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Stabilization of Poly(vinyl Chloride). II. Stabilization Mechanism Through Metal Soaps by Complementary Color Action

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Synopsis

In a previous paper, it was pointed out that the stabilization mechanism through metal soaps might be affected by an effect of complementary color. In this work, the colors of heated poly(vinyl chloride) (PVC) films mixed with various metal soaps were investigated by using a differential colorimeter and a spectrophotometer. Monochromatic coloration was observed with PVC, PVC-Ca stearate, and PVC-Ba stearate systems. On the other hand, the phenomenon of color mixing was observed with PVC-Zn stearate, PVC-Cd stearate, PVC-Zn/Ca stearate, and PVC-Cd/Ba stearate systems. In particular, achromatic color remained with PVC-Zn/Ca stearate and Cd/Ba stearate systems for longer heating periods. This means that the stabilization mechanism for PVC compounded with metal soaps should be effected finally by subtractive complementary colors situated between polyene color and the color effected with the metal complex, in addition to being subject to the usual chemical stabilization mechanisms.

INTRODUCTION

The following facts or phenomena were previously reported[1]: (1) Among the heated poly(vinyl chloride) (PVC) films containing the various metal soaps, a color difference dependent on the added metal soap was observed. (2) The synergetic stabilizers were a mixture of warm color producing soap and cool color producing soap. (3) The decoloration of the films was accelerated remarkably with THF, DMF, acetone, and ammonia. (4) The colored film containing Ba stearate was markedly decolored by mixing with the colored film containing Cd stearate. (5) The heated colorless film containing Cd/Ba stearate was colored slightly and became yellow orange in acetone or ammonia. These results indicate that the stabilization mechanism of metal soaps should be based on an effect of complementary color.

In the present work, films containing Zn stearate, Ca stearate, Cd stearate, Ba stearate, Zn/Ca stearate, or Cd/Ba stearate were investigated by colorimetry.

EXPERIMENTAL

The PVC used in this work was Geon 103 EP. The commercially available reagent of metal soaps and DOP (2-ethylhexyl) was used.

PVC, DOP, and metal stearate were milled on an open roll (4 in. × 8 in.) at 150°C for 5 min. Films about 0.5 mm in thickness were obtained. These films were heated at 160° ± 5°C in a gear oven. During compression of the roll films, the process time was minimized in order to avoid a heat history.

Colorimetry was carried out at room temperature by using a differential colorimeter (Nippon Denshoku, Model CP-6, 102D) and a spectrophotometer (Shimadzu Seisakusho, Model MPS-50L).

RESULTS AND DISCUSSION

PVC films with or without 0.1 phr Zn stearate (Zn-st), 0.1 phr Cd-st, 1 phr Cd-st, 1 phr Ca-st, 1 phr Ba-st, 3 phr Zn/Ca-st (2/1), and 3 phr Cd/Ba-st (2/1) were heated at 160°C in air. DOP, 20 phr, was contained in these films.

Figure 1 represents a plot of chromaticity based on the CIE color system, as a function of heating time. The curves in Figure 1 spiral to the right with increasing heating times, which were 0, 60, 120, 180, 240, 300, and 360

