

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

## I. Sterically Hindered Phenolic Antioxidants

P. KOVAŘÍK, E. KLEIN, and L. VALKO

*Department of Physical Chemistry, Faculty of Chemical Technology,  
Slovak University of Technology, SK-812 37 Bratislava*

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The action of two antioxidants from the sterically hindered phenol group – Irganox 1010 and Topanol CA – has been studied. Twenty-five film samples, which consisted of poly(vinyl chloride), antioxidant, and heat stabilizer systems, have been prepared. The additives used were nontoxic and without ecological hazards. Degradation in real atmosphere was followed potentiometrically. The time of thermal stability  $\tau$  and the gradient of degradation degree  $dx/dt$  were evaluated from the measured kinetic curves. Kinetic models were proposed for the antioxidant as sole additive and for the antioxidant—CaO system to calculate the corresponding rate constants, which allow to compare the effectiveness of the antioxidant and to prove the synergism between CaO and Irganox 1010. Two composite stabilizer systems for long-time stabilization have been found.

Due to low thermal stability heat-treatment of synthetic polymer poly(vinyl chloride) (PVC), usually at the temperature about 180°C, brings about problems. The formation of conjugated polyene sequences (of 1 to 25 double bonds) on thermal degradation of PVC with the evolved hydrogen chloride (HCl) is a complex chain reaction with a special mechanism called “zipper elimination” It may include radical, ionic or molecular mechanisms, which were proposed on the basis of experimental evidences. Each may play predominant role under specific conditions [1]. Oxidative processes based on free radical attack also decrease the utilities of the polymer and the length of service life, especially by outdoor applications exposed to the direct sunlight.

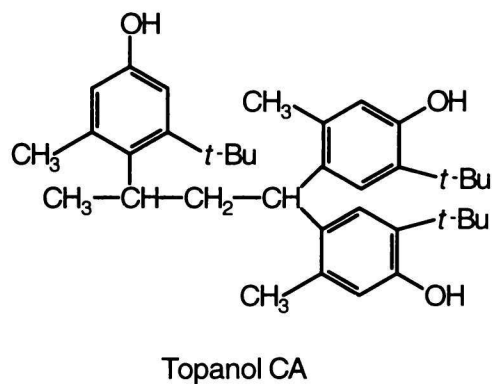
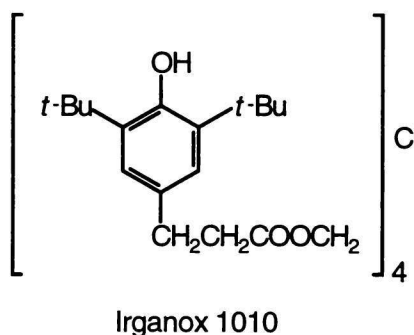
PVC processing and applications are not possible without additives, like stabilizers and antioxidants, since dehydrochlorination (DHC) starts above glass transition temperature (80–84°C) [2]. The presence of impurities reduces the thermal stability of PVC. Susceptibility to thermal degradation increases in the sequence: mass polymer → suspension polymer → emulsion polymer [3]. A good stabilizer should prevent or disrupt the reactions in thermal degradation of PVC. It should rapidly bind and inactivate any reaction product (especially free HCl – autocatalyst of DHC, generated on degradation), which may further impair the stability, deactivate potential initiation sites in the polymer matrix (by substituting stable groups for labile Cl atoms and saturation of double bonds), deactivate oxygen-bearing groups (modification defects in the polymer chain), terminate the

increase of polyene sequences, react with free radicals, and neutralize the destabilizing effects of impurities.

Heat stabilizers from the group of metal compounds (except lead compounds and organotin) and organic stabilizers are usually used in combination with other compounds from these two groups to create composite stabilizer systems, often coupled with synergistic enhance. Calcium/zinc stabilizers are the most widely used nontoxic stabilizers, though they are not the most effective ones. In many cases they are used in conjunction with epoxy co-stabilizers (organic stabilizers) without loss of nontoxic property [3].

Some stabilizers (predominantly those which exhibit also light-stabilizing effects) show antioxidant action in PVC. Antioxidants are often incorporated into composite stabilizer systems. Primary antioxidants act as free radical scavengers to prevent or interrupt oxidation. Secondary antioxidants react with hydrogenperoxide groups, converting them to non-radical reaction products. Primary antioxidants, most used in stabilizer systems, can be divided into two fundamental groups, *i.e.* sterically hindered phenols and secondary aromatic amines. The sterically hindered phenols are of greater importance than the secondary aromatic amines used especially in rubber compositions.

