

Stabilization of Poly(vinyl Chloride). V. Synergism between Metal Soaps and Polyols upon Stabilization of Poly(vinyl Chloride)

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Synopsis

The marked discolorations observed on aged poly(vinyl chloride)(PVC) containing synergetic metal soaps, in the early heating stage, were due to the excessive coloration of π complex of metal chloride and double bonds in the polyene chain. These excessive colorations were inhibited by masking the excessive metal chloride with some masking agents, thereby slowing down the abrupt discoloration of PVC. In this paper, the masking effect of various alcohols such as 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, hexylene glycol, glycerol, 1,2,4-butanetriol, trimethylethane, trimethylpropane, *meso*-erythritol, pentaerythritol, sorbitol, and dipentaerythritol is investigated. The polyhydric alcohols, except dihydric alcohols, showed superior masking effect and markedly improved the thermal stabilization effects of synergetic metal soaps. The mechanism for the synergetic effects between polyols and metal soaps should be based on the masking effect of polyols, owing to the formation of the colorless complex of polyols with excess metal chlorides obtained from the metal soap.

INTRODUCTION

The color of heated poly(vinyl chloride) (PVC) varied with the specific metal salt added. This coloration difference depended on the formation of π complex of double bonds in the polyene chain with metal chloride produced from the corresponding metal salt.¹ Since the synergetic metal soaps are a mixture of cool color-producing soap such as zinc stearate and cadmium stearate and warm color-producing soap such as calcium stearate or barium stearate, the stabilization mechanism for synergetic metal soaps should be based on the effects of complementary colors.²

However, the stabilization effects of synergetic metal soaps were impaired by the excessive production of the cool color-producing metal chloride.² For example, the abrupt discolorations observed on aging PVC compounded with synergetic soaps, such as zinc burning appearing on the PVC containing zinc stearate, were due to the excessive formation of π complex of double bonds with cool color-producing metal chloride converted from the corresponding metal stearate.² Therefore, it is convenient to mask the excessive free metal chloride, which is a cause of harmful coloration of the π complex, with some masking agents in order to prolong the thermal stabilization effects of synergetic metal soaps.

Since the nitrogen-containing agents have exhibited a remarkable masking effect when used with synergetic soaps,^{3,4} it has also been suggested that the polyols might exhibit a similar effect.³ Briggs⁵ and Albarino⁶ have reported stabilization effects of oxygen-containing compounds in the dehydrochlorination

of PVC. In the present work, the masking effect of polyols as one of the oxygen-containing agents is investigated in accordance with the previous deductions.¹⁻⁴

Various polyhydric alcohols, except dihydric alcohols, delay the appearance of excessive or injurious coloration of π complex. Moreover, tri- or more hydric alcohols decolorized a blue that was a mixture of vitamin A and anhydrous zinc chloride. The polyols should stabilize PVC by their masking effect, which is a phenomenon of forming a colorless complex. This deduction is well supported by infrared analysis of compounded PVC containing polyols and metal soaps.

EXPERIMENTAL

Materials

PVC used in this work was Geon 103 EP; also used were commercially available di(2-ethylhexyl)phthalate (DOP), zinc stearate, cadmium stearate, calcium stearate, barium stearate, and polyhydric alcohols.

Preparation of Film Specimens

The mixtures of PVC, DOP, metal stearates, and polyol were milled on an open roll (4 × 8 in.) at 150°C for 5 min. Each PVC film contained 20 phr DOP. The synergetic metal soaps were mixtures of 2 parts zinc stearate and 1 part calcium stearate [Zn/Ca(2/1)-st] or 2 parts cadmium stearate and 1 part barium stearate [Cd/Ba(2/1)-st].

The compounded PVC specimens (about 0.5 mm thick, 50 mm wide, and 60 mm long) were heated at $160 \pm 2^\circ\text{C}$ up to 120 min in the PVC-Zn/Ca(2/1)-st system and up to 6 hr in the PVC-Cd/Ba(2/1)-st system in a circulating air oven.

Colorimetry

PVC films were investigated by colorimetry at room temperature, using a Suga Shikenki model AU-CH-1D differential colorimeter with a specimen holder window 30 mm in diameter. Tristimulus values of each film were obtained by averaging the values recorded from three places on the film surface, using a white-color standard plate ($Y = 84.5$, $X = 82.4$, and $Z = 93.7$) as a reflector.

Infrared Analysis

The compounded PVC specimens before and after heating at $160 \pm 2^\circ\text{C}$ were finely powdered using a fine file and then wafered with dried KBr (1 wt % concentration). These operations were carried out in dried atmosphere. IR spectra were recorded in KBr disks by using a Shimadzu Seisakusho model IR-430 spectrophotometer.

