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# Development of Synergistic Heat Stabilizers for PVC from Zinc Borate-Zinc Phosphate

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*The importance of flame-retardant and smoke-suppressed poly(vinyl chloride) (PVC) compositions is increasing gradually in the polymer industry since PVC releases smoke and toxic gases (hydrogen chloride, HCl) during heating at temperatures above 140°C with the result of dehydrochlorination reaction. In this study, the synergistic effects of zinc borate (ZB)-zinc phosphate (ZP) on the thermal stability of PVC were investigated using thermal techniques. The induction and stability time values of PVC plastigels were obtained at 140° and 160°C. The results revealed that PVC plastigels having only ZP and ZB retarded dehydrochlorination of PVC compared with the unstabilized sample. However, the plastigels with both ZB and ZP had a superior synergistic effect on char formation of PVC. Since the induction periods of the samples having both ZB and ZP were higher than those of the unstabilized samples having only ZB or only ZP, the synergistic effect was observed.*

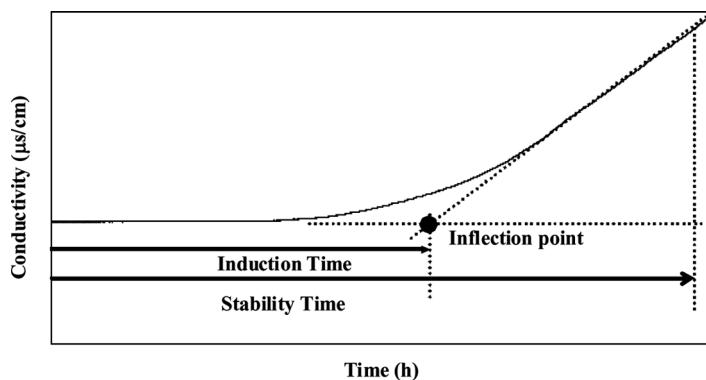
**Keywords** Heat stabilizer; PVC; Thermal degradation; Zinc borate; Zinc phosphate

## Introduction

It is well known that poly(vinyl chloride) (PVC) has high chlorine content, so it is an incombustible material. The construction of buildings often requires the use of fire- or flame-retardant jacketing, facing materials for heating, duct insulation, electrical insulation applications, cables, and domestic uses such as in gutters, doors, profiles, house siding, and similar applications involving plies of combustible sheet material or plies of such sheet materials laminated to various substrates such as aluminum foil and fiberglass batting.

Because of its lower cost and versatility, PVC is often used to prepare such sheet materials by being blended with various additives that are designed to impart the required flame-retardant characteristics. PVC has good flame retardancy because of its high chlorine content, but it is not a safe material in fires because it releases high levels of smoke and toxic gases leading to a color change from brown and even black in the end (Pi et al., 2002; Ning and Guo, 2000; Baltacıoğlu and Balköse, 1999). Additives such as compounds containing metals like antimony, zinc, copper,

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**Figure 1.** A representative curve for PVC Thermomat results.

iron, aluminum, magnesium, and molybdenum are widely used in reducing flammability and in smoke suppression, and the most important commercial smoke suppressants are zinc and aluminum compounds (Pi et al., 2002; Ning and Guo, 2000). One of the most used flame retardants is zinc borate ( $xZnO \cdot yB_2O_3 \cdot zH_2O$ ). Boron can be used as a flame retardant in both the condensed and vapor phases. Under flaming conditions boron and halogens form the corresponding trihalide. Since boron trihalides are effective Lewis acids, they promote cross-linking, minimizing decomposition of the polymer into volatile flammable gases (Schubert, 1995, 1994). Recent studies indicated the synergistic effect of zinc borate and aluminum trihydrate on the flame retardancy and smoke suppression of PVC (Pi et al., 2002; Ning and Guo, 2000).

Zinc phosphate is an anticorrosive white pigment usually produced from zinc oxide and phosphorous acid or zinc salts and phosphates. Smoke densities of smoke-retardant PVC compositions of nickel and zinc salts were evaluated according to their smoke formation during burning in a National Bureau of Standards (NBS) smoke chamber. It has been clearly stated that the compositions with NiO and ZP have reduced smoke generation (Dickens, 1976).

The effects of synergistic fire-retardant additives consisting essentially of boric acid and zinc oxide or zinc phosphate were investigated by determining the limiting oxygen index (LOI) of plasticized PVC samples. In this study, LOI values were obtained in the samples where boric acid and zinc oxide or zinc phosphate were combined. According to the results, the LOI of the control sample was 23.7 and the highest LOI index (29.8), which means more flame and fire retardation, was observed for the plasticized PVC having 30 pbw boric acid and 30 pbw zinc oxide (Ismat, 1977).