In this work we studied the action of two nontoxic, sterically hindered nonvolatile phenols with spherical shape of molecule, and created composite stabilizer systems containing these antioxidants. The first antioxidant, permitted for food packaging plastics, was Irganox 1010, *i.e.* pentaerythritol tetrakis[3-(3,5-di-



*tert*-butyl-4-hydroxyphenyl)propionate] and the second one was Topanol CA, *i.e.* 1,1,3-tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane.

### EXPERIMENTAL

We have prepared 25 specimens (Table 1): 5 with PVC and Irganox (0.5 %, 1 %, 1.5 %, 2 %, and 2.5 %),

5 analogous specimens with Topanol, 3 specimens with 2 % CaO and 0.5 %, 1 % or 2 % of Irganox for kinetic study of the action of the antioxidant and CaO, and 12 specimens with composite stabilizer system (based on Ca/Zn) to get stabilized polymer resistant to long-

**Table 1.** Composition of Samples

Sample	$m_{\text{PVC}}/\text{g}$	$m_{\text{Wax E}}/\text{g}$	$m_{\text{CaO}}/\text{g}$	$m_{\text{ZnSt}}/\text{g}$	$m_{\text{rape oil}}/\text{g}$	$m_{\text{methyl acetoacetate}}/\text{g}$	$m_{\text{Irganox}}/\text{g}$
1	25	0.125	0.0	0.0	0.0	0.0	0.125
2	25	0.125	0.0	0.0	0.0	0.0	0.250
3	25	0.125	0.0	0.0	0.0	0.0	0.375
4	25	0.125	0.0	0.0	0.0	0.0	0.500
5	25	0.125	0.0	0.0	0.0	0.0	0.625
6	25	0.125	0.500	0.0	0.0	0.0	0.125
7	25	0.125	0.500	0.0	0.0	0.0	0.250
8	25	0.125	0.500	0.0	0.0	0.0	0.500
14	25	0.125	0.500	0.250	0.500	0.500	0.125
15	25	0.125	0.500	0.250	0.500	0.500	0.250
16	25	0.125	0.500	0.250	0.500	0.500	0.500

Sample	$m_{\text{PVC}}/\text{g}$	$m_{\text{Wax E}}/\text{g}$	$m_{\text{CaO}}/\text{g}$	$m_{\text{ZnSt}}/\text{g}$	$m_{\text{rape oil}}/\text{g}$	$m_{\text{methyl acetoacetate}}/\text{g}$	$m_{\text{Topanol}}/\text{g}$
9	25	0.125	0.0	0.0	0.0	0.0	0.125
10	25	0.125	0.0	0.0	0.0	0.0	0.250
11	25	0.125	0.0	0.0	0.0	0.0	0.375
12	25	0.125	0.0	0.0	0.0	0.0	0.500
13	25	0.125	0.0	0.0	0.0	0.0	0.625
17	25	0.125	0.500	0.250	0.500	0.500	0.125
18	25	0.125	0.500	0.250	0.500	0.500	0.250
19	25	0.125	0.500	0.250	0.500	0.500	0.500

Sample	$m_{\text{PVC}}/\text{g}$	$m_{\text{Wax E}}/\text{g}$	$m_{\text{CaO}}/\text{g}$	$m_{\text{ZnSt}}/\text{g}$	$m_{\text{methyl acetoacetate}}/\text{g}$	$m_{\text{Edenol}}/\text{g}$	$m_{\text{Irganox}}/\text{g}$
20	50	0.100	0.500	0.250	0.250	0.125	0.500
21	50	0.100	0.500	0.250	0.250	0.250	0.500
22	50	0.100	0.500	0.500	0.300	0.500	0.500
23	50	0.125	1.000	0.125	0.0	1.000	1.000
24	50	0.125	1.000*	0.125	0.500	1.000	1.000
25	50	0.125	1.000	0.125	0.500	1.000	1.000

\* Sample contains 1.000 g of CaSt.