RESULTS AND DISCUSSION

The stabilization effects of typical polyols used with Zn/Ca(2/1)-st or Cd/Ba(2/1)-st are shown in Figures 1 and 2. The effect of each polyol is illustrated with the most effective amount. These figures represent a plot of whiteness in Lab color system [$W(Lab)$], based on the following equations, as a function of heating time:

$$W(Lab) = 100 - [(100 - L)^2 + a^2 + b^2]^{1/2}$$

$$L = 10Y^{1/2}$$

$$a = 17.5[(1.02X) - Y]/(Y^{1/2})$$

$$b = 7.0[Y - (0.847Z)]/(Y^{1/2})$$

where X , Y , and Z are tristimulus values.

Under the present conditions, $W(Lab)$ of PVC films should be always less than 91 because $W(Lab)$ of the white-color standard plate used as a reflector equals 91.0. The $W(Lab)$ is the most convenient value to evaluate the color stabilization of PVC.

In PVC alone and PVC with only polyol $W(Lab)$ decreases with increased heating times owing to the coloration of polyene (yellow-orange). Moreover, the decrease in $W(Lab)$ of PVC with polyol alone is noticeably more than that of unstabilized control. Hence, the polyols do not stabilize PVC without the metal soaps.

PVC compounded with Zn/Ca(2/1)-st or Cd/Ba(2/1)-st alone exhibits abrupt discoloration at 45 min or 4 hr, respectively; this is due to excessive coloration of polyene-zinc chloride complex ($\lambda_d = 475 \text{ nm}$)² and polyene-cadmium chloride complex ($\lambda_d = 485 \text{ nm}$)².

These excessive colorations of polyene-metal chloride complexes decreased $W(Lab)$ markedly and kept an almost invariable $W(Lab)$ after attaining the minimum. Tristimulus values were decreased to a minute size by the appearance of excessive coloration of the π complex such as zinc burning. Therefore, $W(Lab)$ and dominant wavelength λ_d are uncertain in accuracy after the appearance of excessive coloration of the π complexes.

On the other hand, the polyhydric alcohols, except dihydric, inhibit the excessive coloration of the π complexes and slow down the discoloration of PVC with the synergetic soaps. Moreover, the tri- or more hydric alcohols with synergetic soaps prolong the good initial color, in comparison with the nitrogen-containing agents.

Effects of Dihydric Alcohols

The masking effect of 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, and hexylene glycol is summarized in Tables I and II based on Figures 1 and 2. These alcohols neither stabilize PVC without soaps nor exhibit the masking effect even in the systems with synergetic metal soaps.

TABLE I
 Stabilization Effect of Dihydric Alcohols^a

| Additive ^b | phr | W_0 | t_E , min | W_M | t_L , min | W_L | $W_0 - W_M$ | $W_0 - W_L$ | $\lambda d(i)$, nm | $\lambda d(f)$, nm |
|------------------------------|-----|-------|----------------|-------|----------------|-------|-------------|-------------|------------------------|------------------------|
| PVC | — | 88 | — | — | 120 | 52 | — | 36 | 575 | 582 |
| 1,2-Butanediol | 1.0 | 83 | — | — | 120 | 36 | — | 47 | 577 | 589 |
| 1,3-Butanediol | 1.0 | 83 | — | — | 120 | 43 | — | 40 | 574 | 583 |
| 1,4-Butanediol | 1.0 | 83 | — | — | 120 | 44 | — | 39 | 575 | 585 |
| 2,3-Butanediol | 1.0 | 85 | — | — | 120 | 40 | — | 45 | 575 | 587 |
| Hexylene glycol | 1.0 | 85 | — | — | 120 | 48 | — | 37 | 575 | 583 |
| Zn/Ca(2/1)-st | 3.0 | 85 | 45 | 78 | 120 | 8 | 7 | 77 | 574 | 480 |
| 1,2-Butanediol ^c | 0.4 | 86 | 45 | 79 | 120 | 8 | 7 | 78 | 575 | 496 |
| | 1.0 | 87 | 45 | 81 | 120 | 8 | 6 | 79 | 573 | 493 |
| | 2.0 | 88 | 45 | 83 | 120 | 9 | 5 | 79 | 574 | 494 |
| | 3.0 | 87 | 60 | 79 | 120 | 8 | 8 | 79 | 574 | 493 |
| 1,3-Butanediol ^c | 0.4 | 85 | 45 | 75 | 120 | 5 | 10 | 80 | 574 | 490 |
| | 1.0 | 84 | 45 | 76 | 120 | 6 | 8 | 78 | 574 | 492 |
| | 2.0 | 85 | 45 | 77 | 120 | 6 | 8 | 79 | 574 | 490 |
| | 3.0 | 86 | 45 | 79 | 120 | 6 | 7 | 80 | 574 | 491 |
| 1,4-Butanediol ^c | 0.4 | 87 | 45 | 79 | 120 | 8 | 8 | 79 | 574 | 497 |
| | 1.0 | 88 | 45 | 81 | 120 | 8 | 7 | 80 | 574 | 488 |
| | 2.0 | 88 | 45 | 83 | 120 | 8 | 5 | 80 | 574 | 496 |
| | 3.0 | 87 | 45 | 83 | 120 | 9 | 4 | 78 | 574 | 494 |
| 2,3-Butanediol ^c | 0.4 | 86 | 45 | 72 | 120 | 9 | 14 | 77 | 575 | 487 |
| | 1.0 | 86 | 45 | 78 | 120 | 9 | 8 | 77 | 573 | 489 |
| | 2.0 | 86 | 45 | 80 | 120 | 8 | 6 | 78 | 573 | 473 |
| | 3.0 | 87 | 45 | 72 | 120 | 10 | 15 | 77 | 574 | 487 |
| Hexylene glycol ^c | 0.4 | 88 | 45 | 83 | 120 | 10 | 5 | 78 | 574 | 498 |
| | 1.0 | 88 | 45 | 84 | 120 | 8 | 4 | 80 | 574 | 494 |
| | 2.0 | 87 | 60 | 83 | 120 | 8 | 4 | 79 | 574 | 498 |
| | 3.0 | 88 | 60 | 81 | 120 | 9 | 7 | 79 | 574 | 488 |