Thermal stabilization of PVC can be determined by PVC Thermomat equipment. When PVC plastigels are heated in a PVC Thermomat in the presence of nitrogen gas, the conductivity of water, through which nitrogen gas is passed, changes with respect to time. The period when the conductivity starts to increase is called the induction time, and the period when the conductivity value reaches  $50 \mu S/cm$  is called the stability time. This value is the maximum acceptable level of degradation. Rate of dehydrochlorination can be determined by the conductivity of the solution where the evolved HCl gas is transferred (Atakul et al., 2005). A representative curve for PVC Thermomat results is shown in Figure 1.

**Table I.** Plastisol compositions used in the experiments (values in phr)

Sample no.	PVC	DOP	Viscobyk 5025	ZB	ZP
1	100	80	5	—	—
2	100	80	5	—	2.5
3	100	80	5	0.5	2.0
4	100	80	5	1.0	1.5
5	100	80	5	1.25	1.25
6	100	80	5	1.5	1.0
7	100	80	5	2.0	0.5
8	100	80	5	2.5	—

This study aims to investigate the synergistic effect of the combination of zinc borate (ZB) and zinc phosphate (ZP) on flame retardancy. Optimum synergistic composition of ZB and ZP in thermal stabilization of plasticized PVC is determined as well.

## Experimental Section

### Materials

PVC, dioctyl phthalate (DOP), Viscobyk 5025 (BYK Chemicals, Wallingford, USA), different amounts of zinc borate (ZB) ( $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ ), and zinc phosphate (ZP) ( $\text{Zn}_3(\text{PO}_4)_2$ ) were used to produce PVC plastigels. The amounts of additives used in the experiments are given in Table I. A typical emulsion-type commercial PVC resin (Petvinil P.38/74) was used for plastisol preparation. DOP was used as a plasticizer (Merck, Darmstadt, Germany), and its density is 0.98 g/mL and molecular weight is 390.54 g/mol. Viscobyk 5025 was used as a wetting agent having a density (at 20°C) of 0.88 g/mL and refractive index of 1.45. ZB and ZP were supplied from Heron Chemicals and Pigment Sanayi A.Ş., respectively.

### Preparation of PVC Plastisol and PVC Plastigel

The PVC plastisol was prepared by mixing PVC (resin), dioctyl phthalate (DOP) (plasticizer), and Viscobyk 5025 (suspension aid). They were stirred by a mechanical mixer (IKA Labortecnik). Thereafter different amounts of ZB and ZP were added to PVC plastisol samples and they were stirred by a glass rod. All mixtures contained 100 parts PVC, 80 parts DOP, 5 parts Viscobyk 5025, and 2.5 parts ZB, ZP, or their mixtures. The plastisol compositions are listed in Table I. Subsequent to the mixing, the obtained PVC plastisols were poured onto gloss cardboard papers that were then passed through a film applicator at 300 µm from Sheen Instruments (Sheen 113 N), which is capable of sheeting them into forms of thin, self-supporting films. All plastisol films were gelled for 15 min in an air-circulating oven (EV 018) at  $140^\circ \pm 3^\circ\text{C}$ . Since the plasticizer diffused into the particles of PVC resin, the films were gelled and plastigel films were obtained.

### Morphology of Zinc Borate, Zinc Phosphate, and PVC Plastigels

Zinc borate, zinc phosphate powders, and the PVC plastigel films, gelled at 140°C for 15 min and heated at 160°C for 90 min, were studied by scanning electron microscopy

(Philips, XL-30SFG). In order to determine the morphologies of PVC plastigel films, they were cut by sharp scissors to obtain their cross-sectional area. The films were mounted vertically to observe their cross section.

### *Color Measurement*

The yellowness index value, which gives an idea of the physical deterioration of the heated films when compared with the unheated ones, was measured by a fiber optic spectrophotometer (Spectrocam, Avantes) for unstabilized film and heated plastigels at 140° and 160°C.

### *Thermal Stability Test*

The thermal stability tests were carried out using a 763 PVC Thermomat. It is equipped with two heating blocks, each with four measuring positions. Two sets of four samples can be heated and measured at two different temperatures at each block individually or eight samples can be measured at the same temperature. The samples were cut into small squares of 0.5 cm with a weight of 0.5 g, and later they were put into the reaction vessels of the equipment. The reaction vessels were placed in the heating blocks and they were heated at 140°C and 160°C. Distilled water was put into measuring vessels to be able to calculate the conductivity change of water. As shown in Figure 2, the HCl gas formed because of the dehydrochlorination reaction was taken up by a nitrogen gas stream and transferred into the measuring vessels. The deionized water in the measuring vessel absorbed HCl gas, and the conductivity of the solution changed with respect to time. Therefore, the decomposition process was monitored by measuring the conductivity of aqueous HCl solution.