time heat-treatment, which should satisfy the following requirements: the additives must be nontoxic without ecological hazards, heat stabilizers should trap the evolved HCl to eliminate its autocatalytic effect and restrict colour changes induced by degradation. The specimens contain powdered suspension PVC Slovinyl S-622 and the following additives: Wax E (lubricant, montan wax produced by Hoechst [4]), powdered CaO (HCl trapper, component of calcium/zinc stabilizer systems, purity 99 %), zinc stearate (ZnSt, to increase colour stability, purity 99 %), rape oil (cold pressed low erucic oil, unstabilized, acid number a. n. (KOH) = 1.1–1.3 mg g<sup>-1</sup>, for better mechanical properties), ethyl acetoacetate (purity 99 %, for better mechanical properties), Edenol D-81 (co-stabilizer for Ca/Zn system, epoxy-soya oil, extraction resistant,  $M_r = 935$ , epoxy-oxygen content 6.3–7 %, produced by Henkel Plastics & Coatings Technology), and antioxidants Irganox 1010 and Topanol CA (Hoechst). The mixtures were mixed for 2 min to obtain maximum possible homogeneity and then calendred for 3 min at the processing temperature 180°C to get 0.1 mm thick films.

Degradation of samples in real atmosphere was monitored at temperature 180°C. Since HCl is the only degradation product at this temperature, degradation can be followed by detection of the evolved HCl. It is absorbed in AgNO<sub>3</sub> solution and the decrease of Ag<sup>+</sup> concentration is continuously monitored by the electrode system – silver working electrode *vs.* reference saturated calomel electrode [4].

## RESULTS AND DISCUSSION

The Figs. 1–9 show the measured kinetic curves as degradation degree  $x$  (the mole ratio of the evolved HCl and monomer links in the PVC specimen) *vs.* time  $t$ . The kinetic curves of model samples 1–8 and 9–13 have been used to determine the kinetic parameters based on the proposed reaction schemes and the remaining curves to judge the effect of the composite stabilizer systems.

The basic information obtained from kinetic curves are the time of thermal stability and the  $dx/dt$  gradient (Table 2). The time of thermal stability  $\tau$  is the length of time elapsing before perceptible and measurable degradation develops. The observed values of  $\tau$  reached 50–70 % of those found in inert nitrogen atmosphere and the  $dx/dt$  values increased by 150–200 % [5]. These observations agree with well-known fact that PVC degradation in real atmosphere runs faster than degradation in inert atmosphere [6–9]. These results do not affect markedly the utility of the best samples, since their thermal stability values (132 min for 25, 185–273 min for 14–19) are higher than that (60 min) required by producers. Analogous results were expected with samples 14–16 and 17–19, since the structure and action of antioxidants are simi-

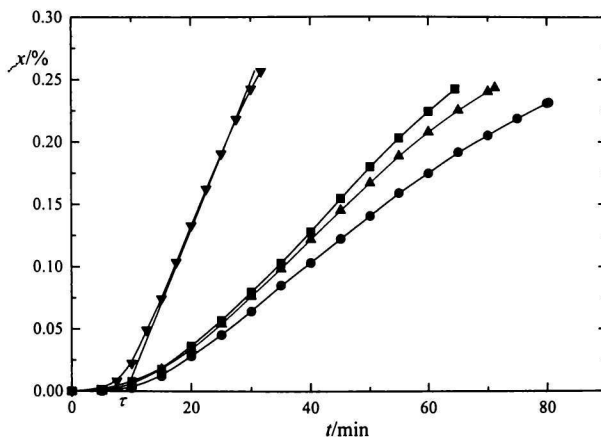


Fig. 1. Kinetic curves of PVC degradation of samples 1 (■), 2 (▲), 3 (●), and pure PVC (▼).

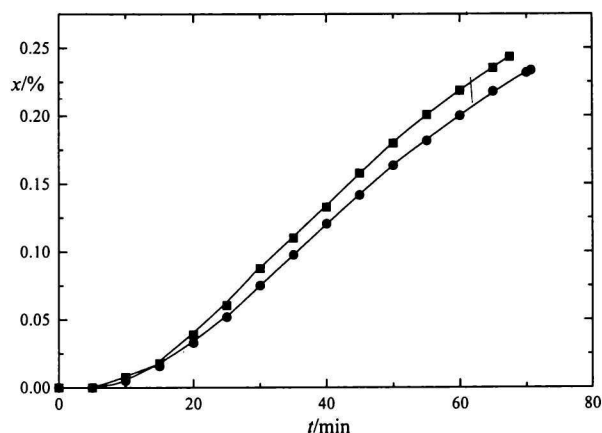


Fig. 2. Kinetic curves of PVC degradation of samples 4 (●) and 5 (■).