^a Heated at 160°C.

^b Each film contained 20 phr DOP.

^c Zn/Ca(2/1)-st, 3.0 phr, was combined with polyol. W_0 represents $W(Lab)$ of unheated film; t_E is the heating time for onset of zinc burning; W_M represents $W(Lab)$ at the heating time just before onset of zinc burning; t_L is the heating time attaining the lowest $W(Lab)$; W_L represents the lowest $W(Lab)$; $\lambda d(i)$ represents the dominant wavelength of unheated film; and $\lambda d(f)$ represents the dominant wavelength of aged film which is heated for 120 min.

TABLE II
 Stabilization Effect of Dihydric Alcohols^a

| Additive ^b | phr | W_0 | t_E , hr | W_M | t_L , hr | W_L | $W_0 - W_M$ | $W_0 - W_L$ | $\lambda_d(t)$, nm | $\lambda_d(f)$, nm |
|------------------------------|-----|-------|---------------|-------|---------------|-------|-------------|-------------|------------------------|------------------------|
| PVC | — | 86 | — | — | 6 | 17 | — | 69 | 574 | 611 |
| 1,3-Butanediol | 1.0 | 82 | — | — | 6 | 10 | — | 72 | 574 | 630 |
| 2,3-Butanediol | 1.0 | 85 | — | — | 6 | 11 | — | 74 | 574 | 637 |
| Cd/Ba(2/1)-st | 3.0 | 85 | 4 | 72 | 6 | 12 | 13 | 73 | 575 | 492 |
| 1,2-Butanediol ^c | 0.4 | 86 | 4 | 73 | 6 | 14 | 13 | 72 | 576 | 497 |
| | 1.0 | 85 | 4 | 74 | 6 | 15 | 11 | 70 | 575 | —545 |
| | 2.0 | 86 | 4 | 74 | 6 | 16 | 12 | 70 | 575 | —558 |
| | 3.0 | 86 | 4 | 74 | 6 | 16 | 12 | 70 | 574 | —540 |
| 1,3-Butanediol ^c | 0.4 | 81 | 4 | 74 | 6 | 18 | 7 | 63 | 574 | 495 |
| | 1.0 | 82 | 4 | 74 | 6 | 11 | 8 | 71 | 574 | 492 |
| | 2.0 | 84 | 4 | 73 | 6 | 12 | 11 | 72 | 574 | 495 |
| | 3.0 | 81 | 4 | 73 | 6 | 14 | 8 | 67 | 574 | 493 |
| 1,4-Butanediol ^c | 0.4 | 87 | 4 | 72 | 6 | 11 | 15 | 76 | 575 | 493 |
| | 1.0 | 86 | 4 | 72 | 6 | 12 | 14 | 74 | 575 | 501 |
| | 2.0 | 86 | 4 | 76 | 6 | 12 | 10 | 74 | 575 | 498 |
| | 3.0 | 85 | 4 | 73 | 6 | 16 | 12 | 69 | 575 | 493 |
| 2,3-Butanediol ^c | 0.4 | 86 | 4 | 68 | 6 | 18 | 18 | 68 | 575 | 498 |
| | 1.0 | 86 | 4 | 69 | 6 | 9 | 17 | 77 | 574 | 500 |
| | 2.0 | 86 | 4 | 67 | 6 | 8 | 19 | 78 | 574 | 507 |
| | 3.0 | 86 | 4 | 68 | 6 | 10 | 18 | 76 | 574 | 496 |
| Hexylene glycol ^c | 0.4 | 86 | 4 | 74 | 6 | 13 | 12 | 73 | 575 | 494 |
| | 1.0 | 86 | 4 | 74 | 6 | 13 | 12 | 73 | 575 | 488 |
| | 2.0 | 86 | 4 | 73 | 6 | 13 | 13 | 73 | 575 | 493 |
| | 3.0 | 85 | 4 | 73 | 6 | 14 | 12 | 71 | 576 | 489 |

^a Heated at 160°C. t_E is the heating time for onset of excessive coloration of polyene-cadmium chloride complex; W_M represents $W(Lab)$ at the heating time just before onset of excessive coloration of polyene-cadmium chloride complex; and $\lambda_d(f)$ represents the dominant wavelength of aged film which is heated for 6 hr.

