

Synergetic Effect of Dimerized Pentaerythritol Esters with Synergetic Metal Soap on the Stabilization of Poly(vinyl chloride)

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ABSTRACT: The synergetic effect of dimerized pentaerythritol esters, as novel costabilizer, with metal soap, the mixture of zinc and calcium stearates, as stabilizer, on the undesirable discoloration of poly(vinyl chloride) (PVC) by heating was investigated. The dimerized pentaerythritol esters were prepared by the esterification of pentaerythritol using stearic acid and the dimerization of the obtained pentaerythritol ester using unsaturated dicarboxylic acid. This dimer was used to improve its poor compatibility with PVC. The degree of esterification for pentaerythritol was varied from half to the full amount of hydroxyl groups. Both stabilizer and costabilizer were compounded into poly(vinyl chloride) through roll mixing. As a result, the dimerized pentaerythritol esters showed good dispersibility in poly(vinyl chloride). The effect of suppressing the discoloration was obtained in the systems used, not only the half-esterified type but also the full-esterified type, although it had no hydroxyl group. The abrupt discoloration was caused by the formation of a π complex between cool color producing metal chloride, i.e., zinc chloride from the metal soap and double bonds from the dehydrochlorination in poly(vinyl chloride) chain. Usually, the hydroxyl group containing compounds are said to be useful for suppressing the discoloration because the hydroxyl group captures the metal chloride. In the costabilizing effect of the full esterified type, it was clarified from the X-ray photoelectron spectroscopic analysis and infrared spectrum observations for the model mixtures, that the decomposition of the ester group could occur, and the excess zinc chloride was captured as colorless zinc carboxylate. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2029–2037, 2001

Key words: poly(vinyl chloride); stabilization; costabilizer; polyols; pentaerythritols

INTRODUCTION

The synergetic metal soap, such as the mixture of zinc and calcium stearates, are widely used as a thermal stabilizer for poly(vinyl chloride) (PVC).

However, the amount of double bond introduced along the dehydrochlorinated PVC chain, i.e., polyene, increased gradually with an increase in the heating time.^{1,2} Simultaneously, the metal chloride was also converted from the corresponding metal soap in the PVC.^{3,4}

Some amount of π complex between the cool color producing metal chloride, such as zinc chloride, and the double bonds in the polyene chains

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were formed during the heat treatment of compounded PVC,^{1,2} and then the color of the system turned abruptly black. In particular, this phenomenon, which appeared on the system containing zinc salts, is called "zinc burning."^{1,2,5} Compounds that contain groups to capture the cool color producing metal chloride should be used as a costabilizer⁶⁻¹¹ were usually used together with the synergetic metal soap to delay the appearance of zinc burning.

Briggs et al.¹² and Albarino et al.¹³ reported that the oxygen-containing compounds had good stabilization effect concerning the dehydrochlorination of PVC. So, we have investigated the effects of polyols on the stabilization of PVC, involving colorimetry.

Our previous articles^{8,14} showed that the lower and higher molecular polyols such as glycerol¹⁴ and poly(vinyl alcohol)⁸ exhibited the good costabilizing effects, to delay the appearance of zinc burning, which should be due to capture of the excess zinc chloride. Their effects were strongly depended upon their dispersibility into the PVC phase. We also pointed out that the pentaerythritol was considered useful as a costabilizer,¹⁵ but it showed lower dispersibility owing to its poor compatibility with PVC. Furthermore, the unperfectly dispersed polyols were unstable in the PVC matrix, then they bloomed or bled onto the surface and stayed on its surface as a contamination. Therefore, it would be difficult to use them as a costabilizer in industrial applications.

In this study, in order to improve the poor compatibility of pentaerythritol with PVC, pentaerythritol esters were prepared, and the influences of their dispersibility upon the costabilization effect for PVC and its mechanism were investigated.

EXPERIMENTAL

Materials

The PVC used in this work was Geon 103 EP (Nippon Zeon Co., Ltd.; \bar{P}_n : 1050). Commercially available di(2-ethylhexyl)phthalate (DOP) as plasticizer, zinc stearate (Zn-st), and calcium stearate (Ca-st) as stabilizer for PVC, and pentaerythritol (PE) as costabilizer, were used as received. Reagent grade stearic acid and unsaturated dicarboxylic acids were used as raw materials.

The pentaerythritol derivatives as costabilizer were prepared as follows, and their formulations

are shown in Figure 1. First, pentaerythritol was esterified with stearic acid with stirring in xylene (5% by weight of pentaerythritol) under nitrogen atmosphere, and it was refracted at $200 \pm 5^\circ\text{C}$ until the theoretical water was discharged. The obtained pentaerythritol stearate (pentaerythritol ester, PEE) was distilled to remove the xylene completely *in vacuo*, then decolorized with activated clay and filtered. Subsequently, dimerization of PEE was carried out by the same methods using three kinds of unsaturated dicarboxylic acids, maleic acid, azelaic acid, and dimeric acid (dimerized linolenic acid) for the MPS, ZPS, and DPS series, respectively. The dimerized PEE was called DPEE. MPS-123 and MPS-126 indicated that the mole ratios of maleic acid, stearic acid, and PE at the syntheses were 1:2:3 and 1:2:6, respectively. The half amount of the hydroxyl group of PE expected to be esterified with stearic acid for MPS-123, and full of them expected to be esterified completely for MPS-126. Therefore, the 123 and 126 series were called DPEE-half and DPEE-full, respectively. Some properties are shown in Table I.