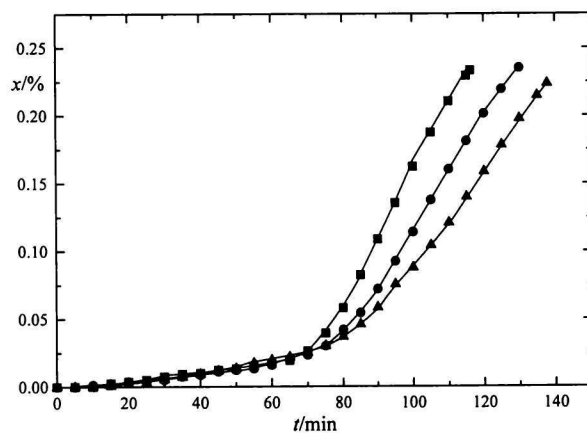


Fig. 3. Kinetic curves of PVC degradation of samples 6 (■), 7 (●), and 8 (▲).

lar. Such high  $\tau$  values are not possible without strong synergism between the compounds used for the com-

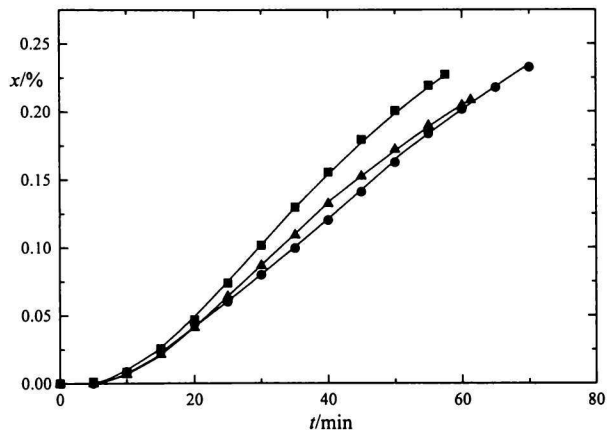


Fig. 4. Kinetic curves of PVC degradation of samples 9 (●), 10 (▲), and 11 (■).

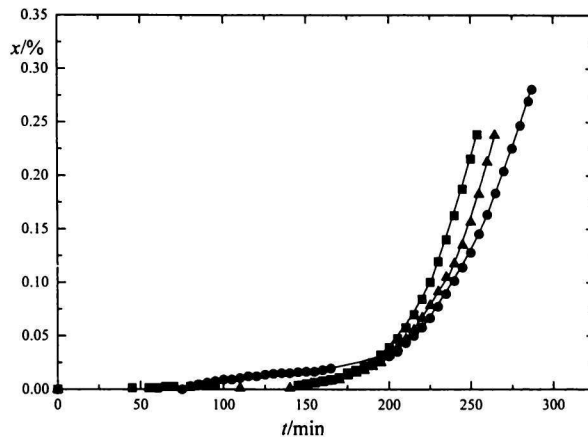


Fig. 7. Kinetic curves of PVC degradation of samples 17 (●), 18 (■), and 19 (▲).

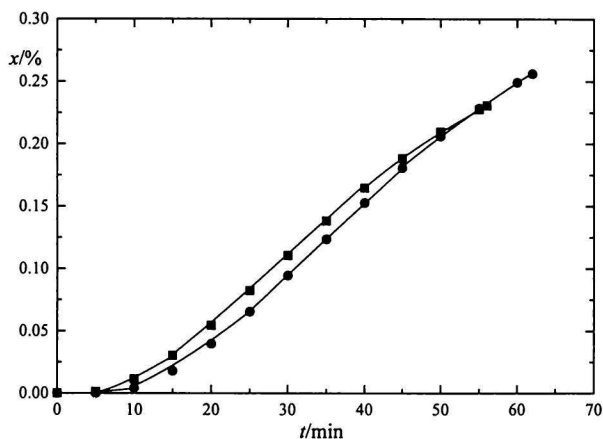


Fig. 5. Kinetic curves of PVC degradation of samples 12 (■) and 13 (●).