^b Each film contained 20 phr DOP.

^c Cd/Ba(2/1)-st, 3.0 phr, was combined with polyol.

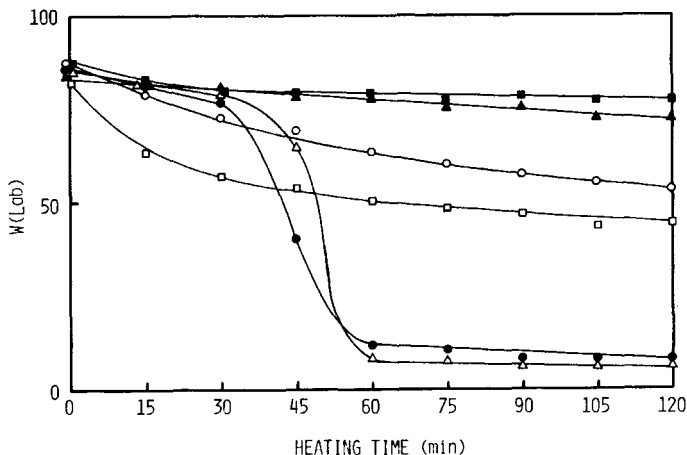


Fig. 1. Stabilization effect of polyols. PVC 100 and DOP 20 (○), PVC 100, DOP 20, and Zn/Ca(2/1)-st 3.0 (●), PVC 100, DOP 20, and *meso*-erythritol 1.0 (□), PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,3-butanediol 3.0 (△), PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and 1,2,4-butanetriol 1.0 (▲), and PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and *meso*-erythritol 1.0 (■) were milled at 150°C for 5 min and heated at 160°C.

Effects of Trihydric Alcohols

The masking effect of glycerol, 1,2,4-butanetriol, trimethylolethane, and trimethylolpropane is summarized in Tables III and IV. In the case of trihydric alcohols without synergetic metal soaps, PVC specimens become brownish and grow deeper in color with increased aging times. The λ_d of each system without soap is turned from $\lambda_d(i) = 575$ nm to $\lambda_d(f) = 583$ –593 nm. This means that the trihydric alcohols do not stabilize PVC without soaps.

Further additions of glycerol, trimethylolethane, and trimethylolpropane result in greater slowing of the discoloration of PVC admixed with Zn/Ca(2/1)-st. For example, 1.0 phr trimethylolpropane with Zn/Ca(2/1)-st delays the appearance

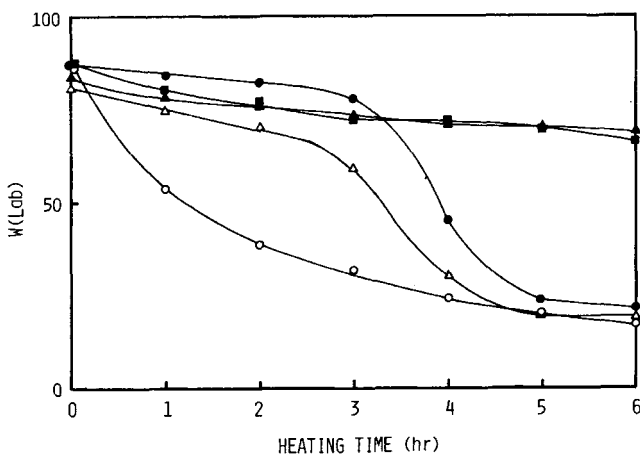


Fig. 2. Stabilization effect of polyols. PVC 100 and DOP 20 (○), PVC 100, DOP 20, and Cd/Ba(2/1)-st 3.0 (●), PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and 1,3-butanediol 0.4 (△), PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and 1,2,4-butanetriol 0.4 (▲), and PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and *meso*-erythritol 0.4 (■) were milled at 150°C for 5 min and heated at 160°C.