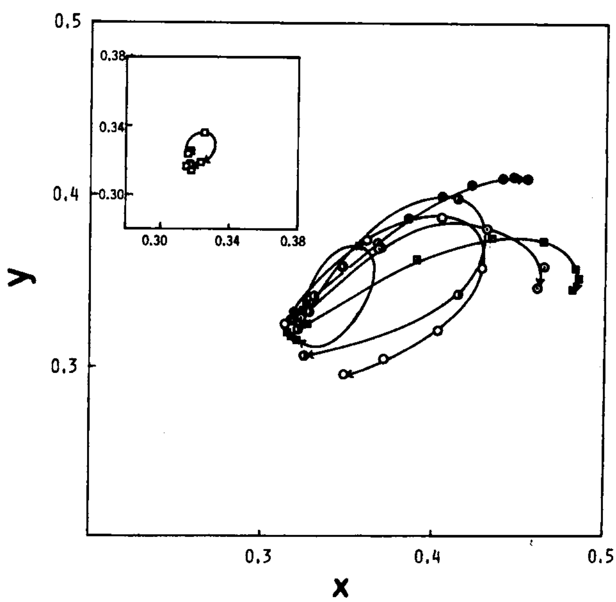

Fig. 1. Chromaticities of each heated PVC film on CIE color system. PVC 100 and DOP 20 (●), PVC 100, DOP 20, and Zn-st 0.1 (□), PVC 100, DOP 20, and Cd-st 0.1 (○), PVC 100, DOP 20, and Ca-st 1 (⊡), PVC 100, DOP 20, and Ba-st 1 (⊙), PVC 100, DOP 20, and Zn/Ca-st(2/1) 3 (◪), and PVC 100, DOP 20, and Cd/Ba-st (2/1) 3 (◑) were milled at 150°C for 5 min and heated at 160°C in air at hourly intervals up to 6 hr (□ and ◪ were plotted every 10 min and every 15 min respectively).

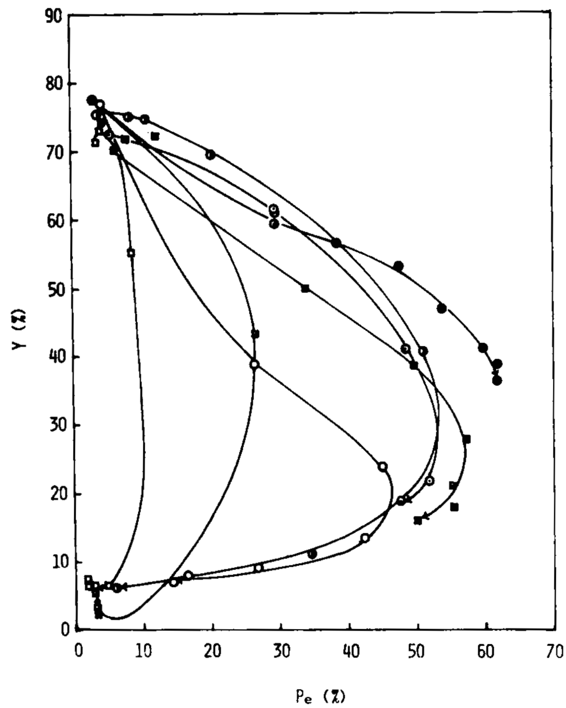

Fig. 2. Plots of Y vs. Pe. Data as in Figure 1.

min. Specifically, the chromaticities for the PVC–Zn-st and PVC–Zn/Ca-st systems are plotted every 10 min up to 60 min and every 15 min up to 90 min, respectively.

The chromaticity for PVC without the metal soap is approximately linear with heating time. The chromaticity diagrams for PVC–Ca-st and PVC–Ba-st systems show almost the same tendency as for PVC without metal soap. Their λ_d are 580–600 nm and are similar to that of PVC alone (λ_d = 580 nm). Their color is a yellow orange which grows deeper with longer heating times.

On the other hand, the chromaticity diagrams for PVC–Zn-st, PVC–Zn/Ca-st, PVC–Cd-st, and PVC–Cd/Ba-st systems markedly deviate from a straight line. Discoloration from yellow orange to bluish green and from yellow orange to purple pink is observed in the chromaticity diagrams for PVC–Zn-st and PVC–Zn/Ca-st films and PVC–Cd-st and PVC–Cd/Ba-st films, respectively. These systems show the phenomenon of color mixing, e.g., the discoloration of the PVC–Zn-st, PVC–Zn/Ca-st, PVC–Cd-st, and PVC–Cd/Ba-st systems depends on the ratio of the color mixture of polyene/polyene-$ZnCl_2$ complex, polyene/polyene-$ZnCl_2$ complex/polyene-$CaCl_2$ complex, polyene/polyene-$CdCl_2$ complex, and polyene/polyene-$CdCl_2$ complex/polyene-$BaCl_2$ complex, respectively.

