

## Stabilization of Poly(vinyl Chloride). I. Change in Color of Poly(vinyl Chloride) Compounded with Some Metal Soaps

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### Synopsis

Poly(vinyl chloride) (PVC) with one or more metal salts added was colored by the action of heat to investigate the stabilization mechanism. The coloration and the color difference of heated PVC compound films varied according to the metal salt added. The decoloration of the colored compound films was advanced markedly in THF, DMF, acetone, and ammonia. On the other hand, the heated achromatic PVC film containing Cd/Ba soaps underwent an opposite change, from colorless to yellow orange, in the above materials. This means that the coloration of heated compound films may result from the formation of some complex (for example,  $\pi$  complex of the polyene with the metal chloride). Furthermore, the colored film with cadmium stearate was decolorated by roll mixing with the colored film containing barium stearate. These results indicate that the stabilization with metal soaps may be founded on a physical phenomenon such as an effect of complementary color.

### INTRODUCTION

In general, the discoloration of poly(vinyl chloride) (PVC) advances during heat and light processes and is due to the formation of longer polyene chains through the zipper-like dehydrochlorination.<sup>1</sup>

Usually, PVC is mixed with one or more stabilizers in order to slow down the discoloration. Metal soaps are the most important stabilizers. In this work, *coloration* is used instead of *discoloration* which is usually employed when discussing the stabilization of PVC. Discoloration indicates the phenomenon whereby a colored material turns into a different color; coloration means the rearrangement from a colorless to a colored matter; and decoloration indicates the disappearance of color as determined by colorimetry.

As stabilization mechanisms of the metal soaps, removal of the hydrogenchloride<sup>2,3</sup> and substitution of RCOO with Cl<sup>4</sup> have been proposed. The present authors have reported a previous paper<sup>5</sup> in which PVC has been pyrolyzed with various metal salts and in which chlorine atoms released from PVC have been recombined with the polyene chains.

In the present work, PVC mixed with one or more metal soaps or oxides is colored by the action of heat in order to investigate the stabilization mech-

anism. It was observed that the treated films underwent a color change which was dependent on the specific metals employed. The fish eyes in the case of the control did not appear on the film surface.

The above color differences are difficult to explain by the usual stabilization mechanism. Therefore, the colored PVC was studied by colorimetry while many of the color changes occurred.

## EXPERIMENTAL

**Materials.** PVC used in this work was Geon 103EP; and the commercially available metal oxides, DOP (2-ethylhexyl), and metal stearates were used.

**Preparation of PVC Film.** PVC and metal soap or oxide were milled on an open roll (4 in.  $\times$  8 in.) at 150°C for 5 min, respectively. Then compound PVC films were heated at 160  $\pm$  5°C in the presence of flowing HCl gas. In this way, the coloration of the film was restricted to the surface and did not occur internally. The color of the film also appeared when exposed to air.

**Colorimetry.** PVC films were investigated by colorimetry at room temperature by using a differential colorimeter. The differential colorimeter used in this work was the Toyo Rika Kogyo, Model AU-SCH-2.

## RESULTS AND DISCUSSION

PVC film milled with 3 phr cadmium stearate (Cd-st), barium stearate (Ba-st), zinc stearate (Zn-st), or calcium stearate (Ca-st) was heated at 160°C in HCl flow until coloration was observed: Zn-st for 1 min, Cd-st and Ba-st for 10 min, and Ca-st for 15 min.

A warm color was observed with PVC and the PVC-Ba-st and PVC-Ca-st systems and a cool color was observed with the PVC-Cd-st and PVC-Zn-st systems.

Table I is a summary of the change in color of these colored films, after being dipped in ethyl ether, acetone, ethanol, 10 wt-% NH<sub>3</sub> aq. solution, 10 wt-% NaOH aq. solution, 10 wt-% NaOH alc. solution, 10 wt-% HCl aq. solution, 10 wt-% HCl alc. solution, 5 wt-% EDTA aq. solution, and 5 wt-% EDTA alc. solution at 30°C for 72 hr., where  $\lambda_d$  (nm),  $Pe$  (%), and  $Y$  (%) correspond to hue, chroma, and value, respectively, according to the CIE color system.

