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Takeo Iida^a; Kunio Goto^a

^a Department of Applied Chemistry, Osaka Institute of Technology, Asahi-ku, Osaka, Japan

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Color Stabilization of Poly(vinyl Chloride) with Heat Treatment

TAKEO IIDA and KUNIO GOTŌ

Osaka Institute of Technology
Department of Applied Chemistry
Asahi-ku, Osaka 535, Japan

ABSTRACT

Stabilization of poly(vinyl chloride) (PVC) containing metal soaps was investigated by psychophysical colorimetry. A color difference observed among heated PVC films containing various metal salts depends on coloration of the π -complex of polyene with metal chloride converted from the metal salt added and that the stabilization effect of synergistic soaps should be based on an effect of complementary colors set up among a polyene color and metal chloride-polyene complex colors. These conclusions are well supported by colorimetry of heated PVC films containing various dyes. The color of heated PVC films containing Zn/Ca and Cd/Ba synergetic soaps markedly deviated from a polyene color with increased heat treatments, owing to greater degree of coloration of Zn complex and Cd complex, respectively. These color deviations usually decrease the thermal stability of PVC. The thermal stability of PVC was markedly improved by the use of synergetic soaps together with masking agent such as triethanolamine, urea, N,N'-dimethylol-urea, and vinylpyridine-methylmethacrylate copolymer, owing to the masking effect of these nitrogen-containing compounds. These masking agents did not slow down the dehydrochlorination of PVC.

INTRODUCTION

As is well known, 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 dehydrochlorination of PVC [1].

PVC is usually mixed with one or more stabilizers in order to retard the discoloration. Metal soaps are the most important stabilizers.

Removal of hydrogen chloride [2, 3], substitution of RCOO with a chlorine atom in PVC chains [4], and recombination of chlorine atoms liberated from PVC with the polyene chains [5] have been proposed as stabilization mechanisms involving the metal soaps.

On the other hand, heat-treated PVC films containing various metal salts have been observed to undergo a color change which is dependent on the specific metals employed [6]. This color difference observed among the heated PVC films containing various metal salts is difficult to explain by the usual stabilization mechanisms [2-5].

Therefore, we tried to investigate the stabilization of PVC from a different view point. Changes in the color of various PVC films were studied by psychophysical colorimetry in order to elucidate the stabilization mechanisms of metal soaps.

Subsequently, it was found that the color difference observed among various heated PVC films depended on the formation of a π -complex of double bonds in polyene chains with metal chloride converted from the corresponding metal soap [6]. It has also been concluded, from the fact that synergistic metal soaps are a mixture of warm color-producing soap and cool color-producing soap, that the stabilization mechanism of synergistic metal soaps should be based on an effect of complementary colors [7].

The possibilities of stabilizing PVC on the basis of complementary colors was previously detailed [8, 9]. These methods employed psychophysical colorimetry in order to keep PVC colorless by the addition of masking agents and colors or various chromophores and developers which set up complementary colors in PVC.

In the present work, the stabilization effects involving dyes and masking agents are investigated. The results of colorimetry obtained from various heated PVC films containing dyes or masking agents well support the conclusions [7] which the stabilization mechanism of synergistic metal soaps should be based on the complementary colors related among polyene color and metal chloride-polyene complex colors.

In this paper, coloration is used instead of the term "discoloration," which is usually employed when discussing the stabilization of PVC. Discoloration indicates a phenomenon involving a change in color of colored material; coloration means the development of color in a

previously colorless material; and decoloration indicates the disappearance of color as determined by colorimetry.

EXPERIMENTAL

Materials

The PVC used in this work was Geon 103 EP; commercially available di(2-ethylhexyl) phthalate (DOP), metal stearates, and other reagents were used.

2-Vinylpyridine and methyl methacrylate were copolymerized in benzene at 60°C by using benzoyl peroxide as an initiator.