### *Thermogravimetric Analysis (TGA)*

TGA was used not only to learn the thermal behavior of the films and but also to expose the char residue. PVC films gelled at 140°C for 15 min were tested in this

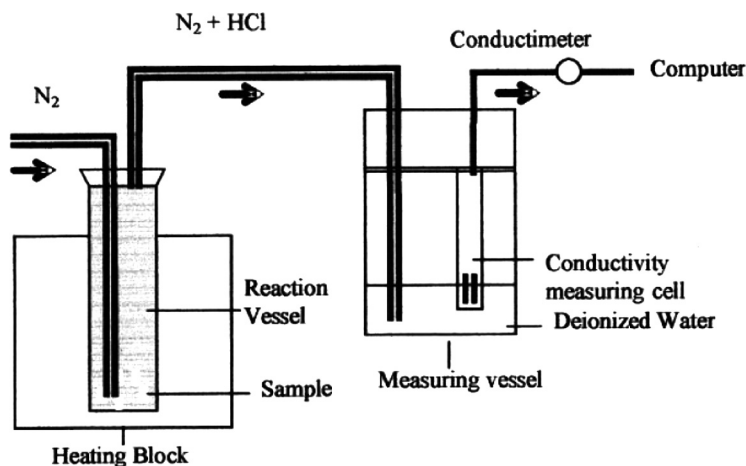


Figure 2. The measuring arrangement of 763 PVC Thermomat.

instrument (Instrument Seteram Labsys) under N<sub>2</sub> atmosphere at a heating rate of 10°C per minute up to 600°C.

## Results and Discussion

The morphology of the materials (ZB and ZP) and the produced PVC plastigel films, the color and the yellowness index values of plastigels, thermal behavior of the films, and the kinetics of degradation were studied to investigate the synergistic effect of zinc borate and zinc phosphate on PVC thermal study. Unlike the similar patent (Ismat, 1977), this study focused on the determination of thermal stability of PVC plastigels stabilized with ZB and ZP by PVC Thermomat. Moreover in the patent, the total amount of flame-retardant additives used for plasticized PVC was in the range of 10–60 parts, whereas in this study the amount was only 2.5 parts for 100 parts resin.

### *Morphology of Zinc Borate, Zinc Phosphate, and PVC Plastigels*

Micrographs of ZB and ZP were obtained by scanning electron microscopy (SEM) to determine particle size of these powders (Figures 3(a) and 3(b)). The average particle size of ZB and ZP powders were determined by taking the averages of the diameters of the particles in micrographs and were 3 µm and 5 µm, respectively.

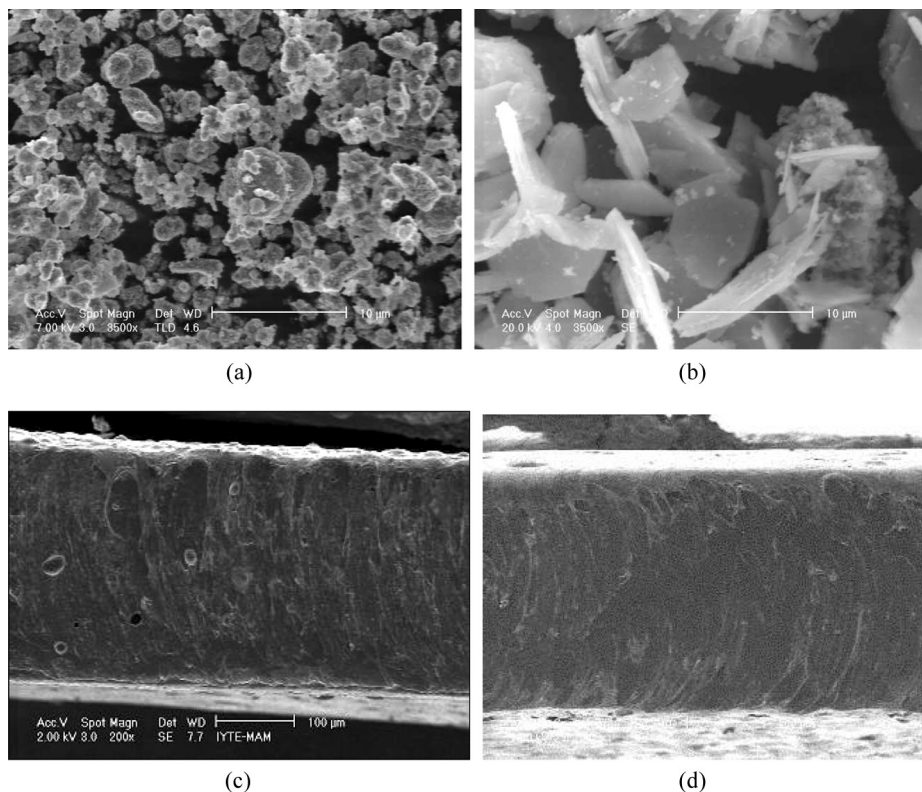
SEM micrographs of cross-sectional areas of PVC plastigels were obtained to examine gelation and fusion behavior of samples. The micrographs of PVC plastigel gelled at 140°C for 15 min and heated at 160°C for 90 min are shown in Figures 3(c) and 3(d). In these micrographs, the dark parts indicate the cross section of the films, and the upper white parts show the surfaces of the films. There are a few pores of 10 µm diameter in the micrograph at 140°C due to entrapped air. The micrograph shows that PVC particles fused to a plastic mass of 300 µm thickness. It is observed that when the temperature and heating periods are increased, the pores between PVC grains disappear and the rough surface of PVC plastigel obtained at 140°C (Figure 3(c)) transforms to a homogeneous surface at 160°C (Figure 3(d)).