The decoloration of the colored film containing Ba-st or Ca-st was slight, because the color of these films was similar to the color of polyenes ( $\lambda_d = 580$  nm). On the other hand, the change in color of the colored film containing Zn-st or Cd-st was significant in acetone and 10 wt-% NH<sub>3</sub> aq. solution, i.e., the discoloration from black to yellow orange ( $\lambda_d = 580$ –600 nm) was observed on these films, but black did not disappear in HCl solution. These changes in color could be observed on the film mixed with corresponding metal oxide or heated in air.

TABLE I  
Effect of Dipping Substances on Change in Color of Colored PVC Films\*

PVC film	Undipped film	Ethyl ether	Acetone	Ethanol	Film dipped in									
					10 wt-% NH <sub>3</sub> aq. soln.	10 wt-% NaOH aq. soln.	10 wt-% NaOH aq. soln.	10 wt-% HCl aq. soln.	10 wt-% HCl aq. soln.	10 wt-% HCl aq. soln.	10 wt-% EDTA aq. soln.	5 wt-% EDTA aq. soln.	5 wt-% EDTA aq. soln.	
Zn-st (3 phr)	400 $\lambda_d$ , nm 3.9 $P_e$ , % 3.60 $Y$ , %	563 3.0 3.22	588 63.8 14.82	562 4.2 3.36	595 37.0 5.61	483 4.4 3.25	472 4.1 3.20	465 3.7 3.61	490 1.0 3.60	477 4.6 2.95	473 4.6 3.38			
Cd-st (3 phr)	584 $\lambda_d$ , nm 28.8 $P_e$ , % 5.60 $Y$ , %	583 37.8 32.30	578 33.2 53.85	583 28.0 6.25	580 57.8 38.92	583 32.8 9.99	581 34.9 8.50	581 25.0 11.90	580 22.8 9.85	581 31.0 14.25	580 21.2 11.30			
Ca-st (3 phr)	587 $\lambda_d$ , nm 56.2 $P_e$ , % 23.95 $Y$ , %	586 34.8 35.31	581 42.3 44.82	584 57.8 24.95	589 47.0 28.25	587 45.0 27.95	587 29.2 35.10	585 59.2 21.70	586 37.2 28.50	584 52.7 21.34	584 62.0 21.98			
Ba-st (3 phr)	587 $\lambda_d$ , nm 51.8 $P_e$ , % 28.82 $Y$ , %	585 24.8 48.51	585 49.0 35.03	585 48.3 28.80	584 55.9 28.42	588 48.6 21.64	588 44.3 33.49	587 45.4 25.07	584 46.0 30.49	587 35.2 27.03	586 50.6 26.12			

\* The films were heated at 160°C in HCl(gas) flow for 1 min (Zn-st), 10 min (Cd-st and Ba-st), and 15 min (Ca-st) and were dipped in the dipping substances at 30°C for 72 hr.

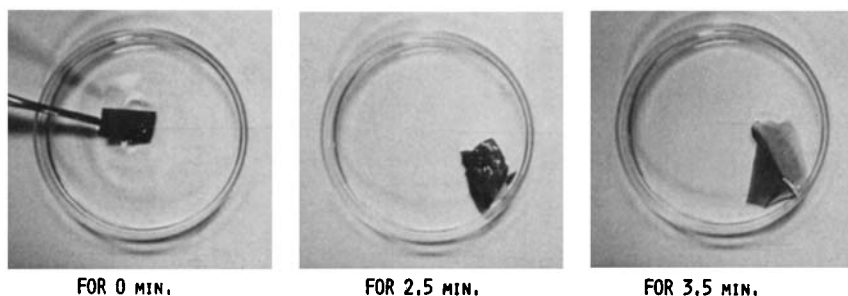


Fig. 1. Change in color of colored PVC film: film containing 3 phr ZnO was dipped in THF at room temperature after the film was colored by heating at 160°C in HCl (gas) flow for 1 min.