The dyes used in this work were Ceres Blue GN (CB), Macro-Lex Red 5B (MLR), Macro-Lex Green 5B (MLG), Macro-Lex Violet 3R (MLV), Thren Blue IRN (TB), and Oplas Violet 230 (OP). No additives were contained in these dyes.

Preparation of PVC Film

PVC, DOP, metal stearate, and dye or masking agent were milled in an open roll (4 in. × 8 in.) at 150°C for 5 min, respectively. Each PVC film contained 20 phr DOP and 3 phr synergetic metal soaps. No synergetic metal soap combined in PVC films containing dye. The compounded PVC films about 0.5 mm in thickness were heated at 160°C in a gear oven. During compression of the roll films, the process time was held constant in order to avoid a heat history difference.

Colorimetry

PVC films were investigated by colorimetry at room temperature by using a differential colorimeter. The differential colorimeter used in this work was the Suga Shikenki, Model Au-CH-LD instrument.

Absorbance of Ultraviolet Spectrum

Ultraviolet absorbances of heated PVC films dissolved in tetrahydrofuran (2 g/liter) were obtained by using a spectrophotometer at room temperature. The spectrophotometer used in this work was a Shimadzu Seisakusho, Model MPS-50L instrument. Each absorbance was corrected for the concentration of PVC.

RESULTS AND DISCUSSION

Color Changes on Heating of PVC Films Containing Dye

From the colorimetry of various heated PVC films [7] it is confirmed that a color mixing phenomenon among a polyene color and metal chloride-polyene complex colors occurs in PVC films containing metal soaps. We therefore investigated color changes in heated PVC films containing various dyes.

PVC films containing 0.01 phr CB, MLR, MLG, MLV, TB, or OP were heated at 160°C for 30, 60, or 90 min. On the other hand, PVC films without dye were also heated under the same conditions as for the films with dye. Then, the unheated film containing the same amount of dye was put on the heated films without dye. The color of the stacked films was the same as the color of the heated film containing corresponding dye. For example, the color of a PVC film compounded with 0.01 phr MLG and then heated at 160°C for 30 min was similar to the color observed when an unheated film containing 0.01 phr MLG was placed on a film without dye heated at 160°C for 30 min.

Similar phenomena were also observed for films containing other dyes and for all heating times except for the films containing CB. This means that the color observed on heated film containing dye is a mixture of the dye color and polyene color.

The discoloration of PVC films with or without dye with heating time is shown in Fig. 1. The plots in Fig. 1 are plotted every 15 min up to 2 hr. Y and P_e correspond to value and chroma, respectively. The Y of all films decreases with increasing heat treatment. This means that the coloration of each film increases progressively on heating. On the other hand, the P_e of each film containing dye has a minimum at 30 min. In particular, the film containing TB or CB turned to an achromatic color after heating at 160°C for 30 min.

As is well known, between a cool color such as a blue and a warm color such as a yellow orange lie the complementary colors.

So, it is concluded that the disappearance of a polyene color in these systems is affected by the complementary color relationships based on the color mixing phenomenon between the polyene color (yellow orange) and the blue of added dyes.

These results support the conclusion [7] that the stabilization effect of Zn/Ca and Cd/Ba synergistic soaps depends on the complementary colors resulting between the polyene color and Zn complex color ($\lambda_d = 475$ nm) or Cd complex color ($\lambda_d = 485$ nm), respectively.

