Stabilization of Poly(vinyl Chloride). IV. Color Changes on Heating Poly(vinyl Chloride)–Dye Systems

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Synopsis

The stabilization of poly(vinyl chloride) (PVC) involving complementary colors has been previously reported. Obliterating polyene color with various dyes containing complementary colors with the polyene color is studied on the basis of colorimetry. The changes in the color of heated PVC containing Thren Blue IRN, Ceres Blue GN, Oplas Violet 730, Macro-Lex Violet 3R, Macro-Lex Green 5B, or Macro-Lex Red 5B were investigated using a differential colorimeter. When the PVCs containing various dyes were heated, the discoloration from the color of each dye to the color mixture of each dye and polyene color was observed with increased heating times for all systems. In particular, an achromatic color has been observed, during the heat treatments, in PVC containing blue dyes such as Thren Blue IRN or Ceres Blue GN, which set up complementary color relationships with the polyene color. Thus the color of polyenes, which appears with advancing dehydrochlorination of PVC, is masked by the blue dyes. It is also apparent that the obliteration of polyene color does not depend on the chemical influences of the dyes added, but by color mixing of polyenes and the dyes. Cool-color dyes markedly slow down the appearance of polyene colors.

INTRODUCTION

The effects of synergetic metal soaps on the stabilization of poly(vinyl chloride)(PVC) were based on the obliteration of polyene color by coloring PVC with the blue produced from soap such as zinc stearate or cadmium stearate.[1,2]

The color of heated PVC containing cadmium stearate/barium stearate or zinc stearate/calcium stearate synergetic soaps changed from the color of polyenes to that of the cadmium and zinc complex colors, respectively, with increased heating times.[2] This was due to the marked formation rate, or coloration rate, of cadmium and zinc complexes, respectively.[2]

The possibility of stabilizing PVC on the basis of colorimetry has been previously proposed.[3–5] In the present paper, the obliteration of polyene color which appears with advancing dehydrochlorination of PVC, is investigated by adding a color which sets up complementary colors with the polyene color. The colorimetry of heating PVC with or without Thren Blue IRN (TB), Ceres Blue GN (CB), Oplas Violet 730 (OV), Macro-Lex Violet 3R (MLV), Macro-Lex Green 5B (MLG), or Macro-Lex Red 5B (MLR) was conducted to ensure the previous deductions.[2–6]

By heating PVC containing a blue dye, the color changed from blue to grey to yellow-orange. Thus the color of polyenes changed by adding a blue color, a phenomenon known as bluing. As for the colorimetry of PVC with or without dyes, the obliteration effect of blue dyes does not depend on their chemical behavior, but is based on the color-mixing phenomenon between the polyene and the blue dye.

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These results fully support the deductions[2–6] that the polyene color compensates with the cool color produced from soaps such as cadmium and zinc stearate, or some chromophores and developers, with advancing dehydrochlorination of PVC.

EXPERIMENTAL

Materials. The PVC used in this work was Geon 103 EP; and commercially available di(2-ethylhexyl)phthalate (DOP) and dyes were used.

Preparation of PVC Film. PVC with or without 0.01 phr TB, CB, OV, MLV, MLG, or MLR were milled on an open roll (4 × 8 in.) at 150°C for 5 min. Each PVC composition was plasticized with 20 phr DOP containing no stabilizers. During the roll mixing, the process time was minimized and held to unity in order to avoid the influence of heat history. The compounded PVC films (about 0.5 mm thick, 60 mm long, and 50 mm wide) were heated at 160 ± 2°C in a circulating air oven.

Colorimetry. PVC films were investigated by colorimetry at room temperature by using a Suga Shikenki model AU-CH-1D differential colorimeter with 45°–0° geometry attached to a 30-mm diameter specimen holder window.

A white color standard plate (Y = 84.5, X = 82.4, and Z = 93.7) was used to reflect light onto the film.[2,6] Tristimulus values for each film were determined by averaging the values obtained from three different places on the film surface.

RESULTS AND DISCUSSION

Changes in Color of Heated PVC With or Without Dyes

The color changes of PVC with or without 0.01 phr of various dyes heated at 160°C up to 120 min are shown in Figure 1. This figure is presented as a CIE chromaticity diagram. Figure 1 is plotted every 15 min from 0 up to 120 min, and the heating times, as for each chromaticity curve, increasing from left to right. The perforated lines represent the distribution of the dominant wavelength and the corresponding color. The × represents the center of the white area.