The film containing 3 phr Zn-st, Cd-st, or their oxides was heated at 160°C in flowing HCl, and then these films were dipped in THF and DMF at room temperature. These colored films turned from black to yellow orange within 5 min. When the metal oxide was combined, the colored skin of the film was stripped off during the dipping in THF for a few minutes. As an example of this phenomenon, the changes observed with PVC-ZnO are shown in Figure 1. The colored skin is decolorized and stripped off, and then a white layer appears.

From these observations, it is deduced that the  $\pi$  complex of polyene with metal chloride, rearranged from metal soap or oxide, will be a color developer. After the  $\pi$  complex in these colored films was ruptured with THF, DMF, acetone, or ammonia, only the polyene color developed on any of the films.

The mixture of ZnCl<sub>2</sub> and vitamin A, used as a model substance for the polyene, shows a blue which appears on the film of the PVC-Zn-st or PVC-ZnO systems early in the heating period; but the blue disappears immediately upon contact with THF, DMF, acetone, or ammonia. Although the presence of the  $\pi$  complex has not been proven, its presence may be concluded from this experiment. Mixtures of vitamin A and CdCl<sub>2</sub>, BaCl<sub>2</sub>, or CaCl<sub>2</sub> are colorless. A longer polyene chain is required to make the  $\pi$  complex a chromophore. Therefore, a long heating time is necessary for Cd-st, Ba-st, and Ca-st. These observations agree with their heat efficiencies.

The film containing a typical synergistic stabilizer Cd/Ba-st was heated at 160°C in flowing HCl. The coloration of this achromatic film, after being dipped in the above liquid materials at 30°C for 24, 72, and 168 hr, is summarized in Table II. A pale yellow orange was observed in acetone or ammonia and developed with increasing treatment period. This pale yellow orange is the typical color of a polyene.

The long-term heat efficiency of Cd/Ba-st should result from the phenomenon whereby the polyene color turns into an achromatic color upon the addition of the color of the corresponding metal complex, a complementary color.

TABLE II  
Effect of Dipping Substances on Coloration of Colorless PVC Film\*

Dipping period	Undipped film	Ethyl ether	Acetone	Ethanol	Film dipped in												
					10			10			10			5			
$\lambda_d$ , nm	$\lambda_d$ , nm	$P_e$ , %	$P_e$ , %	$P_e$ , %	wt-% NH <sub>3</sub>	wt-% NaOH	wt-% HCl	wt-% NaOH	wt-% HCl	wt-% HCl	wt-% EDTA	wt-% EDTA	wt-% EDTA	alc. soln.	alc. soln.	alc. soln.	
24 hr	580	581	577	581	576	578	580	581	580	580	578	578	578	580	580	580	580
	19.0	12.6	13.8	15.8	18.9	15.7	21.0	17.6	17.6	22.0	13.2	13.2	17.0	17.0	17.0	17.0	17.0
	25.14	28.95	63.30	21.60	62.20	43.00	26.60	19.29	19.29	24.40	42.31	42.31	31.52	31.52	31.52	31.52	31.52
72 hr	580	586	576	580	576	579	579	580	579	579	577	577	579	579	579	579	579
	19.0	9.9	9.4	12.0	18.6	19.9	26.4	11.9	11.9	15.8	14.6	14.6	16.8	16.8	16.8	16.8	16.8
	25.14	43.02	64.45	37.15	63.02	22.70	28.35	28.40	28.40	33.26	46.60	46.60	40.12	40.12	40.12	40.12	40.12
168 hr	580	578	574	576	576	578	576	584	584	578	579	579	580	580	580	580	580
(for 1 week)	19.0	14.2	9.9	12.4	22.8	18.8	19.9	7.9	7.9	18.8	14.0	14.0	19.9	19.9	19.9	19.9	19.9
	25.14	48.13	69.18	55.58	61.91	29.60	49.02	39.11	39.11	38.50	32.05	32.05	37.10	37.10	37.10	37.10	37.10

\* The film containing 0.8 phr Cd-stearate and 0.4 phr Ba-stearate was dipped in the substances after the film was heated at 160°C in HCl(gas) flow for 5 min.