TABLE III
Stabilization Effect of Trihydric Alcohols^a

| Additive ^b | phr | W_0 | t_E , min | W_M | t_L , min | W_L | $W_0 - W_M$ | $W_0 - W_L$ | $\lambda_d(i)$, nm | $\lambda_d(f)$, nm |
|---------------------------------|-----|-------|----------------|-------|----------------|-------|-------------|-------------|------------------------|------------------------|
| Glycerol | 1.0 | 86 | — | — | 120 | 48 | — | 38 | 575 | 583 |
| 1,2,4-Butanetriol | 1.0 | 81 | — | — | 120 | 30 | — | 51 | 575 | 593 |
| Trimethylolpropane | 1.0 | 83 | — | — | 120 | 43 | — | 40 | 575 | 583 |
| Trimethylolpropane | 1.0 | 74 | — | — | 120 | 41 | — | 33 | 575 | 585 |
| Glycerol ^c | 0.4 | 87 | 75 | 77 | 120 | 9 | 10 | 78 | 574 | 491 |
| | 1.0 | 88 | 75 | 79 | 120 | 9 | 9 | 79 | 574 | 493 |
| | 2.0 | 89 | 90 | 78 | 120 | 8 | 11 | 81 | 573 | 492 |
| | 3.0 | 88 | 90 | 77 | 120 | 10 | 11 | 78 | 573 | 492 |
| 1,2,4-Butanetriol ^c | 0.4 | 86 | 105 | 78 | 120 | 10 | 8 | 76 | 574 | 493 |
| | 1.0 | 85 | — | — | 120 | 72 | — | 13 | 574 | 576 |
| | 2.0 | 78 | — | — | 120 | 66 | — | 12 | 575 | 578 |
| | 3.0 | 76 | — | — | 120 | 64 | — | 12 | 576 | 578 |
| Trimethylolpropane ^c | 0.4 | 88 | 90 | 71 | 120 | 12 | 17 | 76 | 572 | 492 |
| | 1.0 | 88 | 90 | 73 | 120 | 10 | 15 | 78 | 575 | 487 |
| | 2.0 | 88 | 105 | 78 | 120 | 11 | 10 | 77 | 574 | 498 |
| | 3.0 | 88 | 120 | 77 | 120 | 56 | 11 | 32 | 574 | 577 |
| Trimethylolpropane ^c | 0.4 | 88 | 75 | 82 | 120 | 7 | 6 | 81 | 574 | 496 |
| | 1.0 | 87 | 105 | 72 | 120 | 10 | 15 | 77 | 574 | -500 |
| | 2.0 | 88 | — | — | 120 | 65 | — | 23 | 574 | 576 |
| | 3.0 | 88 | — | — | 120 | 63 | — | 25 | 574 | 576 |

^a Heated 15 160°C. Definitions of abbreviations are same as in Table I.

^b Each film contained 20 phr DOP.

^c Zn/Ca(2/1)-st, 3.0 phr, were combined with polyol.

TABLE IV
Stabilization Effect of Trihydric Alcohols^a

| Additive ^b | phr | W_0 | t_E , hr | W_M | t_L , hr | W_L | $W_0 - W_M$ | $W_0 - W_L$ | $\lambda_d(i)$, nm | $\lambda_d(f)$, nm |
|-----------------------|-----|-------|---------------|-------|---------------|-------|-------------|-------------|------------------------|------------------------|
| Glycerol | 0.4 | 86 | — | — | 6 | 64 | — | 22 | 575 | 577 |
| | 1.0 | 85 | — | — | 6 | 61 | — | 24 | 575 | 578 |
| | 2.0 | 85 | — | — | 6 | 61 | — | 24 | 575 | 578 |
| 1,2,4-Butanetriol | 3.0 | 86 | — | — | 6 | 58 | — | 28 | 575 | 578 |
| | 0.4 | 84 | — | — | 6 | 69 | — | 15 | 575 | 577 |
| | 1.0 | 79 | — | — | 6 | 64 | — | 15 | 576 | 578 |
| Trimethylolpropane | 2.0 | 74 | — | — | 6 | 59 | — | 15 | 577 | 579 |
| | 3.0 | 70 | — | — | 6 | 56 | — | 14 | 578 | 580 |
| | 0.4 | 86 | 5 | 65 | 6 | 18 | 21 | 68 | 575 | -600 |
| Trimethylolpropane | 1.0 | 86 | 6 | 75 | 6 | 45 | 11 | 41 | 575 | 581 |
| | 2.0 | 87 | — | — | 6 | 70 | — | 17 | 575 | 576 |
| | 3.0 | 86 | — | — | 6 | 72 | — | 14 | 575 | 576 |
| Trimethylolpropane | 0.4 | 86 | 5 | 76 | 6 | 16 | 10 | 70 | 575 | 495 |
| | 1.0 | 87 | 6 | 75 | 6 | 46 | 12 | 41 | 575 | 581 |
| | 2.0 | 87 | — | — | 6 | 70 | — | 7 | 575 | 575 |
| | 3.0 | 87 | — | — | 6 | 74 | — | 13 | 575 | 575 |

^a Heated at 160°C. Definitions of abbreviations are same as in Table II.

^b Each film contained 20 phr DOP and 3.0 phr Cd/Ba(2/1)-st.

of zinc burning for 60 min in comparison with the stabilized control. Moreover, 3.0 phr trimethylolpropane completely inhibits the appearance of zinc burning up to 120 min and λ_d remains constant during all heating times.