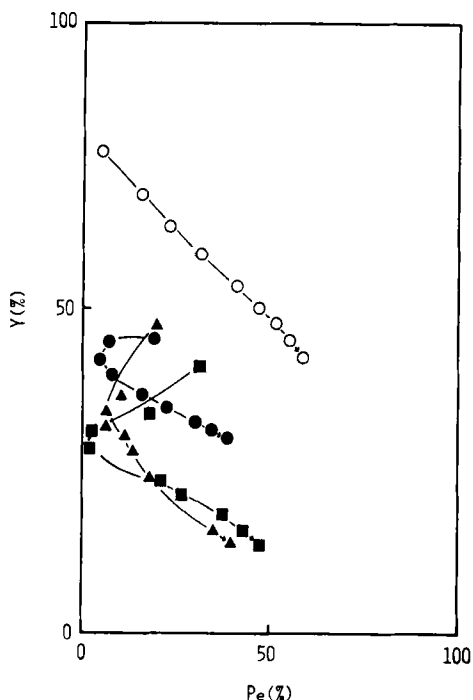


FIG. 1. Stabilization effect of some dyes: (■) PVC 100, DOP 20, Ceres Blue GN 0.01; (●) PVC 100, DOP 20, Thren Blue IRN 0.01; (▲) PVC 100, DOP 20, Macro-Lex Green 5B 0.01; (○) PVC 100, DOP 20. Heated at 160°C in air at 15 min intervals up to 2 hr.

Synergism among Masking Agents and Metal Soaps

Discoloration from the polyene color to the colors of the Zn complex and Cd complex was observed on films containing Zn/Ca or Cd/Ba synergistic soaps under heating and was due to the marked coloration of the Zn and Cd complexes, respectively [6, 7]. These color deviations are usually accompanied by a decrease in the thermal stability of PVC. Discoloration from the yellow orange to the Zn complex color (blue), observed especially on PVC films containing Zn/Ca synergistic soap in the early heating stage, markedly inhibits the stabilization of PVC [7]. This phenomenon appearing in the PVC films compounded with Zn/Ca synergistic soap has been called "zinc burning."

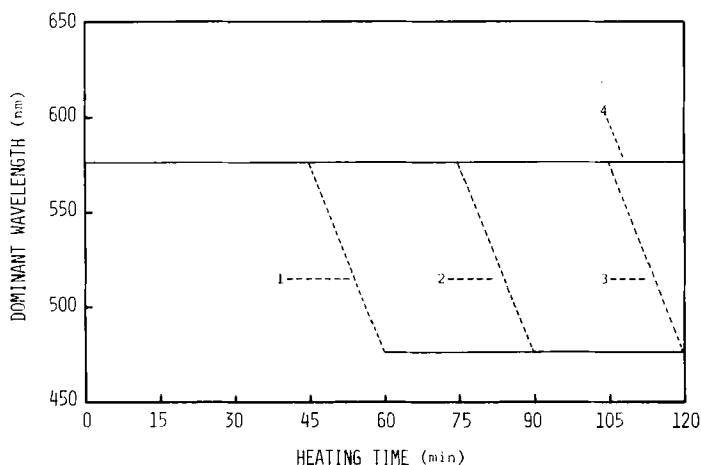


FIG. 2. Masking effect of *N,N'*-dimethylolurea (DMU): (1) PVC 100, DOP 20, Zn/Ca-st(2/1) 3; (2) PVC 100, DOP 20, Zn/Ca-st(2/1) 3, DMU 0.2; (3) PVC 100, DOP 20, Zn/Ca-st(2/1) 3, DMU 0.4; (4) PVC 100, DOP 20, Zn/Ca-st(2/1) 3, and DMU 0.6-3.0. Heated at 160°C in air.

The presence of some compounds which form colorless complexes with metal chlorides is well known. These substances have been called masking agents. Aminopolycarboxylates or urea are most effective.

The thermal stability of PVC containing metal soaps may be improved by the addition of some substances which mask the freely presented metal chloride, converted from the corresponding metal soap, in order to inhibit the excessive formation and coloration of metal π -complex.

The masking effects of *N,N'*-dimethylolurea (DMU), for example, upon the stabilization of PVC containing Zn/Ca and Cd/Ba synergistic soaps are shown in Figs. 2 and 4, respectively. The colorations of Zn-complex and Cd-complex are inhibited by adding suitable amounts of DMU. Moreover, the coloration of PVC is slowed down by the use of synergistic soaps together with DMU, as shown in Figs. 3 and 5. A similar effect was also observed for urea, stearylamine, and tri-ethanolamine.