The color of the metal chloride complex may appear markedly during the heat treatment, since the metal chloride should be converted easily from

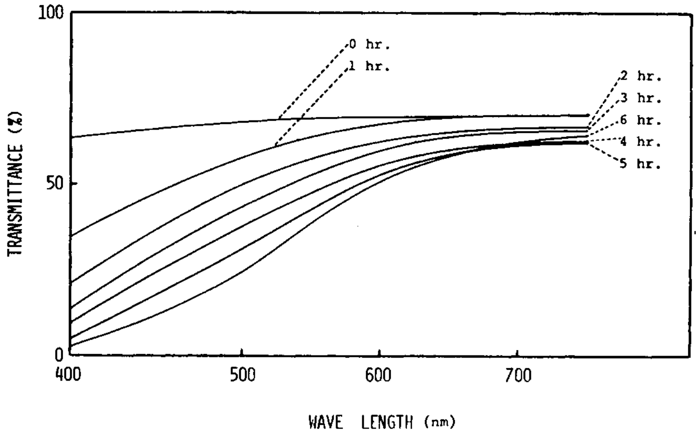

Fig. 3. Transmittances of compounded PVC film. PVC 100 and DOP 20, heated at 160°C in air.

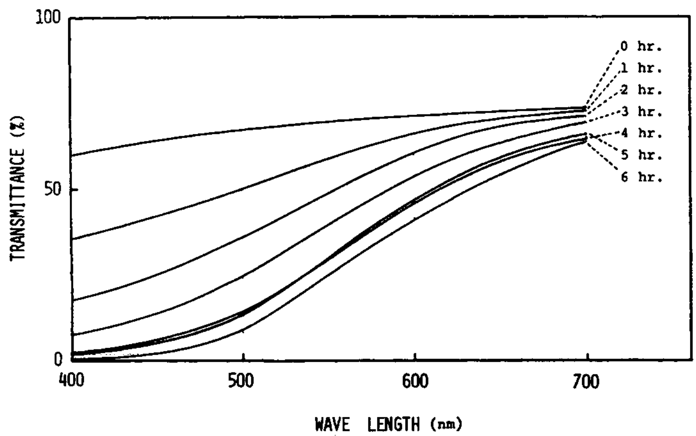

Fig. 4. Transmittances of compounded PVC film. PVC 100, DOP 20, and Ca-st. 1, heated at 160°C in air.

the corresponding metal soap under the above conditions. From the chromaticity diagram it is concluded that the color of the Cd complex has a complementary wavelength.

The relation between Y and Pe based on the CIE color system is shown in Figure 2.

The metal soaps which tend to have no decrease in Y and no increase in Pe are observed simultaneously when the increased heating periods in this relation are the most effective ones for heat stability.

Figure 2 shows that PVC–Cd/Ba-st and PVC–Zn/Ca-st systems stabilize the PVC for 2 hr and 30 min, respectively. These systems exhibit marked decrease in Y and increased in Pe with increasing heat treatment. These observations indicate that the subtractive complementary colors are

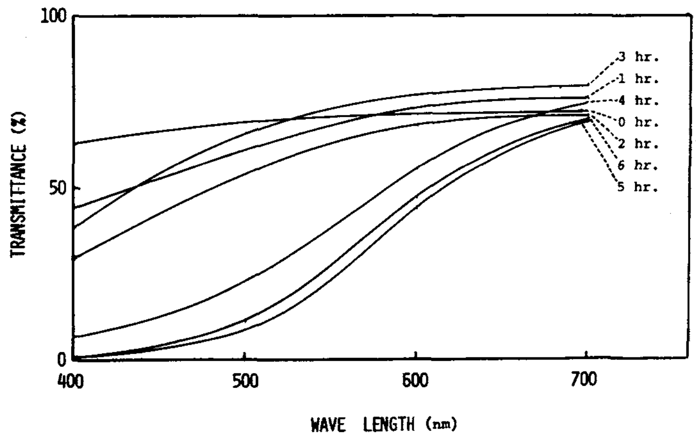

Fig. 5. Transmittances of compounded PVC film. PVC 100, DOP 20, and Ba-st. 1 heated at 160°C in air.