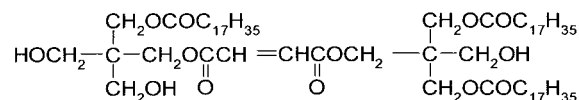
Sample Preparation

PVC, DOP (20 parts per hundred parts of resin by weight, phr), synergetic metal soap, which was mixture of 2 parts of Zn-st and 1 part of Ca-st [called Zn/Ca(2/1)-st, powder, 3 phr], and the costabilizer (powder, 0.4–3 phr) were dry blended, and then the mixture was milled using an open roll at 150°C for 5 min. The compounded PVC sheet, about 0.5 mm thickness, was prepared and cut into the rectangular sheet (50×70 mm). The obtained sheet was heated at $160 \pm 2^\circ\text{C}$ for 120 min in an oven. These procedures were described in detail in the previous article.¹⁰

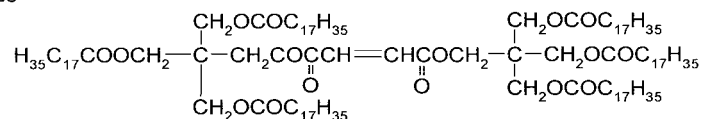
Colorimetry

The whiteness of heated sheets at room temperature was measured using a differential colorimeter (Model SM-4-CH color computer, Suga Shikenki Co., Ltd.) with Purity-I 84 software mounting a specimen holder window of 30 mm in diameter in the same method shown in the previous articles.¹⁰ The tristimulus values of each sheet were determined by averaging the measured values at three different places on the sheet's surface, using a white color standard plate ($X = 82.4$, $Y = 84.5$, $Z = 93.7$) as a reflector. The measured data was shown in "W(Lab)," which means the whiteness in Lab color system.

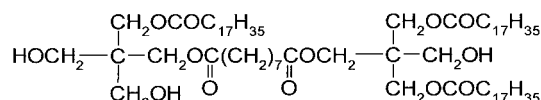
MPS-123



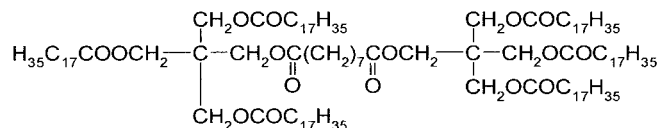
MPS-126



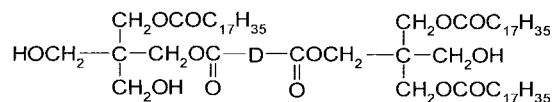
ZPS-123



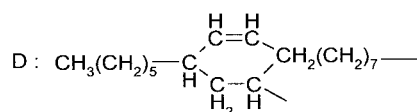
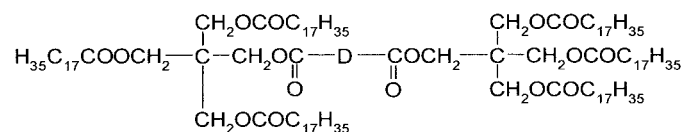
ZPS-126



DPS-123



DPS-126


Figure 1 Structural formulations of the dimerized pentaerythritol esters (DPEE).

Evaluation of Dispersibility

The dispersibility of the costabilizers in the compounded PVC was evaluated using an image processing analysis system (Model TVIP-2000 image processor, Nippon Avionics Co., Ltd.) with Image Command 98 software in the same way as the previous articles⁸⁻¹⁰ equipped with an electron probe microanalyzer (EPMA, DX-4 type, Philips Japan, Ltd.). In the optical photomicrograph of the compounded PVC sheets, the shadows of the costabilizer were recognized and they were utilized for the anal-

ysis. The total area of the recognized unperfectly dispersed costabilizer phase per 1 mm² (ΣA), the average area of the unperfectly dispersed particles (A), and the average distance to the nearest center of gravity (NCG) were evaluated.⁸⁻¹⁰ In this study, the particles above diameter of 1 μm were recognized as the unperfectly dispersed particles.