In the trihydric alcohol-Zn/Ca(2/1)-st systems, the good initial color is markedly prolonged. For example, the rate of decreasing $W(Lab)$ from 0 min up to 120 min ($W_0 - W_L$) as for the PVC-Zn/Ca(2/1)-st system containing 3.0 phr trimethylolpropane is only 25, compared to 36 for PVC alone, 33 for PVC with only 1.0 phr trimethylolpropane, and 77 for the stabilized control (Tables I and III). Moreover, decrease in $W(Lab)$ from 0 min to the heating time just prior to zinc burning ($W_0 - W_M$) is only 15 as for the system of PVC-Zn/Ca(2/1)-st containing 1.0 phr trimethylolpropane.

On the other hand; further additions of 1,2,4-butanetriol shorten the good initial color with which W_0 and W_L are decreased and $\lambda_d(f)$ is shifted to the higher wavelength. The most effective amount in this system is 1.0 phr, and $W_0 - W_L$ is only 13.

With regard to the PVC-Cd/Ba(2/1)-st system, further additions of trimethylolethane and trimethylolpropane improve the stabilization effects of synergetic soap. On the other hand, increased additions of glycerol and 1,2,4-butanetriol increase the discoloration of PVC. The most effective amount of these alcohols is 0.4 phr (Table IV). The different effect observed between trimethylolethane and trimethylolpropane is caused by compatibility difference.

Effect of Tetra- or More Hydric Alcohols

The masking effect of *meso*-erythritol, pentaerythritol, sorbitol, and dipentaerythritol is summarized in Tables V and VI.

As for the PVC-Zn/Ca(2/1)-st system, *meso*-erythritol, pentaerythritol, and sorbitol exhibit synergism. These polyols decrease the good initial color with increased additions, and the most effective amount in each case is 1.0, 0.4, and 0.2 phr, respectively.

With regard to the PVC-Cd/Ba(2/1)-st system, all of them except dipentaerythritol exhibit a marked effect; and the stabilization effect of these polyols is almost invariable with the amounts added. The poor effect of dipentaerythritol observed on both systems is due to its poor compatibility with PVC, since undispersed powders are observed in the compounded PVC films even with the naked eye.

From these results it is necessary, in order to keep PVC colorless, that suitable amounts of polyols should be compounded to retain the effective cool color of the metal chlorides.

Stabilization Mechanisms for Polyols

The remarkable stabilization effects of tri- or more hydric alcohols could not be observed on the PVC films without synergetic soaps, while the stabilization of PVC was markedly improved by the combined use of these polyols and the synergetic metal soaps. Moreover, the blue, which was observed in a mixture of vitamin A and anhydrous zinc chloride, disappeared upon the addition of these polyols.

TABLE V
 Stabilization Effect of Tetra- or More Hydric Alcohols^a

| Additive ^b | phr | W ₀ | t _E , min | W _M | t _L , min | W _L | W ₀ - W _L | W ₀ - W _M | λ _d (i), nm | λ _d (f), nm |
|--------------------------------------|-----|----------------|-------------------------|----------------|-------------------------|----------------|---------------------------------|---------------------------------|---------------------------|---------------------------|
| <i>meso</i> -Erythritol | 1.0 | 83 | — | — | 120 | 43 | — | 40 | 574 | 585 |
| Pentaerythritol | 1.0 | 86 | — | — | 120 | 39 | — | 47 | 573 | 588 |
| Sorbitol | 1.0 | 82 | — | — | 120 | 32 | — | 50 | 575 | 589 |
| Dipentaerythritol | 1.0 | 86 | — | — | 120 | 45 | — | 41 | 575 | 585 |
| <i>meso</i> -Erythritol ^c | 0.4 | 87 | 120 | 75 | 120 | 66 | 12 | 21 | 574 | 576 |
| | 1.0 | 87 | — | — | 120 | 77 | — | 10 | 574 | 574 |
| | 2.0 | 87 | — | — | 120 | 75 | — | 12 | 574 | 575 |
| | 3.0 | 88 | — | — | 120 | 71 | — | 17 | 574 | 575 |
| Pentaerythritol ^c | 0.2 | 87 | 75 | 78 | 120 | 16 | 9 | 71 | 573 | 471 |
| | 0.4 | 87 | — | — | 120 | 75 | — | 12 | 574 | 574 |
| | 0.6 | 86 | — | — | 120 | 76 | — | 10 | 572 | 573 |
| | 0.8 | 87 | — | — | 120 | 75 | — | 12 | 573 | 574 |
| | 1.0 | 87 | — | — | 120 | 74 | — | 13 | 573 | 573 |
| | 2.0 | 87 | — | — | 120 | 72 | — | 15 | 573 | 573 |
| | 3.0 | 87 | — | — | 120 | 71 | — | 16 | 573 | 573 |
| Sorbitol ^c | 0.1 | 85 | 75 | 79 | 120 | 8 | 6 | 77 | 574 | 497 |
| | 0.2 | 86 | — | — | 120 | 72 | — | 14 | 574 | 575 |
| | 0.4 | 82 | — | — | 120 | 56 | — | 26 | 575 | 579 |
| | 1.0 | 84 | — | — | 120 | 52 | — | 32 | 575 | 579 |
| | 2.0 | 82 | — | — | 120 | 50 | — | 32 | 575 | 580 |
| | 3.0 | 83 | — | — | 120 | 51 | — | 32 | 574 | 580 |
| Dipentaerythritol ^c | 0.4 | 86 | 60 | 79 | 120 | 11 | 7 | 75 | 574 | 487 |
| | 1.0 | 87 | 75 | 78 | 120 | 49 | 9 | 38 | 574 | 513 |
| | 2.0 | 87 | — | — | 120 | 72 | — | 15 | 574 | 575 |
| | 3.0 | 85 | — | — | 120 | 70 | — | 15 | 574 | 576 |