The color of PVC without dye turns from colorless to yellow orange, which is the color of polyenes, and grows deeper with increased heating time. On the other hand, the color changes of PVC with various dye combinations show the phenomenon of color mixing. Color changes from the color of the dye to the color mixture of polyene plus dye (Fig. 1).

In particular, PVC containing a blue dye such as TB or CB, which set up complete colors complementary with the polyene color (yellow orange: λd = 580–600 nm), reveal the polyene color, after a grey (achromatic color) appears at 45 min. Hence relationships involving subtractive complementary colors exist in these systems because the mixture of chromatic colors, which is achromatic, corresponds to the complementary colors in a subtractive color mixture.

The changes in color of PVC with various dyes, therefore, are due to the color-mixing phenomenon of dye and polyene which appears with increased heating.

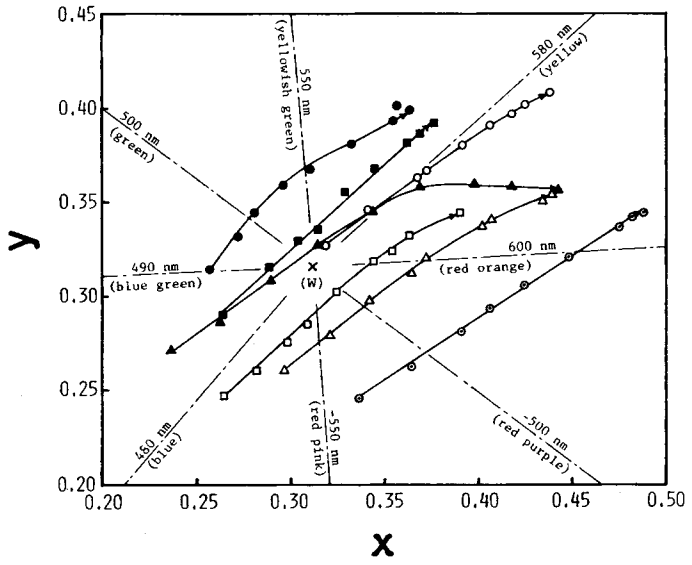

Fig. 1. Color changes of PVC films without (○) and with various dyes: 0.01 phr TB (■), CB (▲), OV (□), MLV (△), MLG (●), and MLR (⊙). Each PVC film contained 20 phr DOP.

Obliteration of Polyene Color with Dyes

The discoloration of heated PVC with or without 0.01 phr cool color dyes such as TB, CB, OV, MLV, or MLG is shown in Figure 2. Figure 2 represents a plot of whiteness [$W(BY)$] based on the ASTM E 313 equation a function of heating time:

$$W(BY) = 4(0.847Z) - 3Y \tag{1}$$

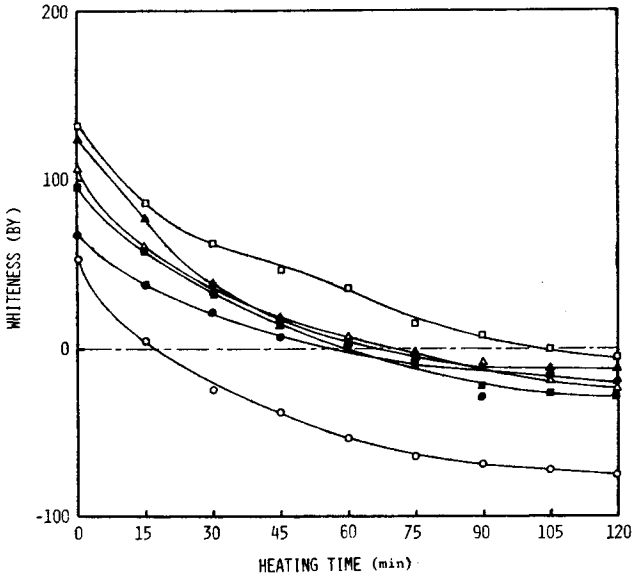

Fig. 2. Obliteration of polyene color without (○) and with various dyes: with 0.01 phr TB (■), CB (▲), OV (□), MLV (△), or MLG (●). Each PVC film contained 20 phr DOP. Films heated at 160°C.

where Z and Y represent the Z and Y tristimulus values, respectively.

PVC without dyes shows the polyene color at 15 min, which grows deeper with increased heating times; while each PVC with dye requires more than 90 min of heating time for the polyene color to appear (Fig. 2). No polyene color is observed in PVC containing OV even at 120 min.