### *Color Measurement*

The main outward indicators of thermal degradation of PVC are the evolution of hydrogen chloride, deterioration of physical, chemical, and electrical properties, and the development of color (from light yellow through reddish brown, to almost black in severe cases) (Titov, 1985). The development of color is attributed to the conjugated double bond systems formed in this process. The process starts with a chlorine atom activated by an adjacent allylic bond configuration where that is already present in mid-chain. The yellowness index is the extent of degradation of the films as there is a color change on the films due to heat. In order to observe the change of colors of PVC plastigels heated at 140° and 160°C for different time periods up to 90 min, their yellowness index (YI) values were calculated from data obtained by fiber optic spectrophotometer (Equation (1)):

$$YI = \frac{(128X - 106Z)}{Y} \quad (1)$$

where X, Y, and Z are tristimulus values according to 2° observer and C illuminant.



**Figure 3.** Scanning electron micrographs of the ZB and ZP powders and PVC control sample: (a) ZB, 3500 $\times$  magnified; (b) ZP, 3500 $\times$  magnified; (c) PVC plastigel heated at 140 $^{\circ}$ C for 15 min; and (d) PVC plastigel heated at 160 $^{\circ}$ C for 90 min.

Yellowness index measures the degree of yellowness of a sample. The colors and the yellowness index values of the films having different amounts of ZP and ZB and heated at 140 $^{\circ}$  and 160 $^{\circ}$ C for 90 min are listed in Table II. In this table, higher numbers of yellowness index indicate that the samples have more yellow color. On the other hand, for brown and black samples yellowness index has no physical meaning. According to these results, the sample having 0.68 wt.% ZB + 0.68 wt.% ZP has the lowest yellowness index value and the color of the film heated for 90 min is white at 140 $^{\circ}$ C. However when this sample is heated at 160 $^{\circ}$ C for the same time period, the film becomes brown, indicating that the sample is highly degraded. At 160 $^{\circ}$ C, the synergistic effect of ZB and ZP on the improvement of color of PVC plastigel is obtained for the composition of 1.29 wt.% ZB + 0.27 wt.% ZP. The yellowness index of this sample is  $-3.7$ . Nevertheless, the results in Table II reveal that the addition of zinc phosphate to PVC plastisol decreases the yellowness index of PVC control film at 140 $^{\circ}$  and 160 $^{\circ}$ C, whereas the addition of zinc borate to PVC plastisol increases the yellowness index, and the color of the film having 1.36 wt.% ZB became light yellow at 140 $^{\circ}$ C.

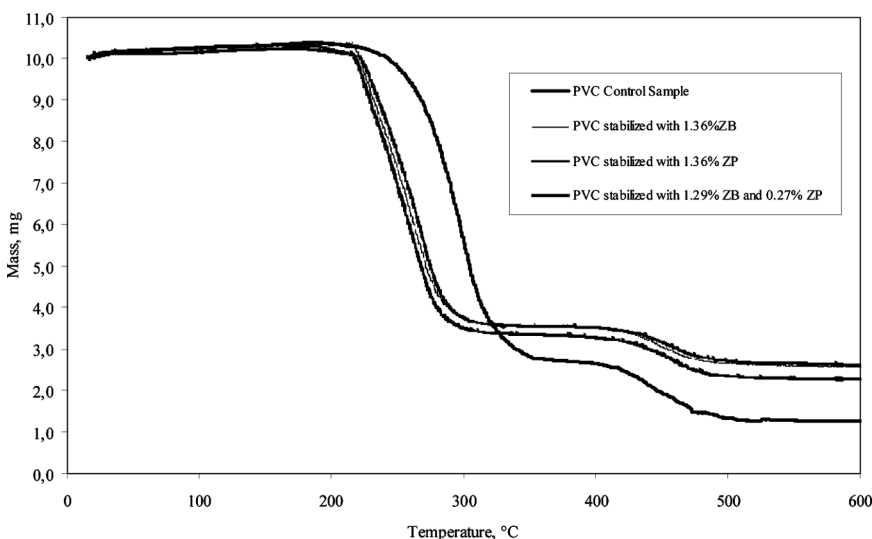
**Table II.** Colors, yellowness index values, and residual mass % of PVC plastigels

