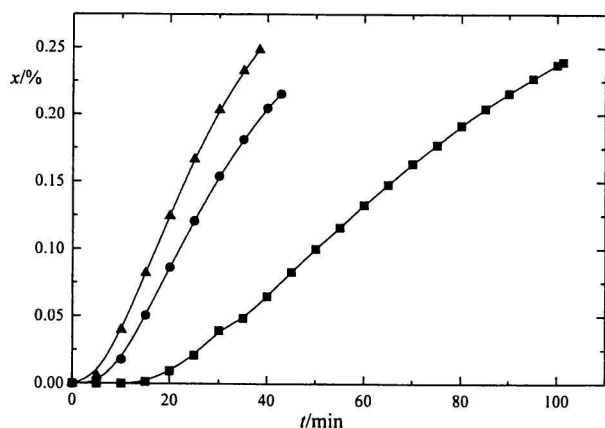


Fig. 1. Kinetic curves of PVC degradation of samples 1 (■), 2 (●), and 3 (▲).

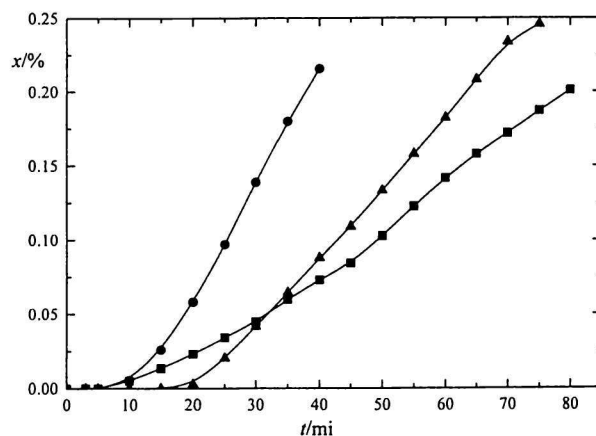


Fig. 2. Kinetic curves of PVC degradation of samples 7 (▲), 8 (■), and 9 (●).

## RESULTS AND DISCUSSION

Measured kinetic curves are shown in Figs. 1—5 as degradation degree  $x$  (the mole ratio of the evolved HCl and monomer links in the PVC sample) *vs.* time  $t$ . The values of the thermal stability time  $\tau$  [5] were not higher than 20 min (Table 2). That means, no tested mixture can be used with success for long-time stabilization. Synergistic effect between components of composite stabilizer system (mixtures 7—9, 13—15) was not observed, even the stability of polymer was worse than stability of the model samples, where the stabilizer system consisted of CaO and Irganox 1010 (2

% CaO and 0.5 % Irganox 1010,  $\tau = 64$  min [5]). Samples 1—5 behaviour was unexpected. Higher amounts of Stobadine dipalmitate caused problems by calendaring and a massive degradation of samples 4 and 5 made impossible to get specimens suitable for our kinetic study. The rate of dehydrochlorination (DHC) of sample 6 was higher than those of samples 4 or 5. CaO was replaced in sample 15 with 0.5 % CaSt without a great improvement. Samples 16 and 17 contained MgSt. The use of MgSt also did not lead to a synergistic effect of additives action.

Although development of degradation of the model sample 1 was slower than DHC of model samples con-

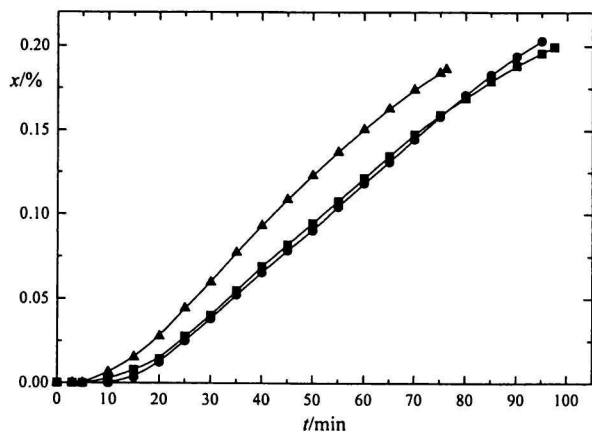


Fig. 3. Kinetic curves of PVC degradation of samples 10 (■), 11 (●), and 12 (▲).

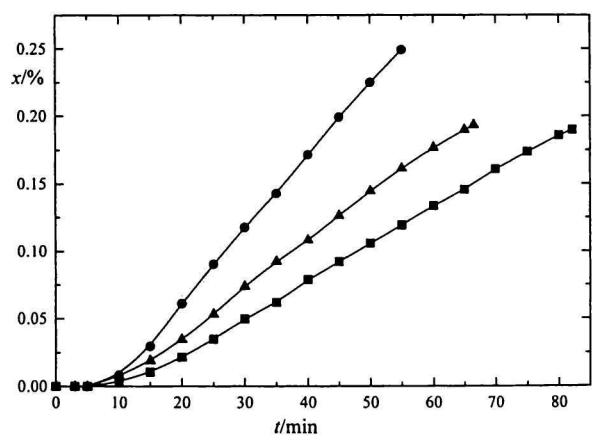


Fig. 4. Kinetic curves of PVC degradation of samples 13 (■), 14 (●), and 15 (▲).