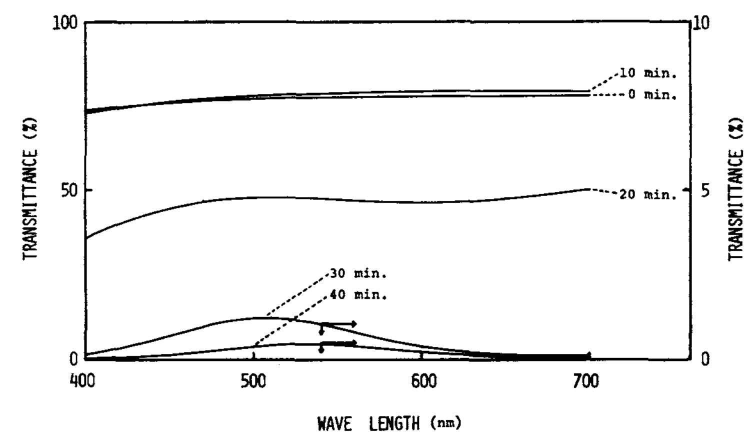

Fig. 6. Transmittances of compounded PVC film. PVC 100, DOP 20, and Zn-st. 0.1. heated at 160°C in air.

strongly related to the polyene color and the corresponding metal complex color.

Figures 3–10 represent the transmittances of each film in the visible range. A pale yellow orange appears after 1 hr and then grows deeper in PVC and in the PVC–Ca-st and PVC–Ba-st systems as shown in Figures 3–5.

No transmittance at the longer wavelength band can be observed for any heating periods, and transmittance of a bluish green (λ_d, about 500 nm) appears with longer heating times in the PVC–Zn-st system as shown in Figure 6. Between a yellow orange (λ_d = 580 nm) and a bluish green (λ_d = 470–500 nm) lie the subtractive complementary colors.

Figures 3 and 6 indicate that the polyene color (yellow orange) is compensated completely by addition of a blue color-producing soap (Zn-st). This technique has been called "blueing."

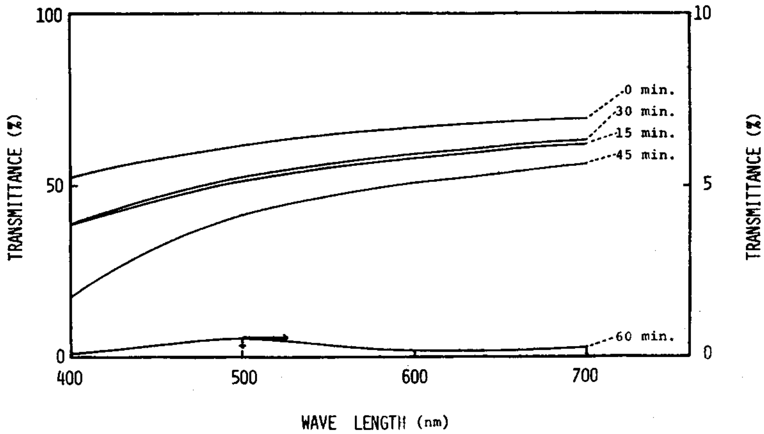

Fig. 7. Transmittances of compounded PVC film. PVC 100, DOP 20, and Zn/Ca-st. (2/1)3, heated at 160°C in air.

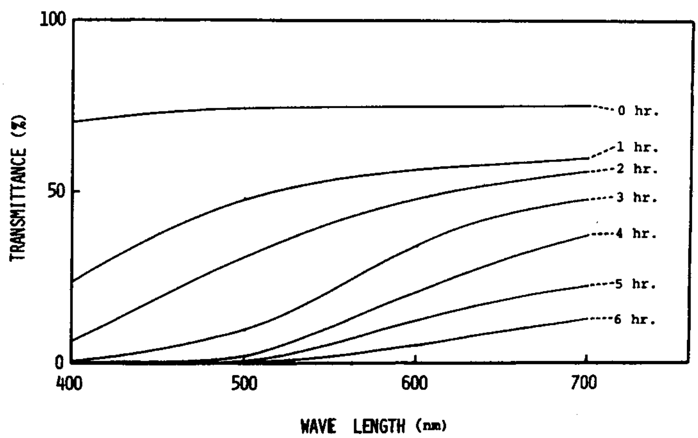

Fig. 8. Transmittances of compounded PVC film. PVC 100, DOP 20, and Cd-st. 0.1, heated at 160°C in air.