Sample no.	Sample composition		140°C, 90 min		160°C, 90 min		Residual mass % at 600°C
	ZB wt. %	ZP wt. %	Color	Yellowness index	Color	Yellowness index	
1	0.00	0.00	White	7.8	Black	1.6	12.50
2	0.00	1.36	White	-0.7	White	-5.2	22.80
3	0.27	1.29	Yellowish	11.6	Light brown	36.8	19.60
4	0.54	0.81	White	3.6	White	-4.9	23.85
5	0.68	0.68	White	-2.6	Brown	106.8	18.10
6	0.81	0.54	Yellowish	5.7	White	-6.0	19.10
7	1.29	0.27	Yellowish	10.5	White	-3.7	26.30
8	1.36	0.00	Light yellow	41.2	Light brown	82.1	25.80

### Thermogravimetric Study of PVC Plastigels

The thermal decomposition of PVC is a two-stage process: thermal decomposition in the first stage is mainly the evolution of HCl and the thermal decomposition in the second stage is mainly cyclization of conjugated polyene sequences to form aromatic compounds. It is known that zinc-containing compounds can greatly reduce smoke formation. Zinc chloride, which is formed along with the thermal decomposition of PVC, acts as an effective catalyst for the ionic dehydrochlorination of PVC due to its strong Lewis acidity, resulting in an increase in char formation and a decrease in smoke production (Ning and Guo, 2000).

The remaining mass versus temperature graph of PVC plastigels is shown in Figure 4. The PVC control sample started to lose its mass at 180°C, whereas the

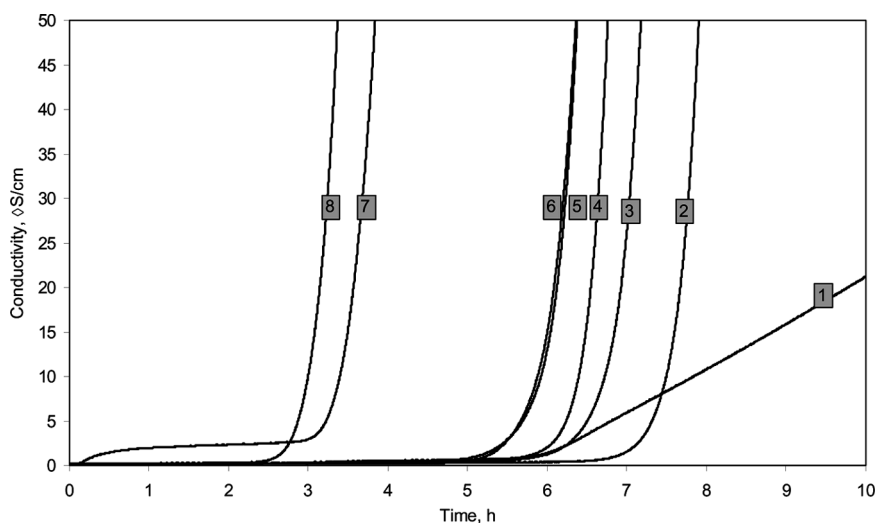
**Figure 4.** TGA curves of the unstabilized sample and the samples stabilized with ZB and ZP.



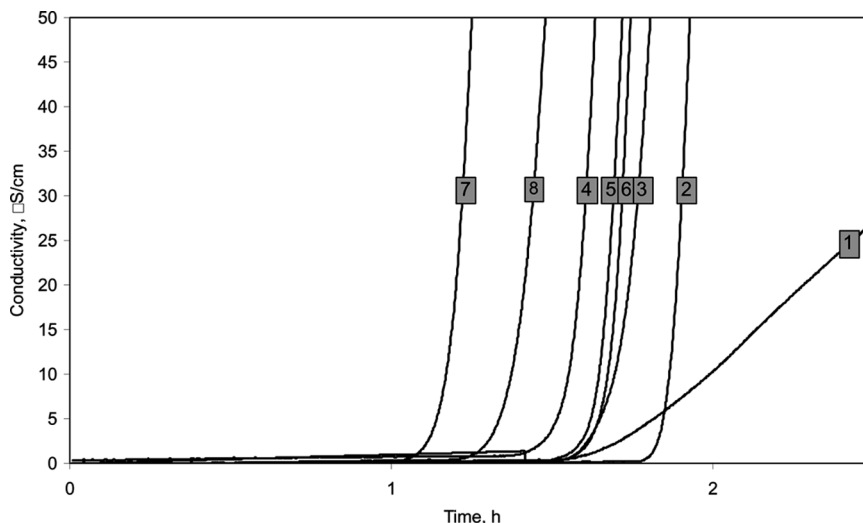
samples having only 1.36 wt.% ZB and 1.36 wt.% ZP had higher onset temperatures of 214° and 185°C, respectively. Among the samples, the film having 1.29 wt.% ZB + 0.27 wt.% ZP had the highest onset temperature (225°C). The char residues of the samples, which are residual mass values, are tabulated in Table II. The highest char residue values were obtained as 26.36% and 23.85% for the samples having 0.54 wt.% ZB + 0.81 wt.% ZP and 1.29 wt.% ZB + 0.27 wt.% ZP, respectively. Since the formed  $\text{ZnCl}_2$  suppressed the formation of smoke and catalyzed the char formation, all of the samples having ZB and/or ZP gave higher char residues than the control sample.