The compatibility of some masking agents with PVC was poor. Therefore, we tried to synthesize macromolecular masking agents containing nitrogen atoms, hydroxy groups, or carboxyl groups in order to improve the compatibility with PVC.

The masking effect of 2-vinylpyridine-methyl methacrylate copolymer, P(VP-MMA), ($\bar{P}_n = 500$, 1:1 composition by mole) upon

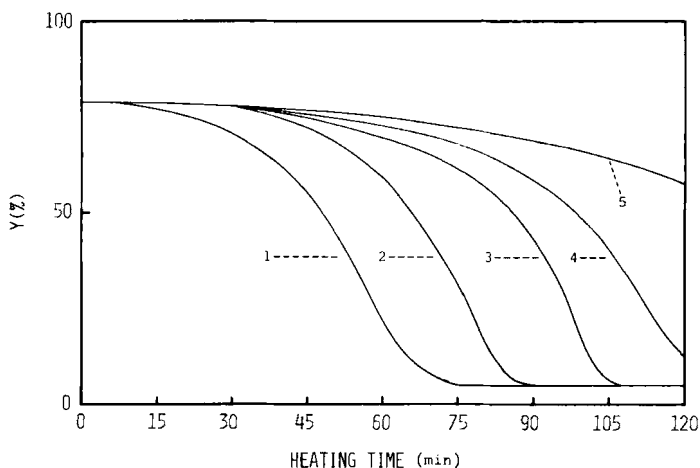


FIG. 3. Stabilization effect of *N,N'*-dimethylolurea (DMU), evaluated by Y: (1) PVC 100, DOP 20, and Zn/Ca-st(2/1) 3; (2) PVC 100, DOP 20, Zn/Ca-st(2/1) 3, and DMU 0.2; (3) PVC 100, DOP 20, Zn/Ca-st(2/1) 3, and DMU 0.4; (4) PVC 100, DOP 20, Zn/Ca-st(2/1) 3, and DMU 0.6-0.8; (5) PVC 100, DOP 20, Zn/Ca-st(2/1) 3, and DMU 1.0-3.0. Heated at 160°C in air.

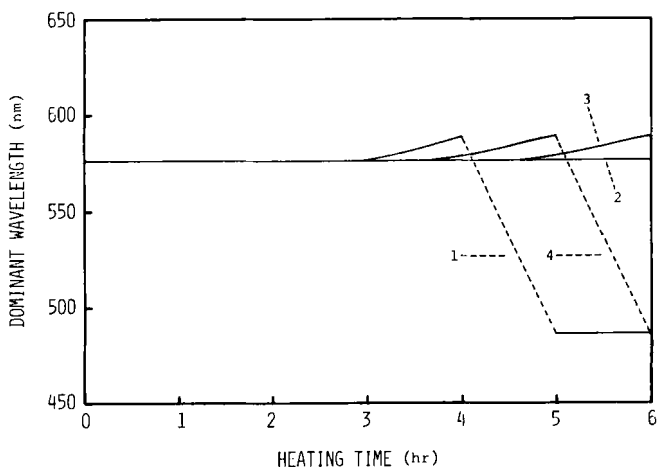


FIG. 4. Masking effect of *N,N'*-dimethylolurea (DMU): (1) PVC 100, DOP 20, Cd/Ba-st(2/1) 3; (2) PVC 100, DOP 20, Cd/Ba-st(2/1) 3, DMU 0.2; (3) PVC 100, DOP 20, Cd/Ba-st(2/1) 3, DMU 0.4-1.0; (4) PVC 100, DOP 20, Cd/Ba-st(2/1) 3, DMU 2.0-3.0. Heated at 160°C in air.