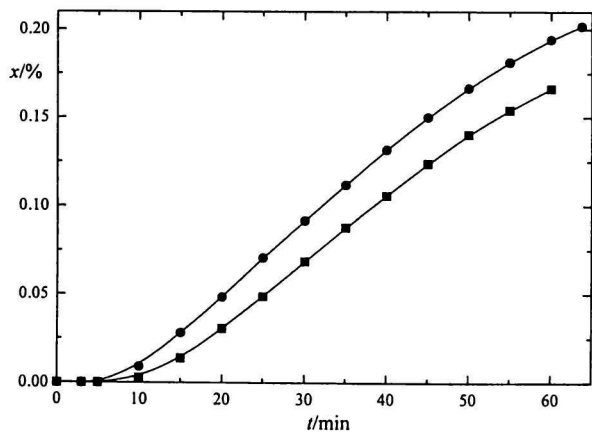
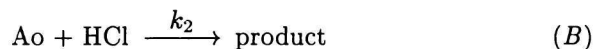


Fig. 5. Kinetic curves of PVC degradation of samples 16 (■) and 17 (●).

sisting of antioxidant Irganox 1010 or Topanol CA (with antioxidant amounts 10 times higher [5, 6]), degradation of samples 2 and 3 was comparable with DHC of pure unstabilized PVC [5]. Higher amounts

of Stobadine dipalmitate caused also a worse initial colour of samples. Calculations of the effective rate constants based on simple reaction scheme



where dePVC means degraded polymer, have shown great differences between sample 1 and samples 2, 3 (Table 3). For the pure PVC  $k_1 = 9.59 \times 10^{-5} \text{ min}^{-1}$ . Amount of Stobadine dipalmitate in sample influences the rate of DHC very strongly.

The relative mole fractions of components are designated as follows:  $X_1$  – calculated conversion of DHC,  $X_2$  – splitting-off HCl in polymer,  $X_3$  – double bonds in polymer,  $X_4$  – antioxidant. HCl is evolved from the polymer when the relative mole fraction  $X_2$  has reached a critical value  $X_c$  and then can be detected [5, 6]. Kinetic equations for the aforementioned scheme are

$$1. X_2 < X_c$$

$$dX_1/dt = 0$$

$$dX_2/dt = k_1(1 - X_3) - k_2X_2X_4$$

$$2. X_2 = X_c$$

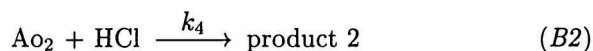
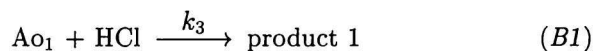
$$dX_1/dt = k_1(1 - X_3) - k_2X_2X_4$$

$$dX_2/dt = 0$$

$$dX_3/dt = k_1(1 - X_3)$$

$$dX_4/dt = -k_2X_2X_4$$

$dx/dt$  Values of samples 10–12 indicate lower rate of DHC than that of sample 1. These samples contain antioxidant system consisting of 0.125 % of Stobadine dipalmitate and 0.25 %, 0.5 %, or 1 % of Irganox 1010. These two antioxidant systems are much more effective than 2.5 % of Irganox 1010 as a sole antioxidant.  $dx/dt$  Gradients are about 1/3 lower than  $dx/dt$  reached by model samples containing 0.5–2.5 % of Irganox 1010 or Topanol CA [5]. Increase of amount of Irganox 1010 negatively influences the rate of DHC. The reaction scheme analogous to the previous one



was proposed to judge mutual influence of Stobadine dipalmitate (designated as  $\text{Ao}_1$ ) and Irganox 1010 (designated as  $\text{Ao}_2$ ) and analogous kinetic equation

**Table 2.** Time of Thermal Stability  $\tau$  and Gradient  $dx/dt$  Values

Sample	$(dx/dt) \times 10^3/\text{min}^{-1}$	$\tau/\text{min}$	Sample	$(dx/dt) \times 10^3/\text{min}^{-1}$	$\tau/\text{min}$
1	2.86	15.0	11	2.41	11.4
2	6.03	5.7	12	2.80	7.6
3	7.44	3.7	13	2.63	9.8
7	4.50	19.4	14	5.27	7.6
8	2.94	12.7	15	3.35	7.8
9	7.24	10.8	16	3.31	8.77
10	2.54	13.7	17	3.66	5.80

**Table 3.** Kinetic Parameters Calculated for Samples 1–3

Sample	$k_1 \times 10^5/\text{min}^{-1}$	$k_2/\text{min}^{-1}$	$X_c \times 10^4$
1	2.83	0.460	3.21
2	6.14	19.6	2.63
3	7.50	20.0	1.74

**Table 4.** Kinetic Parameters Calculated for Samples 10–12

Sample	$k_1 \times 10^5/\text{min}^{-1}$	$k_3/\text{min}^{-1}$	$k_4/\text{min}^{-1}$	$X_c \times 10^4$
10	2.50	25.0	200	2.00
11	2.60	25.0	190	2.20
12	3.47	17.0	192	2.09

system has been proposed. The system of differential equations was solved using the least-squares method. Rate constants and  $X_c$  values were searched. The computation results are shown in Table 4. The results were confirmed by Simplex fit. These simple schemes certainly do not comprehend DHC processes in specimens in detail, but they allow basic comparison of effectiveness of antioxidants.

## CONCLUSION

No synergistic enhancement (to obtain long-time stabilizer system) of stabilizing power between Sto-

badine dipalmitate and such components of composite stabilizer systems as CaO, zinc stearate, calcium stearate, magnesium stearate, ethyl acetoacetate, and/or Irganox 1010, has been found. Processing and mechanical properties of samples are problematic. Samples are brittle, presence of Stobadine dipalmitate causes low colourfastness, similar to secondary aromatic amines. Increase of Stobadine dipalmitate amount in model samples markedly decreases the thermal stability of the samples. On the other hand, very low Stobadine dipalmitate quantity – 0.125 % in model samples containing also Irganox 1010 caused a significant decrease of the DHC rate. Higher amounts of Irganox 1010 in the presence of Stobadine dipalmitate caused an increase of the rate constant of DHC.

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