### *Kinetic Study of PVC Plastigels*

The thermal degradation of PVC is substantially a two-step process. The first step mainly involves progressive unzipping of neighboring labile chlorine atoms along the polymer chain by heat, while PVC undergoes a partial carbonization with the release of benzene and other aromatics (Frye and Horst, 1959). In this part of the study, the kinetic theory of degradation of PVC plastigels was evaluated by the change of conductivity of aqueous solution due to evolved HCl gas during heating, as shown in Figure 1. The conductivity change of PVC plastigels stabilized with different amounts of ZB and ZP versus time curves for 140° and 160°C are shown in Figures 5 and 6. By using these curves, kinetic rate constants and the activation energies of dehydrochlorination reaction were evaluated. The steps used in the calculation of rate constants of degradation reaction were described in a recent study (Atakul et al., 2005). In this model, it was assumed that the degradation of PVC was a first-order reaction. The rate constant was related to the concentration of HCl in water ( $C_{\text{HCl}}$ ), potential double bonds to be formed when 100% of HCl



**Figure 5.** Change of conductivity of aqueous solution with respect to time at 140°C for PVC plastigels stabilized with ZB and ZP: 1, PVC control sample; 2, 0.54% ZB + 0.81% ZP; 3, 1.36% ZB; 4, 0.27% ZB + 1.29% ZP; 5, 0.27% ZP + 1.29% ZB; 6, 0.81% ZB + 0.54% ZP; 7, 0.68% ZB + 0.54% ZP; 8, 1.36% ZP.



**Figure 6.** Change of conductivity of aqueous solution with respect to time at 160°C for PVC plastigels stabilized with ZB and ZP: 1, PVC control sample; 2, 0.54 wt.% ZB + 0.81 wt.% ZP; 3, 1.36 wt.% ZB; 4, 0.27 wt.% ZB + 1.29 wt.% ZP; 5, 0.27 wt.% ZP + 1.29 wt.% ZB; 6, 0.81 wt.% ZB + 0.54 wt.% ZP; 7, 0.68 wt.% ZB + 0.54 wt.% ZP; 8, 1.36 wt.% ZP.

was eliminated per 1 g of PVC ( $C_o$ ), moles of evolved HCl gas ( $n_{HCl}$ ), and mass of plastigels in reaction vessel ( $m$ ):

$$k = \frac{dC_{HCl}}{dt} \cdot \frac{1}{C_o} = \frac{dn_{HCl}}{dt} \cdot \frac{1}{m \cdot CF} \cdot \frac{1}{C_o} \quad (2)$$

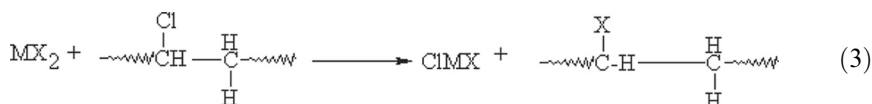
where CF is the correction factor based on the fraction of PVC amount in PVC plastisols.

The dehydrochlorination curves, indicated in Figures 5 and 6, were separated into two parts: initial region and linear region. Therefore, two rate constants were evaluated for each reaction. Initial rate constants were obtained from the slopes of the initial region of the curves where the release of HCl gas started; linear region rate constants were determined from the slopes of the linear region where the release of HCl gas accelerates. Tables III and IV show the kinetic results corresponding to these regions. It was obvious that the PVC control sample had the longest stability time of 15 h at 140°C. However, if the induction times were examined, the film having only 1.36 wt.% of ZB had a higher value than the control sample but the film having only ZP did not. PVC plastigels stabilized with 0.54 wt.% ZB + 0.81 wt.% ZP, 0.81 wt.% ZB + 0.54 wt.% ZP, and 0.27 wt.% ZB + 1.29 wt.% ZP also had higher induction time values than the control sample. At 160°C, PVC films having 0.54 wt.% ZB + 0.81 wt.% ZP, 0.81 wt.% ZB + 0.54 wt.% ZP, and 0.27 wt.% ZB + 1.29 wt.% ZP had the highest values, but in general all of the compositions had better results than the PVC control sample. All of the films showed similar results due to the release of HCl gas. Similar to the former case, again 0.54 wt.% ZB + 0.81 wt.% ZP composition especially showed synergism compared to the sample having only 1.36 wt.% ZB or 1.36 wt.% ZP in its composition. According to the Frye-Horst mechanism (Titow, 1985; Frye and Horst, 1959), anions exchange with