X-Ray Photoelectron Spectroscopy (XPS)

The compounded PVC sheets were powdered and dried *in vacuo* in the presence of phosphorus

Table I Some Properties of the Dimerized Pentaerythritol Esters

| Costabilizer | Acid Value | Saponification Value | Hydroxyl Value | Average Molecular Weight | Melting Point (°C) |
|--------------|------------|----------------------|----------------|--------------------------|--------------------|
| MPS-123 | 6.4 | 232 | 113 | 1137 | 49–50 |
| ZPS-123 | 2.1 | 232 | 123 | 1191 | 40–43 |
| DPS-123 | 1.4 | 173 | 90 | 1583 | 40–42 |
| MPS-126 | 2.1 | 228 | 20 | 1754 | 55–56 |
| ZPS-126 | 4.2 | 214 | 21 | 1808 | 54–60 |
| DPS-126 | 2.6 | 190 | 16 | 2200 | 50–60 |

penta oxide. XPS was measured by the powder method under 10^{-5} Pa using Model ESCA-750 XPS with ESCAPAC-760 data measurement system (Shimadzu Corp.). $MgK\alpha$ (1253.6 eV) was used as X-ray source.

Infrared (IR) Spectrum

The IR spectrum for the mixture of pentaerythritol derivative and Zn-st were measured using Model FTIR-8100M spectrophotometer (Shimadzu Corp.) by the potassium-bromide tablets method.

RESULTS AND DISCUSSION

Synergetic Effect of DPEE

Figure 2 shows the effect of DPEE-half (half esterified dimerized pentaerythritol ester, MPS-, ZPS-, and DPS-123) compounded with Zn/Ca(2/1)-st on the whiteness of PVC. This figure represented the whiteness in Lab color system $[W(\text{Lab})]^{8,14}$ as a function of heating time at 160°C. Under the present condition, the $W(\text{Lab})$ value of PVC sheet should be below 91, because the value of the standard white color plate used as a reflector was 91. The $W(\text{Lab})$ value decreased gradually with time for the PVC control. The value decreased abruptly at 45 min and remained almost invariable value after attaining the minimum for the PVC stabilized with Zn/Ca(2/1)-st alone, whereas there was no decrease like the above until 120 min in the $W(\text{Lab})$ value for those stabilized with DPEE-half combined with Zn/Ca(2/1)-st. In our previous article,¹⁴ it was clear that the abrupt discoloration was ascribed to the excess formation of cool color producing π complex, namely zinc burning. That is, it became clear that DPEE-half combined with Zn/Ca(2/1)-st was effective to delay the zinc burning.

Figure 3 shows the synergetic effect of DPEE-full (completely esterified dimerized pentaerythritol ester, MPS-, ZPS-, and DPS-126) combined with Zn/Ca(2/1)-st for PVC. This result is similar to that shown in Figure 2 was obtained and these compounds were also recognized to be useful as a costabilizer despite them not having a hydroxyl group.

Table II shows other results of the colorimetry with various combinations and DPEE content. For the PVC as an unstabilized control experiment, the $W(\text{Lab})$ value decreased from 83 to 49 and the dominant wavelength (λ_d) shifted from 578 to 586 nm (warm color, yellow orange). This result indicated the formation of polyene in the PVC. For the PVCs added with DPEE without

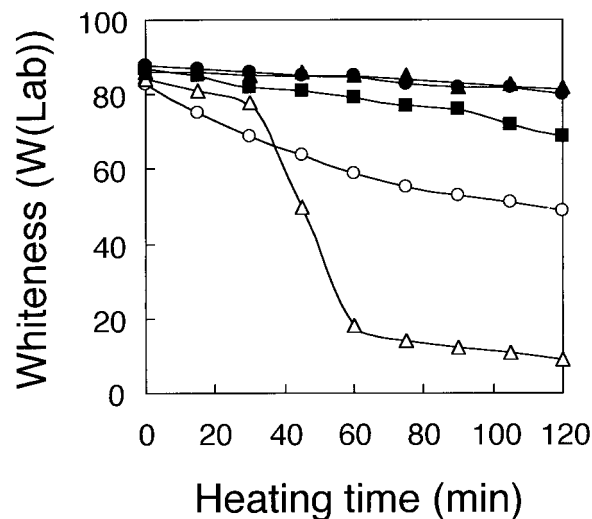


Figure 2 Effect of DPEE-half on the whiteness of PVC sheets heated at 160°C: PVC stabilized with Zn/Ca(2/1)-st alone (Δ , 3 phr), stabilized with Zn/Ca(2/1)-st (3 phr) and DPEE-half (3 phr) (\bullet : MPS-123; \blacktriangle : ZPS-123; \blacksquare : DPS-123), and PVC control (\circ). Base resin was PVC containing 20 phr of DOP. The mixture was milled at 150°C for 5 min.