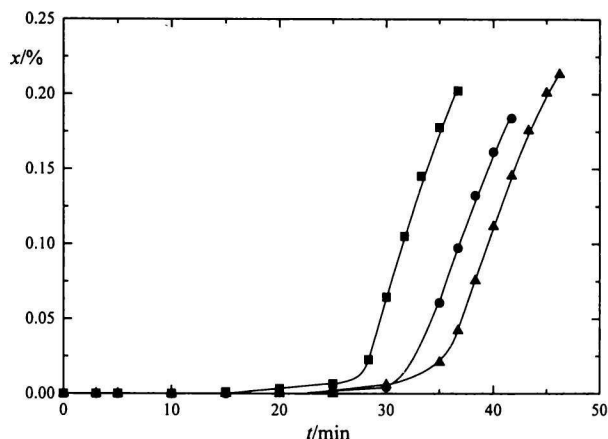


Fig. 8. Kinetic curves of PVC degradation of samples 20 (■), 21 (●), and 22 (▲).

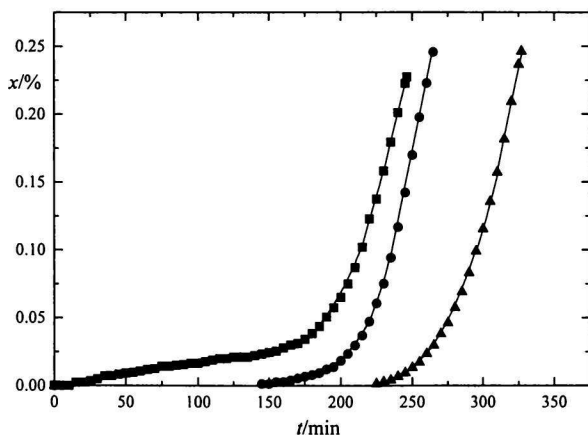


Fig. 6. Kinetic curves of PVC degradation of samples 14 (■), 15 (▲), and 16 (●).

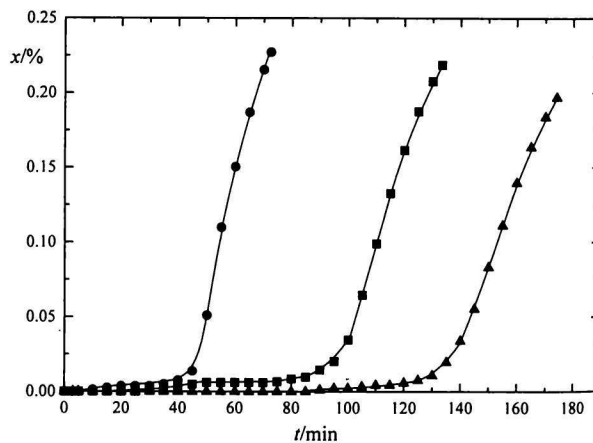


Fig. 9. Kinetic curves of PVC degradation of samples 23 (■), 24 (●), and 25 (▲).

posite stabilizer systems. Comparison of the best specimens with pure suspension PVC ( $\tau = 6.5$  min,  $dx/dt$

$= 9.26 \times 10^{-3} \text{ min}^{-1}$ ) shows a decreasing  $dx/dt$  gradient, the values being approximately one half of the

Table 2. Thermal Stability  $\tau$  and Gradient  $dx/dt$  of Samples 1—25

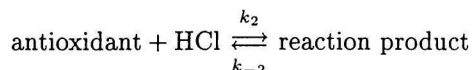
Sample	$dx/dt \times 10^3/\text{min}^{-1}$	$\tau/\text{min}$
1	4.54	9.6
2	4.11	10.5
3	3.32	8.9
4	3.85	9.1
5	4.21	8.6
6	4.53	64.8
7	3.96	70.1
8	3.35	72.1
9	3.79	7.8
10	3.98	7.9
11	4.67	7.8
12	4.82	7.1
13	4.93	9.5
14	3.64	185.0
15	4.50	273.0
16	4.83	214.0
17	3.73	214.0
18	4.55	203.0
19	4.98	217.0
20	20.80	26.6
21	18.60	31.5
22	18.10	34.0
23	5.54	92.2
24	6.70	37.9
25	4.84	132.2