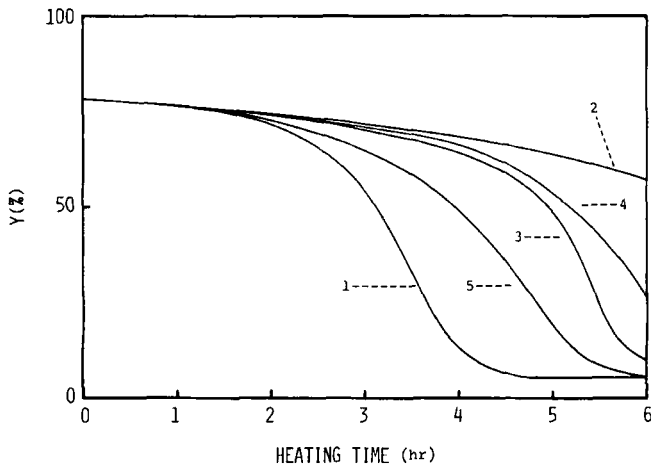


FIG. 5. Stabilization effect of *N,N'*-dimethylolurea (DMU), evaluated by Y: (1) PVC 100, DOP 20, Cd/Ba-st(2/1) 3; (2) PVC 100, DOP 20, Cd/Ba-st(2/1) 3, DMU 0.2; (3) PVC 100, DOP 20, Cd/Ba-st(2/1) 3, DMU 0.4-0.6; (4) PVC 100, DOP 20, Cd/Ba-st(2/1) 3, DMU 0.8-1.0; (5) PVC 100, DOP 20, Cd/Ba-st(2/1) 3, DMU 2.0-3.0. Heated at 160°C in air.

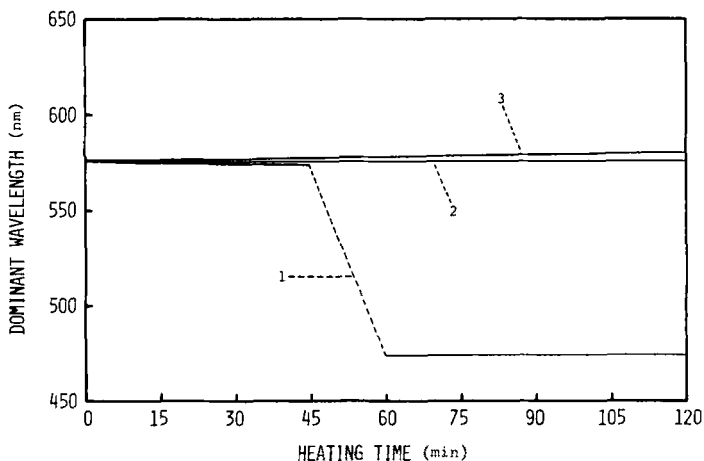


FIG. 6. Masking effect of 2-vinylpyridine-methyl methacrylate copolymer, P(2-VP-MMA): (1) PVC 100, DOP 20, Zn/Ca-St(2/1) 3; (2) PVC 100, DOP 20, Zn/Ca-St(2/1) 3, P(2-VP-MMA) (1:1) 0.4-1.0; (3) PVC 100, DOP 20, Zn/Ca-St(2/1) 3, P(2-VP-MMA) (1:1) 2.0. \bar{P}_n of this copolymer was 500; heated at 160°C in air