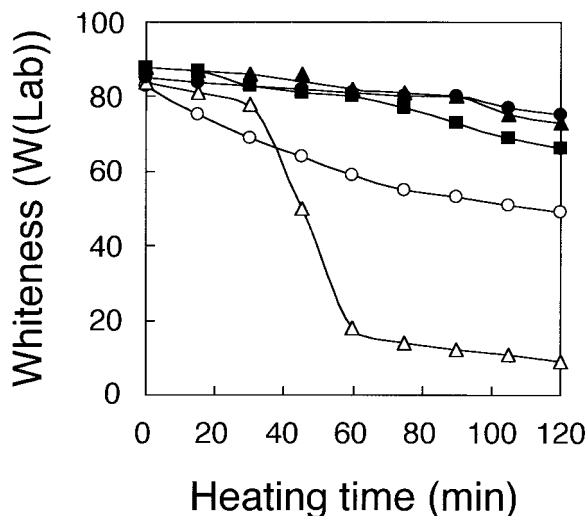


Figure 3 Effect of DPEE-full on the whiteness of PVC sheets heated at 160°C: PVC stabilized with Zn/Ca(2/1)-st alone (Δ , 3 phr), stabilized with Zn/Ca(2/1)-st (3 phr) and DPEE-full (3 phr) (\bullet : MPS-126; \blacktriangle : ZPS-126; \blacksquare : DPS-126), and PVC control (\circ). Base resin was PVC containing 20 phr of DOP. The mixture was milled at 150°C for 5 min.

Zn/Ca(2/1)-st, the $W(\text{Lab})$ values also decreased from 85–80 to 53–39; thus there was no effect on delaying the discoloration. In the case of the PVC stabilizing with Zn/Ca(2/1)-st alone (stabilized control), the abrupt decrease in the $W(\text{Lab})$ at 45 min and the λ_d change to 473 nm (cooler color, blue) were ascribed to the zinc-burning as clarified in the previous article.¹⁴

On the other hand, in the PVCs stabilized with DPEE and Zn/Ca(2/1)-st, the degree of the decrease in the $W(\text{Lab})$ [$(W_0 - W_L)/W_0$] was smaller than that for other systems, especially at the higher costabilizer (DPEE) content. A similar tendency was observed in the λ_d change. That is, these systems showed the significant synergistic effect of DPEE combined with the synergistic metal soap. Both DPEE-half and DPEE-full showed the excellent synergetic effect on delaying the discoloration of PVC by heating. However, the costabilizing effect was slightly higher in DPEE-half (123 series) than in DPEE-full (126 series) and in the order of MPS > ZPS > DPS. These results were in accordance with the hydroxyl group content in the added amount of DPEE.

Dispersibility of DPEE

The image processing analysis of the optical photomicrographs for the compounded PVC sheets

was carried out, to compare with the dispersibility of DPEE in the PVC.

Figure 4 shows the relationship between the total area of the recognized imperfectly dispersed costabilizer particles per 1 mm² ($\Sigma A/\text{mm}^2$) and the added costabilizer content (phr) for DPEE-half (123 series). The ($\Sigma A/\text{mm}^2$) of imperfectly dispersed PE increased with an increase in its content. On the other hand, the ($\Sigma A/\text{mm}^2$) values of DPEE-half were far lower than that of PE, and the degree of the increase in the ($\Sigma A/\text{mm}^2$) value with their content was also smaller in DPEE-half than in the PE. The dispersibility of DPEE-half was superior to that of PE. The imperfectly dispersed particles for PE were easily found with the naked eye. There was no significant difference between MPS-, ZPS-, and DPS-123 on the value. The lines for DPEE-half crossed the origin; however, that for PE never crossed the origin. This result indicated that the particle size of DPEE-half was finer than that of PE, and the size distribution was sharp for DPEE-half, while broad for PE. And in our previous article,¹⁶ it was already clarified that the dispersibility of PEE was almost the same level as that of DPEE shown in Figure 4.

Figure 5 shows the result of the ($\Sigma A/\text{mm}^2$) values for DPEE-full (126 series). The obtained results were similar to those for DPEE-half (123 series) shown in Figure 4.

The average area of the imperfectly dispersed particles (A), the distance to the nearest center of gravity (NCG) and the numbers of imperfectly dispersed particles per 1 mm² (N) at the same costabilizer content of 3 phr were shown in Table III. From these results, there was no significant difference between the dispersibility of DPEE-half and DPEE-full, and that of MPS, ZPS, and DPS. In our previous article,^{15,16} it was clarified that the compounds having hydroxyl groups, such as PE, act as a good costabilizer. However, most of them had poor dispersibility in the PVC.¹⁶ The esterification of PE (i.e., PEE) was an effective way to improve the dispersibility, whereas it reduced the stabilizing effect,¹⁶ because hydroxyl group captured the excess metal chloride. In this study, it became clear that DPEE-full possessed both an excellent dispersibility and a stabilizing ability, although it had no hydroxyl groups, and was quite different from the case of the completely esterified PEE clarified in the previous article.^{15,16}

Table IV shows the slopes [$(\Sigma A/\text{mm}^2)/\text{phr}$] and the extrapolated values to 0 of the costabilizer