pure PVC  $dx/dt$  value. The main components used in mixtures 14—16, *i.e.* CaO, ZnSt, and Irganox, have been combined in samples 20—25 with co-stabilizer Edenol D-81 and CaO has been replaced in sample 24 with calcium stearate. Lower level of synergism was observed in samples 20—22 than in samples 14—16, but specimens 20—22 contained much less additives, especially metal compounds. These samples have also very good clarity and transparency, better than samples 14—16. Higher quantity of ZnSt in mixture 22 has no effect on initial colour and increases the DHC rate on longer heat-treatment (ZnCl<sub>2</sub> catalyst) [10]. Sample 23 contains a similar stabilizer system as samples 20—22 except of ethyl acetoacetate. Higher quantity of metal compounds and different ratio between the Ca- and Zn-compound,  $w_r = 8:1$ , cause significant increase of thermal stability. The same stabilizer system with 1 % ethyl acetoacetate acts more effectively – the time of thermal stability has been increased in specimen 25. Lower ratio between Ca<sup>2+</sup> and Zn<sup>2+</sup> decreases the quality of the stabilizer system (mixture 24 with CaSt).

Our results and the published data [6—8] lead us to the suggestion of the following reaction scheme of thermal DHC of PVC in the presence of antioxidant as only additive (samples 1—5, 9—13)



where dePVC means dehydrochlorinated PVC.



We propose the reversible reaction between the antioxidant and HCl on the basis of the following facts. The structures of these phenolic antioxidants, which are components of composite stabilizer system, and their ability to react with HCl are fairly analogous, as evident from the kinetic curves of 14—16 (Fig. 6) and 17—19 (Fig. 7). The lower effectiveness of Topanol is evident from kinetic curves of model samples 1—5 (Figs. 1 and 2) and 9—13 (Figs. 4 and 5). It can be explained by lower sterical hindrance of the —OH group in the Topanol molecule, which can also predict a higher decomposition rate of the HCl and antioxidant product. If we neglect the reversible reaction, the values of effective rate constants  $k_2$  will be absolutely different in spite of similar molecular structures of antioxidants.

In the reaction scheme the catalytic effect of the eliminated HCl is not considered, since in such thin films the autocatalytic effect is negligible [4, 7] and HCl reacts immediately with additives in the sample. The ability of Irganox 1010 and Topanol CA to terminate the growth of polyene sequences has been described. Using the rate constants of initiation  $k_i$ , propagation  $k_p$ , and termination  $k_t$ , the effective rate constant  $k_1$  can be expressed [9]

$$k_1 = k_i \left( 1 + \frac{k_p}{k_t} \right)$$

Growth rate of the polyene sequences (zippers growth rate) in the polymer with antioxidant can be expressed

$$dz/dt = k_i(1 - x) - k_t z - k_{A_0} x_{A_0} z$$

where  $z$  means relative mole fraction of polyenes and  $k_{A_0}$  antioxidant effect. DHC rate can be expressed using steady-state condition by the following formula

$$dx/dt = k_i \left[ 1 + \frac{k_p}{k_t + k_{A_0} x_{A_0}} \right] (1 - x)$$

The relative mole fractions of components are designated as follows:  $X_1$  – calculated conversion of DHC,  $X_2$  – splitting-off of HCl in polymer,  $X_3$  – double bonds in polymer,  $X_{A_0}$  – antioxidant, and  $X_{\text{prod}}$  – reaction product of HCl and antioxidant.

As soon as the degradation starts, no HCl can be detected because it reacts in the polymer with the components of the stabilizer system and the  $X_2$  value rises. HCl is evolved from the polymer and can be detected when the mole fraction  $X_2$  has reached the critical value  $X_c$ .