TABLE III  
Change in Color of the Colored PVC Films by Remilling\*

Factor	A	B	C <sub>C</sub>	C <sub>L</sub>	D	E	F
$\lambda_d$ , nm	580	580	577	573	580	581	576
Pe, %	23.3	27.0	20.6	8.9	20.7	28.0	22.8
Y, %	55.00	25.20	48.75	67.35	59.90	17.35	51.80

\* PVC, 20 phr DOP, and 1.2 phr Ba-st (A), 1.2 phr Cd-st (B), 0.4 phr Ba-st/0.8 phr Cd-st (C), 0.4 phr Ba-st (D), and 0.8 phr Cd-st (E) were milled at 150°C for 5 min, and these films were heated at 160°C for 110 min in air; 1 part of A and 2 parts of B were milled at 150°C(F).

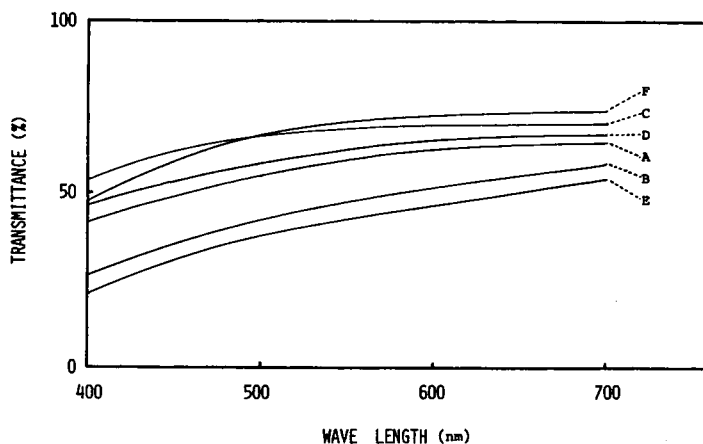


Fig. 2. Transmittance of PVC film: PVC, 20 phr DOP and 1.2 phr Ba-st (A), 1.2 phr Cd-st (B), 0.4 phr Ba-st/0.8 phr Cd-st (C), 0.4 phr Ba-st (D), and 0.8 phr Cd-st (E); 1 part A and 2 parts of B were milled at 150°C (F).

Film A (consisting of PVC 100, DOP 20, and Ba-st 1.2), film B (consisting of PVC 100, DOP 20, and Cd-st 1.2), film C (consisting of PVC 100, DOP 20, and Cd/Ba-st (2/1) 1.2), film D (consisting of PVC 100, DOP 20, and Ba-st 0.4), and film E (consisting of PVC 100, DOP 20, and Cd-st 0.8) were heated at  $160^\circ \pm 5^\circ\text{C}$  for 110 min in air. Every film except C was colored. One part of A and 2 parts of B were remilled on the open roll at 150°C for 3 min (film F). The composition of F corresponds to C, and the amount of each metal soap in C and F also correspond to D and E, respectively. Films A to E were remilled at 150°C for 3 min in order to make their heat history the same. A part of C was also colorless in this treatment (C<sub>L</sub>), but a part was slightly colored (C<sub>C</sub>).

The change in color for each film is summarized in Table III. The decoloration of A and B was observed by blending them. The color of F is paler than that of any of the films except C. Moreover, the color of F is deeper than C<sub>L</sub> but is the same as C<sub>C</sub>.

The transmittance of each film in the visible range is illustrated in Figure 2. The transmittance of F is greater than that of A, B, D, and E and de-

creases at 400–500 nm. For these data, it is apparent that the dilution effect between A and B does not occur.

It may be concluded that the stabilization mechanism of the metal soaps can be explained by an effect of complementary color.

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