Table II Synergetic Effects of the Dimerized Pentaerythritol Esters with Synergetic Metal Soap^a

| Stabilizer ^b | Costabilizer | Costabilizer | | t_E^d (min) | W_M^e | t_L^f (min) | W_L^g | $(W_0 - W_M)/$ W_0 (%) | $(W_0 - W_L)/$ W_0 (%) | $\lambda_d(i)^h$ (nm) | $\lambda_d(f)^i$ (nm) |
|-------------------------|--------------|------------------|---------|------------------|---------|------------------|---------|-----------------------------|-----------------------------|--------------------------|--------------------------|
| | | Content (phr) | W_0^c | | | | | | | | |
| — | — | — | 83 | — | — | 120 | 49 | — | 41 | 578 | 586 |
| — | MPS-123 | 1.0 | 85 | — | — | 120 | 53 | — | 35 | 573 | 582 |
| — | ZPS-123 | 1.0 | 81 | — | — | 120 | 39 | — | 39 | 570 | 582 |
| — | DPS-123 | 1.0 | 83 | — | — | 120 | 46 | — | 45 | 570 | 584 |
| — | MPS-126 | 1.0 | 80 | — | — | 120 | 45 | — | 46 | 568 | 585 |
| — | ZPS-126 | 1.0 | 84 | — | — | 120 | 46 | — | 42 | 574 | 584 |
| — | DPS-126 | 1.0 | 84 | — | — | 120 | 45 | — | 46 | 568 | 583 |
| Zn/Ca(2/1)-st | — | — | 84 | 45 | 78 | 120 | 9 | 7 | 89 | 571 | 473 |
| Zn/Ca(2/1)-st | MPS-123 | 0.4 | 87 | 105 | 65 | 120 | 58 | 25 | 33 | 574 | 481 |
| | | 1.0 | 86 | — | — | 120 | 75 | — | 13 | 576 | 575 |
| | | 2.0 | 88 | — | — | 120 | 85 | — | 3 | 575 | 574 |
| | | 3.0 | 88 | — | — | 120 | 80 | — | 9 | 566 | 574 |
| Zn/Ca(2/1)-st | ZPS-123 | 0.4 | 77 | 120 | — | 120 | 50 | 18 | 35 | 578 | 579 |
| | | 1.0 | 81 | — | — | 120 | 74 | — | 9 | 577 | 577 |
| | | 2.0 | 79 | — | — | 120 | 75 | — | 5 | 576 | 577 |
| | | 3.0 | 86 | — | — | 120 | 82 | — | 5 | 568 | 574 |
| Zn/Ca(2/1)-st | DPS-123 | 0.4 | 86 | 105 | 69 | 120 | 58 | 20 | 33 | 579 | 483 |
| | | 1.0 | 87 | — | — | 120 | 70 | — | 20 | 576 | 532 |
| | | 2.0 | 87 | — | — | 120 | 75 | — | 14 | 576 | 575 |
| | | 3.0 | 87 | — | — | 120 | 69 | — | 21 | 569 | 577 |
| Zn/Ca(2/1)-st | MPS-126 | 0.4 | 86 | 105 | 76 | 120 | 67 | 12 | 22 | 578 | 480 |
| | | 1.0 | 87 | — | — | 120 | 79 | — | 9 | 577 | 484 |
| | | 2.0 | 88 | — | — | 120 | 76 | — | 14 | 575 | 543 |
| | | 3.0 | 85 | — | — | 120 | 75 | — | 12 | 570 | 574 |
| Zn/Ca(2/1)-st | ZPS-126 | 0.4 | 87 | 105 | 76 | 120 | 15 | 13 | 83 | 575 | 486 |
| | | 1.0 | 86 | 120 | 73 | 120 | 46 | 15 | 47 | 577 | 488 |
| | | 2.0 | 86 | 120 | 76 | 120 | 59 | 12 | 31 | 576 | 481 |
| | | 3.0 | 88 | — | — | 120 | 73 | — | 16 | 572 | 576 |
| Zn/Ca(2/1)-st | DPS-126 | 0.4 | 82 | 105 | 71 | 120 | 10 | 13 | 88 | 575 | 486 |
| | | 1.0 | 86 | 120 | 75 | 120 | 43 | 13 | 50 | 576 | 486 |
| | | 2.0 | 87 | 120 | 76 | 120 | 59 | 13 | 32 | 576 | 493 |
| | | 3.0 | 88 | — | — | 120 | 66 | — | 25 | 568 | 577 |

^a Compounded with 20 phr of DOP. Specimens were heated at 160°C.^b Content: 3.0 phr.^c W_0 : $W(\text{Lab})$ of unheated specimen.^d t_E : The heating time for the onset of zinc burning.^e W_M : $W(\text{Lab})$ at the heating time just before the onset of zinc burning.^f t_L : The heating time attaining the lowest $W(\text{Lab})$.^g W_L : The lowest $W(\text{Lab})$.^h $\lambda_d(i)$: The dominant wavelength of unheated specimen.ⁱ $\lambda_d(f)$: The dominant wavelength of heated specimen for 120 min.