Kinetic equations for the above described reaction scheme

$$1. X_2 < X_c$$

$$dX_1/dt = 0$$

$$dX_2/dt = k_1(1 - X_3) - k_2X_2X_{Ao} + k_{-2}X_{prod}$$

$$2. X_2 = X_c$$

$$dX_1/dt = k_1(1 - X_3) - k_2X_2X_{Ao} + k_{-2}X_{prod}$$

$$dX_2/dt = 0$$

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

$$dX_{Ao}/dt = -k_2X_2X_{Ao} + k_{-2}X_{prod}$$

$$dX_{prod}/dt = k_2X_2X_{Ao} - k_{-2}X_{prod}$$

The dominant role of CaO in stabilizer system has been acknowledged by computation of the effective rate constant  $k_{CaO}$  value of the reaction of CaO and HCl in the second kinetic model, proposed for the antioxidant—CaO system (samples 6—8). Reaction schemes



The kinetic equations ( $X_{CaO}$  means the relative mole fraction of CaO)

$$1. X_2 < X_c$$

$$dX_1/dt = 0$$

$$dX_2/dt = k_1(1 - X_3) - 2 k_{CaO} X_2^2 X_{CaO} - k_2 X_2 X_{Ao}$$

$$2. X_2 = X_c$$

$$dX_1/dt = k_1(1 - X_3) - 2 k_{CaO} X_2^2 X_{CaO} - k_2 X_2 X_{Ao}$$

$$dX_2/dt = 0$$

$$3. t > \tau$$

$$dX_1/dt = k_1(1 - X_3) - k_2 X_2 X_{Ao}$$

$$dX_2/dt = 0$$

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

$$dX_{Ao}/dt = -k_2 X_2 X_{Ao}$$

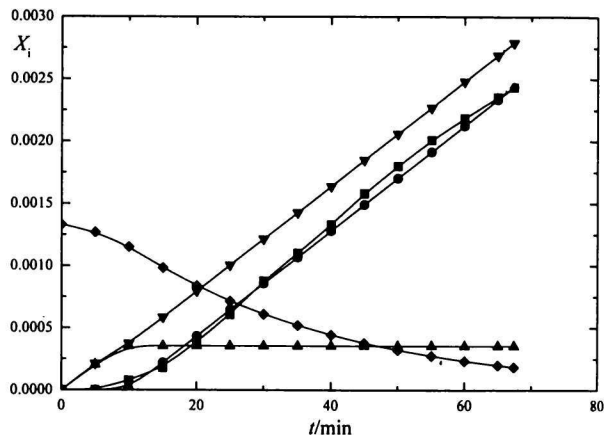
$$dX_{CaO}/dt = -k_{CaO} X_2^2 X_{CaO}$$

We propose that the effect of CaO stabilizer ends at the time exceeding thermal stability. It is supported by experimental observations, *i.e.* very similar curves of samples 6—8 before reaching the time of thermal stability. In these samples the quantity of CaO is equal, only the amounts of antioxidant are different. Development of DHC after reaching  $\tau$  continues in samples 1—5.

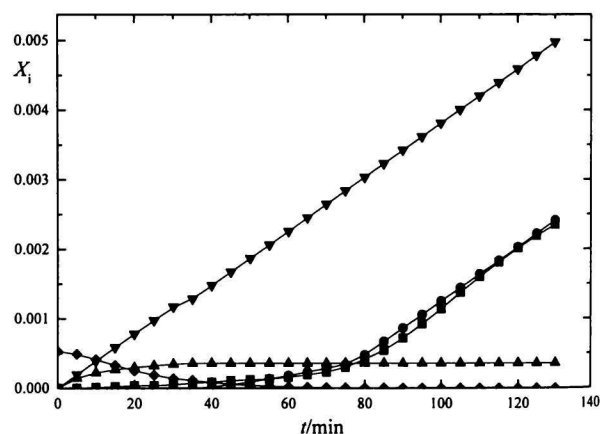
The system of differential equations was solved using the least-squares method with Powell's algorithm. Rate constants and  $X_c$  values were searched. The computation results are shown in Table 3 for samples with Irganox (1—5) and Topanol (9—13). Irganox seems to be a more effective antioxidant than Topanol, since decomposition of the Irganox and HCl reaction product proceeds at lower rate. The results for CaO and Irganox stabilizer system are:  $k_1 = 3.93 \times 10^{-5} \text{ min}^{-1}$ ,  $k_{CaO} = 4960 \text{ min}^{-1}$ ,  $k_2 = 185 \text{ min}^{-1}$ , and  $X_c = 3.63$

**Table 3.** Kinetic Parameters Calculated for Samples 1—5, 9—13

Sample	$k_i/\text{min}^{-1}$	$k_p/k_t$	$k_{Ao}/k_t$	$k_2/\text{min}^{-1}$	$k_{-2}/\text{min}^{-1}$
1—5	$2 \times 10^{-6}$	3.00	50.0	108.0	4.96
9—13	$2 \times 10^{-6}$	3.30	55.8	84.8	25.80



**Fig. 10.** Calculated time dependences of relative mole fractions for dehydrochlorination in air for sample 5.  $X_1$  - conversion of dehydrochlorination, experimental kinetic curve (■), calculated kinetic curve (●);  $X_2$  - HCl in polymer (▲);  $X_3$  - double bonds in polymer (▼);  $X_{Ao}$  - antioxidant (◆).