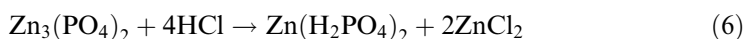
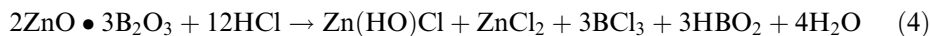
**Table III.** Induction and stability periods, initial and linear rate constants of PVC plastigels at 140°C

Sample no.	Sample composition		Induction time, h	Stability time, h	Initial rate constant $\times 10^7, \text{min}^{-1}$	Linear rate constant $\times 10^4, \text{min}^{-1}$
	ZB wt.%	ZP wt.%				
1	0.00	0.00	2.99	15.21	4.02	0.05
2	0.00	1.36	4.17	4.22	23.09	1.85
3	0.27	1.29	6.72	6.76	7.67	3.14
4	0.54	0.81	7.86	7.91	15.42	2.96
5	0.68	0.68	3.53	3.84	13.85	1.32
6	0.81	0.54	6.37	6.36	27.71	2.40
7	1.29	0.27	6.25	6.38	5.26	1.61
8	1.36	0.00	7.04	7.18	5.36	1.89

labile chlorine atoms next to double bonds or carbonyl substituents. The ZB and ZP in the system react with the HCl released from the system during heating by exchanging their borate and phosphate ions, respectively.



where X is the phosphate or borate anion. The bond between C and phosphate or borate anions are more stable than the C–Cl bond. At long heating times, this bond will be broken also and HCl gas will be released. The reactions occurring in the PVC system are as follows:

**Table IV.** Induction and stability periods, initial and linear rate constants of PVC plastigels at 160°C

Sample no.	Sample composition		Induction time, h	Stability time, h	Initial rate constant $\times 10^6, \text{min}^{-1}$	Linear rate constant $\times 10^4, \text{min}^{-1}$
	ZB wt.%	ZP wt.%				
1	0.00	0.00	1.49	3.35	4.86	0.3
2	0.00	1.36	1.22	1.25	9.24	7.31
3	0.27	1.29	1.59	1.64	2.72	8.72
4	0.54	0.81	1.87	1.93	12.15	10.28
5	0.68	0.68	1.20	1.25	12.31	9.51
6	0.81	0.54	1.69	1.75	10.26	11.08
7	1.29	0.27	1.66	1.72	5.14	8.15
8	1.36	0.00	1.77	1.81	4.62	7.48

ZnCl<sub>2</sub>, which is a strong Lewis acid, formed in reactions (4)–(6), and once its concentration exceeds a certain level it accelerates the dehydrochlorination of PVC.

The activation energies and pre-exponential factors of dehydrochlorination reactions were calculated for the films heated at 140°C and at 160°C by use of the Arrhenius equation at two different temperatures (Equation (7)):

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (7)$$

where  $k$ ,  $A$ ,  $E$ ,  $R$ , and  $T$  are rate constant, pre-exponential factor or frequency, activation energy (J/mol), universal gas constant (8.314 J/mol · K), and temperature (K), respectively. The evaluated values of activation energies and pre-exponential factors are shown in Table V. The results revealed that the activation energies of the linear region were lower than those of the initial region due to the consumption of the additives in the initial region and the acceleration effect of HCl gas. When the activation energies were compared with each other according to the sample compositions, the highest values were found in the sample having 0.81 wt.% ZB + 0.54 wt.% ZP and the sample having 0.27 wt.% ZB + 1.29 wt.% ZP. These values were also consistent with the values in the linear region. The sample stabilized with 0.27 wt.% ZB and 1.29 wt.% ZP had the lowest values, indicating that they decreased the required energy for the release of HCl. Furthermore, kinetic compensation effect was examined to verify the consistency of the calculated values of activation energies and pre-exponential factors with the literature. It has been found that for polymer decomposition, the kinetic parameters, i.e., the pre-exponential factor  $A$  and the activation energy  $E$ , often exhibit the following relationship:

$$\ln A = aE + b \quad (8)$$

where  $a$  and  $b$  are constant coefficients for a series of related rate processes. This relationship is referred to as the “kinetic compensation effect” (KCE), and here the so-called compensation means that the reduction in rate expected to result from an increase in activation energy does not occur for the set of reactions obeying Equation (8) due to a compensatory increase of  $A$  (Lui et al., 2002). Figure 7 shows that