content $[(\Sigma A/\text{mm}^2)_{\text{phr} \rightarrow 0}]$, the intercepts with the vertical axis) obtained from the lines in Figures 3 and 4. In our previous articles,^{8–10} the relation between the costabilizing effect and the dispersibility for a few oxygen-containing compounds such as poly(vinyl alcohol),⁸ saponificated poly(vinyl acetate),⁹ and ethylene-vinyl alcohol copolymer¹⁰ was investigated. As a result, the compounds exhibited the excellent costabilizing effect and the effect increased with an increase in their dispersibility—namely, with a decrease in the above values, $(\Sigma A/\text{mm}^2)/\text{phr}$ and $(\Sigma A/\text{mm}^2)_{\text{phr} \rightarrow 0}$.

That is, the above thing was an important factor as values to evaluate the dispersibility of the costabilizer. The values for DPEE shown in Table IV were smaller than those for above oxygen-containing compounds which was obtained previously^{8–10} or almost the same level with those things. Therefore, the sufficient dispersibility of DPEE in PVC as costabilizer was confirmed.

Synergetic Mechanism of DPEE

The XPS and IR for the model mixture of DPEE-full and zinc chloride (ZnCl_2 ; 1/1, mol ratio) were

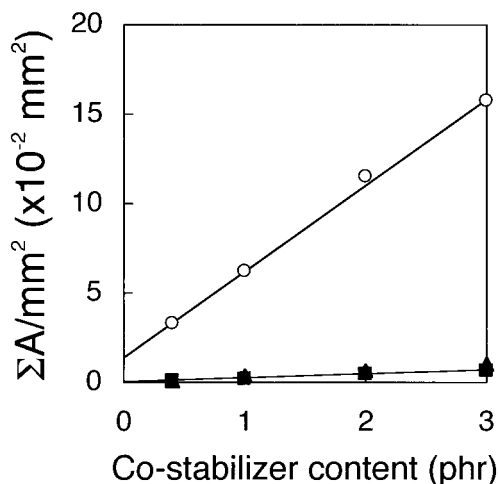


Figure 4 Total area (ΣA) of DPEE-half in PVC sheets: PVC mixed with Zn/Ca(2/1)-st (3 phr) and PE (○). Those mixed with Zn/Ca(2/1)-st (3 phr) and DPEE-half: (●) MPS-123, (▲) ZPS-123, and (■) DPS-123. Base resin was PVC containing 20 phr of DOP. The mixture was milled at 150°C for 5 min. The particles above diameter 1 μm were recognized as the imperfectly dispersed particles.

carried out to clarify their costabilizing mechanism, and compared with the result for the mixture of the completely esterified PE (PEE-full) and ZnCl_2 .

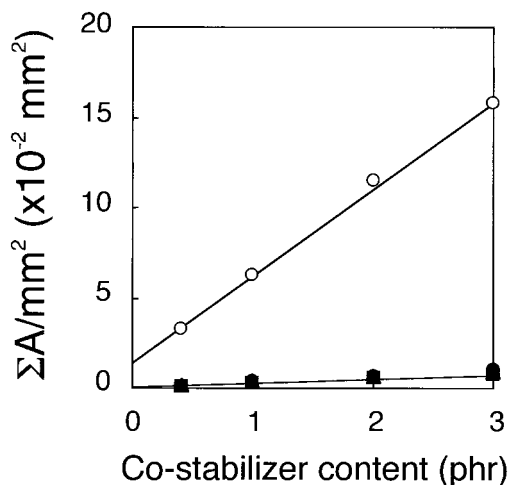


Figure 5 Total area (ΣA) of DPEE-full in PVC sheets: PVC mixed with Zn/Ca(2/1)-st (3 phr) and PE (○). Those mixed with Zn/Ca(2/1)-st (3 phr) and DPEE-full: (●) MPS-126, (▲) ZPS-126, and (■) DPS-126. Base resin was PVC containing 20 phr of DOP. The mixture was milled at 150°C for 5 min. The particles above diameter 1 μm were recognized as the imperfectly dispersed particles.

Table III Dispersibility of the Dimerized Pentaerythritol Esters in PVC Sheets^a

| Costabilizer ^b | $A^c (\times 10^{-3} \text{ mm}^2)$ | NCG ^d (mm) | Number (per mm^2) |
|---------------------------|-------------------------------------|-----------------------|-----------------------------|
| MPS-123 | 0.72 | 0.04 | 9 |
| ZPS-123 | 0.74 | 0.05 | 13 |
| DPS-123 | 0.70 | 0.03 | 10 |
| MPS-126 | 0.71 | 0.06 | 14 |
| ZPS-126 | 0.64 | 0.07 | 12 |
| DPS-126 | 0.65 | 0.05 | 12 |

^a The particles above diameter of 1 μm were recognized as the undispersed particles. Compounded with 20 phr of DOP and 3.0 phr of Zn/Ca(2/1)-st.