**Fig. 11.** Calculated time dependences of relative mole fractions for dehydrochlorination in air for sample 7.  $X_1$  - conversion of dehydrochlorination, experimental kinetic curve (■), calculated kinetic curve (●);  $X_2$  - HCl in polymer (▲);  $X_3$  - double bonds in polymer (▼);  $X_{Ao}$  - antioxidant (◆).

$\times 10^{-4}$  (samples 6—8). The results were confirmed by Simplex fit and are in good agreement with experimental curves (Figs. 10—12).

As expected, the rate constant value of DHC is in

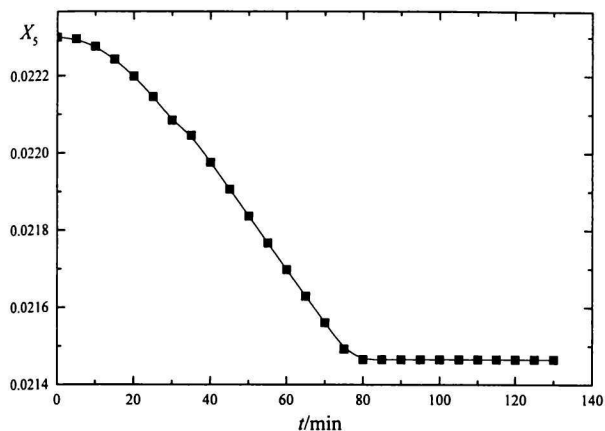


Fig. 12. Calculated time dependence of CaO relative mole fraction  $X_{\text{CaO}}$  (■) for dehydrochlorination of sample 7 in real atmosphere.

both cases lower than in the case of pure PVC ( $k_1 = 9.59 \times 10^{-5} \text{ min}^{-1}$ ). The  $k_2$  and  $k_{-2}$  values for samples 1—5 do not vary in such a narrow interval as  $k_i$ ,  $k_p/k_t$  and  $k_{\text{AO}}/k_t$  (equal for all 5 specimens) or  $k_2$  and  $k_{\text{CaO}}$  for samples 6—8. This fact is caused by absence of experimental data for reactions of HCl with additives. Our experimental data do not allow to ascertain, which process is dominant: termination of polyene sequences or HCl trapping. The ability of CaO to react with the evolved HCl (the reaction has been finished after reaching the time of thermal stability) is limited due to CaO exhausting on granule surface and granules covered with the reaction product,  $\text{CaCl}_2$ . It means that only a small portion of the total CaO amount is active in DHC. The expected synergism between Irganox and CaO is supported by increased  $k_2$  value (of the Irganox and HCl reaction) in comparison with  $k_2$  value of samples 1—5.

### CONCLUSION

The action of the antioxidants Irganox 1010 and Topanol CA either as single additives or as a component of composite stabilizer systems has been studied.

Kinetic schemes for the action of sole antioxidant and of the antioxidant—CaO system have been proposed and the corresponding rate constants have been calculated. These parameters allow to compare the effectiveness of the antioxidants. Irganox 1010 is more effective than Topanol CA. Calculations for the CaO—Irganox 1010 stabilizer system proved the considered synergism between these additives. The rate constant  $k_2$  value of the Irganox 1010 and HCl reaction rose.

Two composite stabilizer systems for long-time stabilization were prepared. The first one with  $\tau = 185$ —273 min consisted of 2 mass % CaO, 1 % zinc stearate, 2 % ethyl acetoacetate, 2 % rape oil, and 0.5—2 % antioxidant (Irganox 1010 or Topanol CA). The second one with  $\tau = 132$  min contained 2 % CaO, 0.25 % zinc stearate, 2 % ethyl acetoacetate, 2 % Edenol D-81, and 2 % Irganox 1010. The advantages of the second stabilizer system are lower amount of metal compound, better clarity, and better initial colour.

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