**Table V.** Activation energies and pre-exponential factors for initial and linear regions of dehydrochlorination reaction

Sample no.	Sample composition		Activation energy (kJ/mol)		Pre-exponential factor (s <sup>-1</sup> )	
	ZB wt. %	ZP wt. %	Initial region	Linear region	Initial region	Linear region
1	0.00	0.00	185.3	135.4	2.15 × 10 <sup>-28</sup>	1.42 × 10 <sup>-21</sup>
2	0.00	1.36	103.1	102.2	3.41 × 10 <sup>-18</sup>	3.38 × 10 <sup>-16</sup>
3	0.27	1.29	94.0	75.9	1.23 × 10 <sup>-17</sup>	6.01 × 10 <sup>-13</sup>
4	0.54	0.81	153.4	92.7	3.78 × 10 <sup>-24</sup>	6.77 × 10 <sup>-15</sup>
5	0.68	0.68	162.4	146.8	3.15 × 10 <sup>-25</sup>	1.85 × 10 <sup>-21</sup>
6	0.81	0.54	97.3	113.7	1.86 × 10 <sup>-17</sup>	2.13 × 10 <sup>-17</sup>
7	1.29	0.27	169.3	120.5	1.92 × 10 <sup>-26</sup>	2.38 × 10 <sup>-18</sup>
8	1.36	0.00	160.1	102.3	2.22 × 10 <sup>-25</sup>	3.38 × 10 <sup>-16</sup>

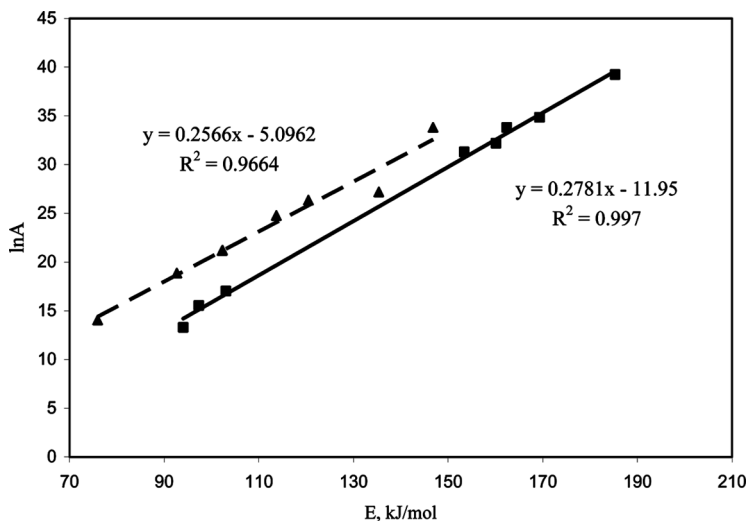


Figure 7. Kinetic compensation effect for PVC plastigels stabilized with ZB and ZP.

there is a linear relationship between activation energy and pre-exponential factor, indicating consistency with the literature (Atakul et al., 2005; Gupta and Viswanath, 1998). The equations obtained from the compensation effect are:

$$y = 0.2781x - 11.95 \text{ (initial region)} \quad (9)$$

$$y = 0.2566x - 5.0962 \text{ (linear region)} \quad (10)$$

By using these linear equations, different parameters under different experimental conditions could be calculated in the heterogeneous reaction; hence, the kinetic compensation effect in fact provided a possible means to predict the effects of experimental factors on kinetic parameters. These linear relations indicated the kinetic compensation effect, showing that dehydrochlorination occurred with different reaction mechanisms with different stabilizers since the activation and the pre-exponential factor values were different for each PVC film.

## Conclusion

The development of heat stabilizers (ZB and ZP) for PVC was studied in different respects. At higher temperatures, the color of PVC plastigels films became brown due the formation of polyene sequences. The color measurement test revealed that the sample having 1.29 wt.% ZB and 0.27 wt.% ZP had small yellowness index values at 160°C. According to the thermogravimetric study, the sample having 1.29 wt.% ZB and 0.27 wt.% ZP showed the highest onset temperature and residual mass percentage at 600°C. Measurements in PVC Thermomat gave information about the release of HCl from PVC plastigels to the surroundings. At 160°C, the sample having 0.54 wt.% ZB and 0.81 wt.% ZP had the highest induction period, 1.87 h, while the induction time value of the PVC control sample was 1.49 h. The synergistic effect of ZB and ZP could not be observed at all levels of stabilizers due to heterogeneous reaction, which involved gas, liquid, and solid.

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