^b Content: 3.0 phr.

^c The average area of dispersed particles.

^d The average distance to nearest center of gravity.

Figure 6 shows the XPS result for the two model mixtures of DPEE-full and ZnCl_2 , and PEE-full and ZnCl_2 in the binding energy (E) of $\text{Zn}(2p)$ orbit. The E of $\text{Zn}(2p)$ began to depart from ZnCl_2 and approach to ZnO , then returned to ZnCl_2 with heating time for the DPEE-full and ZnCl_2 mixture. On the other hand, the E of $\text{Zn}(2p)$ for the PEE-full and ZnCl_2 mixture began to depart from ZnCl_2 to ZnO more slowly than that for the DPEE-full and ZnCl_2 mixture, and never returned to E of ZnCl_2 . These results indicated that the decomposition of ester group occurred readily in DPEE-full, whereas it occurred in PEE-full, with difficulty.

Figure 7 shows the IR spectra of DPEE-full (ZPS-126) alone (I) and the mixture of DPEE-full and ZnCl_2 (II) heated at 160°C. The sharp peak

Table IV Evaluation on Dispersibility of the Dimerized Pentaerythritol Esters in PVC Sheets^a

| Costabilizer | $(\Sigma A/\text{mm}^2)/\text{phr} (\times 10^{-2})$ | $(\Sigma A/\text{mm}^2)_{\text{phr} \rightarrow 0} (\times 10^{-2} \text{ mm}^2)$ |
|-----------------|--|---|
| MPS-123 | 0.22 | 0.00 |
| ZPS-123 | 0.34 | 0.00 |
| DPS-123 | 0.23 | 0.00 |
| MPS-126 | 0.35 | 0.00 |
| ZPS-126 | 0.27 | 0.00 |
| DPS-126 | 0.26 | 0.00 |
| PE ^b | 4.83 | 1.35 |

^a The particles above diameter of 1 μm were recognized as the undispersed particles. Compounded with 20 phr of DOP and 3.0 phr of Zn/Ca(2/1)-st.

^b Pentaerythritol.

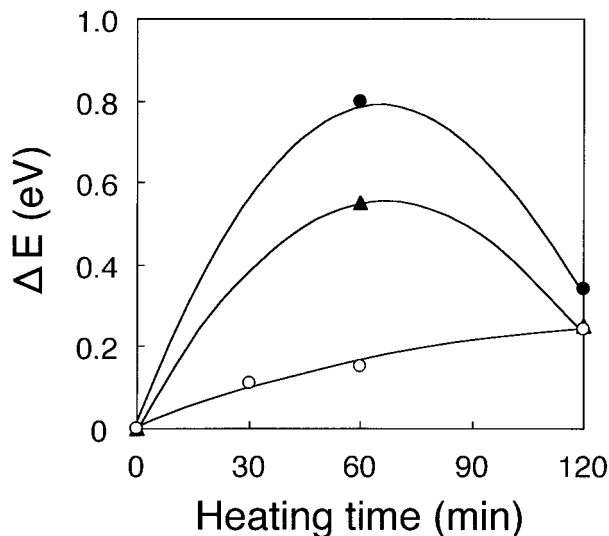


Figure 6 Peak shift of binding energy for Zn(2_p) measured by X-ray photoelectron spectroscopic analysis: mixtures of DPEE-full (●: MPS-126; ▲: ZPS-126) and ZnCl₂, and PEE (○) and ZnCl₂, heated at 160°C. Their mol ratio was 1:1.

arising from diester was clearly observed at near 1600 cm⁻¹ only in the mixture of DPEE-full and ZnCl₂ (II). The peak was never observed in DPEE-full alone (I).

Figure 8 shows the IR spectra of PEE-full alone

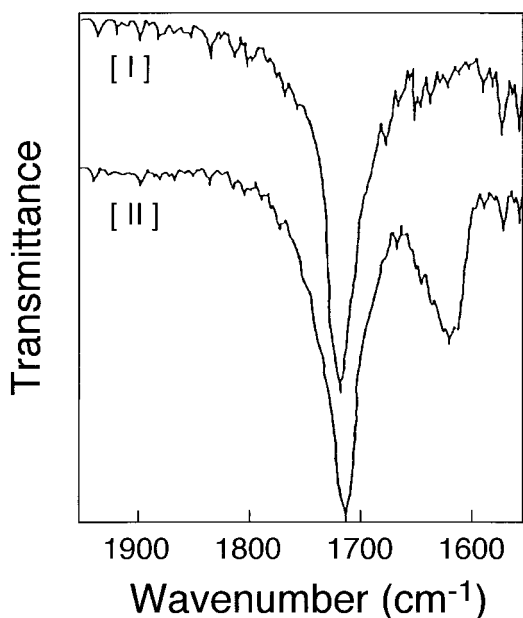


Figure 7 Infrared spectra of DPEE-full (ZPS-126) alone (I) and the mixture of ZPS-126 and ZnCl₂ (mol ratio of 1:1, II) heated at 160°C.