^a Heated at 160°C. Definitions of abbreviations are same as in Table I.

^b Each film contained 20 phr DOP.

^c Zn/Ca(2/1)-st, 3.0 phr, was combined with polyol.

TABLE VI
Stabilization Effect of Tetra- or More Hydric Alcohols^a

| Additive ^b | phr | W_0 | t_E , hr | W_M | t_L , hr | W_L | $W_0 - W_M$ | $W_0 - W_L$ | $\lambda_d(i)$, nm | $\lambda_d(f)$, nm |
|-------------------------|-----|-------|---------------|-------|---------------|-------|-------------|-------------|------------------------|------------------------|
| <i>meso</i> -Erythritol | 0.4 | 87 | — | — | 6 | 67 | — | 20 | 575 | 577 |
| | 1.0 | 86 | — | — | 6 | 66 | — | 20 | 575 | 578 |
| | 2.0 | 87 | — | — | 6 | 67 | — | 20 | 575 | 577 |
| Pentaerythritol | 3.0 | 88 | — | — | 6 | 66 | — | 22 | 575 | 577 |
| | 0.2 | 88 | — | — | 6 | 65 | — | 23 | 571 | 576 |
| | 0.4 | 88 | — | — | 6 | 74 | — | 14 | 573 | 574 |
| | 0.6 | 87 | — | — | 6 | 72 | — | 15 | 573 | 574 |
| | 0.8 | 88 | — | — | 6 | 72 | — | 16 | 572 | 574 |
| | 1.0 | 88 | — | — | 6 | 71 | — | 17 | 574 | 574 |
| Sorbitol | 2.0 | 89 | — | — | 6 | 71 | — | 18 | 573 | 574 |
| | 3.0 | 89 | — | — | 6 | 70 | — | 19 | 573 | 574 |
| | 0.4 | 84 | — | — | 6 | 54 | — | 30 | 572 | 577 |
| | 1.0 | 85 | — | — | 6 | 57 | — | 28 | 575 | 577 |
| | 2.0 | 84 | — | — | 6 | 61 | — | 23 | 575 | 575 |
| | 3.0 | 85 | — | — | 6 | 60 | — | 25 | 575 | 577 |
| Dipentaerythritol | 0.2 | 88 | 4 | 72 | 6 | 18 | 16 | 70 | 573 | 484 |
| | 0.4 | 88 | 5 | 67 | 6 | 18 | 21 | 70 | 573 | 488 |
| | 0.6 | 88 | 5 | 68 | 6 | 19 | 20 | 69 | 573 | 482 |
| | 0.8 | 88 | 6 | 60 | 6 | 23 | 28 | 65 | 573 | 598 |
| | 1.0 | 88 | 6 | 63 | 6 | 39 | 25 | 49 | 573 | 584 |
| | 2.0 | 88 | 6 | 66 | 6 | 54 | 22 | 34 | 574 | 579 |
| 3.0 | 88 | — | — | 6 | 63 | — | 25 | 574 | 577 | |

^a Heated at 160°C. Definitions of abbreviations are same as in Table II.

^b Each film contained 20 phr DOP and 3.0 phr Cd/Ba(2/1)-st.

The stabilization mechanism indicates that these polyols form a colorless complex with excessive free zinc chloride or cadmium chloride converted from the corresponding soaps. This deduction is well supported by the fact that the $\lambda_d(f)$ of the most effective systems are not shifted to the lower wavelength corresponding to the color of polyene-zinc chloride and polyene-cadmium chloride complexes (Tables III-VI).