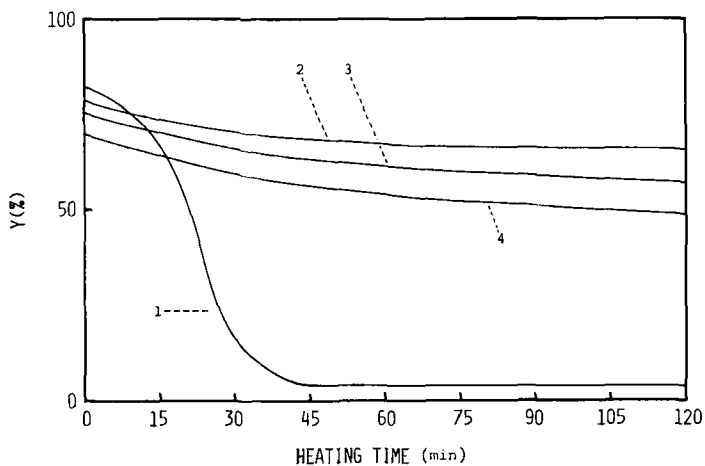


FIG. 7. Stabilization effect of 2-vinylpyridine-methyl methacrylate copolymer, evaluated by Y: (1) PVC 100, DOP 20, and Zn/Ca-St(2/1) 3; (2) PVC 100, DOP 20, Zn/Ca-St(2/1) 3, P(2-VP-MMA) (1:1) 0.4; (3) PVC 100, DOP 20, Zn/Ca-St(2/1) 3, P(2-VP-MMA) (1:1) 1.0; (4) PVC 100, DOP 20, Zn/Ca-st(2/1) 3, and P(2-VP-MMA) (1:1) 2.0. Heated at 160°C in air.

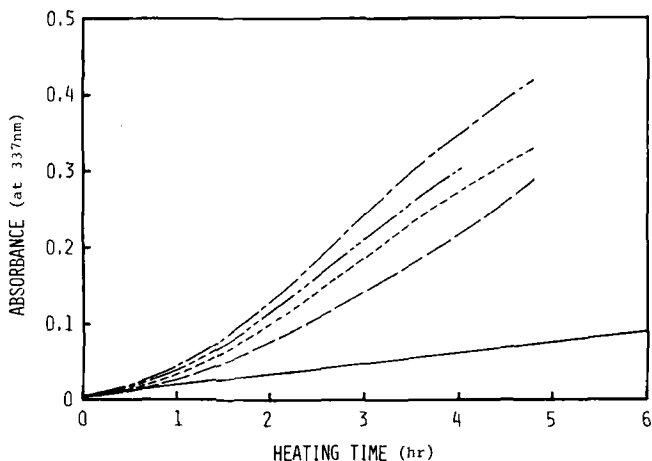


FIG. 8. Effect of masking agents upon the dehydrochlorination of PVC: (—) PVC 100, DOP 20; (---) PVC 100, DOP 20, triethanolamine 1; (- - -) PVC 100, DOP 20, N,N'-dimethylolurea 1; (- -) PVC 100, DOP 20, urea 1; (- -) PVC 100, DOP 20, and stearylamine 1. Heated at 160°C in air.

the stabilization of PVC containing Zn/Ca synergistic soap, for example, is shown in Fig. 6.

The P(VP-MMA) completely inhibits the zinc burning phenomenon, as shown in Fig. 6. A marked stabilization effect was also observed on use of P(VP-MMA) together with synergistic soap, owing to the great masking effect of P(VP-MMA), (Fig. 7).

Effects of some nitrogen-containing masking agents upon the dehydrochlorination of PVC are shown in Fig. 8. These masking agents did not slow down the dehydrochlorination of PVC. As shown in Fig. 8, these masking agents stabilize PVC in spite of their ability to accelerate dehydrochlorination of PVC. Moreover, no stabilization effect of nitrogen-containing low molecular and macromolecular masking agents could be observed on PVC films without metal soaps. This means that the stabilization effect of these substances should be based on their masking effects.

It is concluded from these results that a suitable amount of masking agent serves to inhibit the excessive coloration of the π -complex and to retain the efficient π -complex color which keeps PVC colorless by virtue of complementary colors with the polyene color in PVC.

Blooming and plate-out phenomena appeared when low molecular masking agents added to PVC are retarded by the use of a macromolecular masking agent containing segments very compatible with PVC, such as P(VP-MMA).

CONCLUSIONS

The results described in this paper support the fact that the stabilization mechanism of synergistic metal soaps is based on the complementary color relationship set up among polyene color and the corresponding metal chloride-polyene complex colors.

It is also concluded that a color mixing phenomenon takes place during heat treatment of PVC containing various colors or developers and chromophores. Therefore, PVC should be stabilized by the addition of color or developer and a chromophore which shows a color the complementary colors to the polyene color.

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