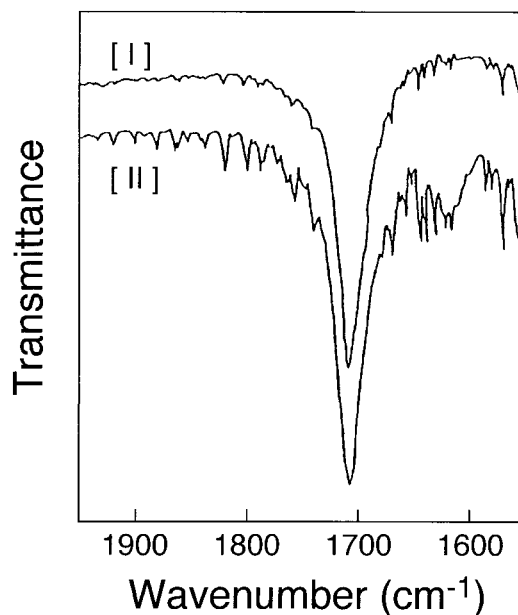
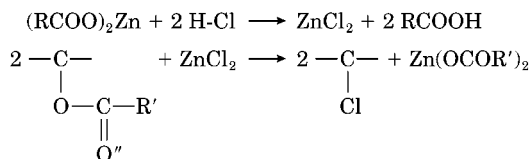


Figure 8 Infrared spectra of PEE (I) and the mixture of PEE and ZnCl₂ (mol ratio of 1:1, II) heated at 160°C.

(I) and the mixture of PEE-full and ZnCl₂ (II). The peak, which appeared near 1600 cm⁻¹ was far smaller than the mixture of DPEE-full and ZnCl₂ (Fig. 7, II). These results supported the above aspect that the decomposition of ester group occurred readily in DPEE-full.

Figure 9 shows the IR spectra of *n*-hexyl acetate alone (I) and the mixture of *n*-hexyl acetate and ZnCl₂ (II) heated at 160°C. The sharp peak arising from alkyl chloride at near 750 cm⁻¹ appeared only in the mixture of *n*-hexyl acetate and ZnCl₂ (II).

From the results above, the following reaction should occur in the heated PVC sheet:



The costabilization mechanism of DPEE-full was in good accordance with that of polyacrylates.¹⁷ There was no costabilizing effect in the PVC combined with PEE and Zn/Ca(2/1)-st^{15,16}; therefore, the decomposition of the ester group in PEE was subject to occur with an increase in its molecular weight, by the dimerization with the fatty acid. Marked differences between PEE and DPEE-full, as to their costabilization effect, were

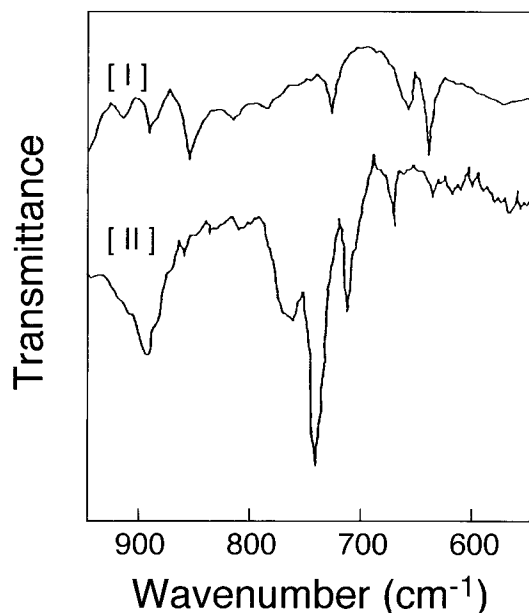


Figure 9 Infrared spectra of *n*-hexyl acetate (I) and the mixture of *n*-hexyl acetate and ZnCl_2 (mol ratio of 1:1, II) heated at 160°C .

due to the ease with which the ester groups of the dimerized part in DPEE-full seemed to be decomposed by ZnCl_2 .¹⁷

CONCLUSION

The effect of dimerized pentaerythritol esters, DPEE-half, and DPEE-full, as novel costabilizer for PVC was investigated, and the following results were obtained:

1. Both DPEE-half and DPEE-full showed good dispersibility in PVC.
2. The effect of delaying the zinc-burning was obtained in the PVC stabilized with $\text{Zn}/\text{Ca}(2/1)$ -st when combined not only with

DPEE-half but also with DPEE-full, although it has no hydroxyl group.

3. The costabilizing effect of DPEE-full was explained by the decomposition of the ester group with ZnCl_2 in DPEE-full and the excess ZnCl_2 was captured simultaneously as colorless zinc carboxylate, as identified from the XPS and IR observations.

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