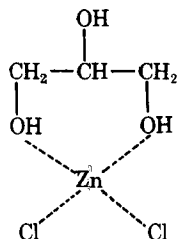
It is difficult to isolate or characterize the chelating compounds of polyols with metal chloride in the heated compounded PVC. The extraction of the complex from compounded PVC is unsuitable because the labile complex of polyols with metal chloride in the PVC specimen should be broken down easily in polar solvents which are good solvents for PVC. Even if the complex, which has been formed in the aged PVC compound, is extracted, it is difficult to keep the extracted complex stable and to disturb simultaneously the formation of complex that is able to form between extracted uncoordinating polyols and free metal chlorides in the extract. Accordingly, it is necessary to determine the polyol-metal chloride complex in the compound PVC specimens.

We have tried to determine the presence of these polyol complexes in the compound PVC using an x-ray diffractometer and an x-ray microanalyzer. Satisfactory results were not obtained, since the signals of the complex are hindered by the resin background even in the presence of maximum amounts of polyol and metal stearate. Therefore, we tried to investigate the IR spectra of PVC containing large amounts of polyols and zinc stearate.

Absorbance at 1540 cm^{-1} (νCOO^-) which appeared on PVC containing metal soap decreased with increased heat treatments in PVC-zinc stearate-1,3-butanediol and PVC-zinc stearate-glycerol systems. Hence, the zinc stearate in the compounded PVC is converted to zinc chloride by the liberated hydrogen chloride in the system. In particular, the decrease of absorbance at 1540 cm^{-1} was greatest in the system containing glycerol rather than the system containing 1,3-butanediol.

The absorbance ratios between 3440 cm^{-1} (νOH) and 2920 cm^{-1} (νCH_2) are illustrated in Figure 3. The absorbance at 3440 cm^{-1} for the system of PVC-zinc stearate-glycerol decreased with increased heat treatments, while the absorbance at 3440 cm^{-1} concerning PVC-zinc stearate-1,3-butanediol system is almost invariable. On the other hand, the absorbance at 1260 cm^{-1} (νCO) is also invariable in all the systems.

Although these results are qualitative, the decrease of absorbance at 3440 cm^{-1} is due to the formation of the complex, which is a six-membered ring of glycerol with zinc chloride as the following shows:



The complex of zinc chloride and 1,3-butanediol, which exhibits no effect, is not formed in the compound PVC.

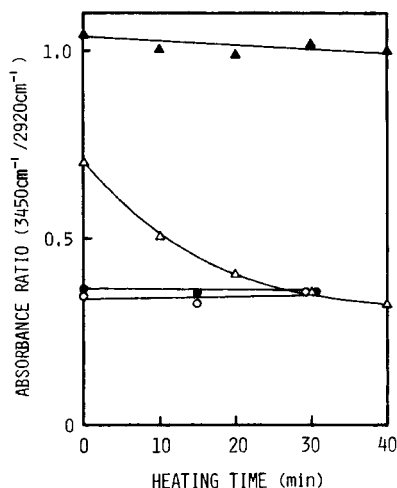


Fig. 3. Variation of absorbance ratio. PVC 100, DOP 20, and 1,3-butanediol 5.0 (●), PVC 100, DOP 20, 1,3-butanediol 5.0, and zinc stearate 5.0 (○), PVC 100, DOP 20, and glycerol 5.0 (▲), and PVC 100, DOP 20, glycerol 5.0, and zinc stearate 5.0 (Δ) were milled at 150°C for 5 min and heated at 160°C.

Since two neighboring hydroxy groups in polyols should be as far apart as possible in zigzag transplanar structure, at least two hydroxy groups in tri- or more hydric alcohols may be oriented on the same side. The effects of synergetic metal soaps are not improved even by adding 2,3-butanediol, which is a mixture of DL and meso forms and which contains two hydroxy groups situated on the secondary carbons. No masking effect for dihydric alcohols therefore, should not depend on their steric hindrance. The different masking effect observed among various polyols and the result of IR analysis are fairly consistent with their steric structure differences.

Although the stabilization mechanism based on delaying dehydrochlorination of stabilized PVC had been proposed by Briggs,⁵ the marked synergetic effect of tri- or more hydric alcohols with the synergetic metal soaps is found in their remarkable masking effect.

CONCLUSIONS

The marked stabilization effects of polyols depend mainly on their masking effects, which form the colorless complex with excessive zinc chloride or cadmium chloride in order to inhibit the unnecessary or injurious coloration of the π complex. Therefore in order to keep PVC colorless, it is necessary that suitable amounts of polyols should be combined to retain the efficient zinc chloride or cadmium chloride, which keep PVC colorless by complementary colors effect with the polyene in PVC.

This conclusion is well supported even by the fact that the increased additions of tri- or more hydric alcohols generally accelerate the appearance of polyene color of PVC admixed with synergetic metal soaps. The decrease in good initial color is caused by their excessive masking action to the cool color-producing metal chloride.

The polyols are suitable masking agents because the good initial color of PVC

is retained in comparison with nitrogen-containing agents. But some polyols exhibit poor compatibility with PVC. Modification of polyols, therefore, should be carried out in order to improve their compatibility with PVC.

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