The transmittance curves are an almost linear curve for all heating times and the achromatic discoloration (white → grey → black) appears markedly in the PVC–Zn-st system. The relationship involving subtractive complementary colors exists in this system because the mixture of chromatic colors, which is achromatic, corresponds to the complementary color in a subtractive color mixture.

As shown in Figure 7, by adding Ca-st, the phenomenon of the complementary color remains after longer heating periods than for the PVC–Zn-st system and the bluish green also appears after a long heating time in the PVC–Zn/Ca-st system. No coloration of this system is observed for 30 min during the initial stage.

The transmittance distribution curves for the PVC–Cd-st system are shown in Figures 8 and 9. The transmittance at the longer wavelength is

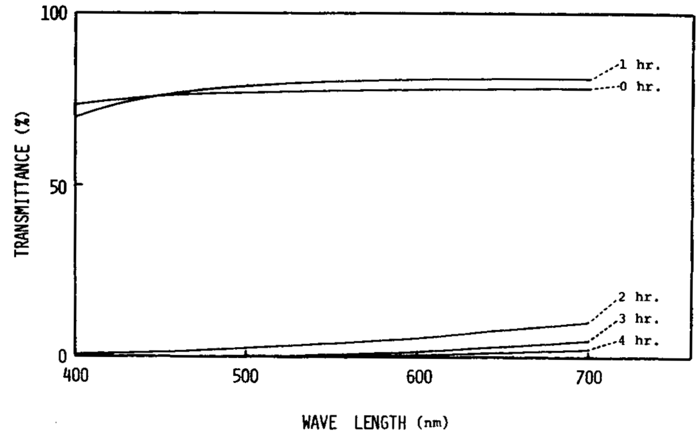

Fig. 9. Transmittances of compounded PVC film. PVC 100, DOP 20, and Cd-st. 1, heated at 160°C in air.

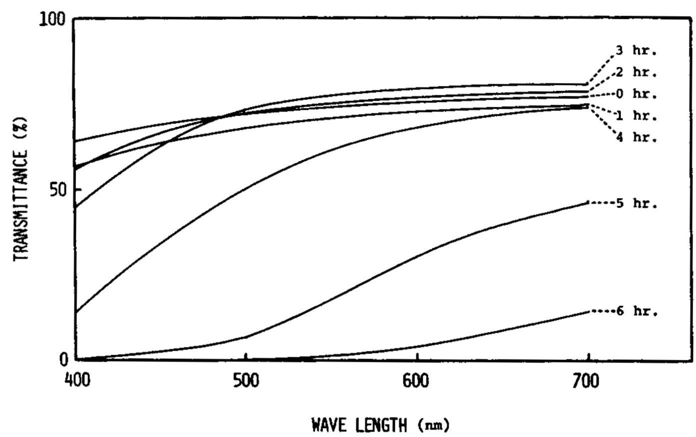

Fig. 10. Transmittances of compounded PVC film. PVC 100, DOP 20, and Cd/Ba-st.(2/1) 3, heated at 160°C in air.

observed on the film containing small amounts of Cd-st after the longer heating time, but it is compensated by adding large amounts of Cd-st at any heating time. The PVC–Cd/Ba-st system has a linear transmittance curve within 2 hr, as shown in Figure 10. This means that the color of the Cd complex is compensated by adding Ba-st.

From these results, the stabilization mechanism of metal soaps can be explained by the effect of complementary color which occurs among the polyene color and the colors of corresponding polyene–metal chloride complex.

No marked decoloration of the colored film containing Zn-st was observed by mixing it with the colored film containing Ca-st; and the color appearing on the milled film with individual Cd-st and Ba-st was deeper than the color which appeared on the PVC–Cd/Ba-st film.[1] Therefore, a stabilization mechanism based on chemical reactions[2-5] is impossible to deny. It may be concluded that these chemical reactions serve to control the coloration of each component in a compound PVC film in order to set up the complementary colors.

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