The polyene color which should appear with heating is masked by additives containing complementary colors. This technique has been called bluing.

The relationships between Y and Pe on the basis of colorimetry are shown in Figure 3. Figure 3 is plotted every 15 min from 0 to 120 min. The heating times increase in the direction of the arrow. Y and Pe correspond, respectively, to value and chroma based on colorimetry. The Y of all systems decreases with increased heating due to the coloration of PVC (Fig. 3). The Pe of PVC without dye increases with increasing heating. The polyene color grows more intense with increased heating times. On the other hand, the Pe of PVC containing green, blue, or violet dyes decreases during the initial stage and then increases with additional heating after attaining a minimum Pe. The Pe of PVC containing CB, TB, MLV, or MLG attains a minimum at 30–45 min. Moreover, the Pe of PVC containing OV reaches a minimum at 60 min (Fig. 3).

Polyene color which should appear during the initial stage is obliterated by adding colors which complement the color of polyenes. The increase of Pe, after attaining a minimum, is due to the excess polyene color, related to the amount of dye.

Hence subtractive complementary colors exist in these systems (except in PVC without dyes) because the mixture of chromatic colors, which is achromatic, corresponds to the complementary colors.

PVC containing a blue dye such as TB and CB shows the obvious discoloration of blue (chromatic) to grey (achromatic) to yellow orange (chromatic) during

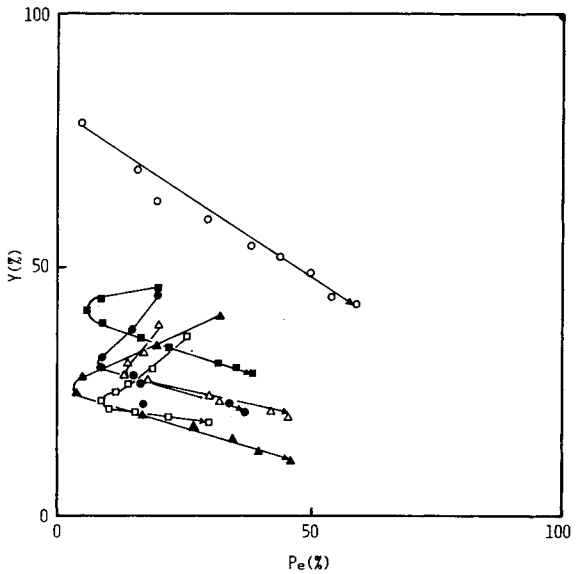

Fig. 3. Evaluation of complementary colors between polyene and dyes in PVCs without (○) and with various dyes: 0.01 phr TB (■), CB (▲), OV (□), MLV (△), or MLG (●). Each PVC film contained 20 phr DOP. Films heated at 160°C.

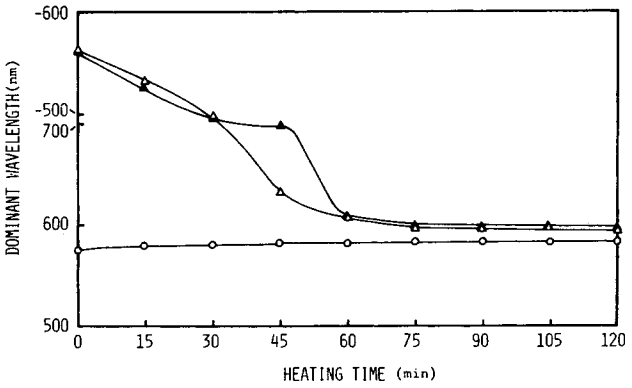

Fig. 4. Appreciation of color-mixing phenomenon evaluated by dominant wavelength in PVCs without (○) and with various dyes: 0.01 phr MLV (△) and the layered system of $(PVC)_t/(PVC–MLV)_0$ (▲). Each PVC film contained 20 phr DOP. Films heated at 160°C.

heating, since a blue dye is complementary to the color of polyenes. On the other hand, the discoloration of PVC containing green or violet is less remarkable than of PVC containing the blue dye. The color of green or violet dyes remains through the longer heat treatments, because the green or violet deviate slightly from the complete complementary color relationships with the polyene color (Fig. 1). Therefore, it is preferable to use green or violet dyes as practical bluing agents.

Evaluation of Color Mixing Phenomena

From the colorimetry of various heated PVC films, the color-mixing phenomenon related between the polyene color and the color of dye should occur during heating of PVC.

Evaluations, therefore, were carried out in order to determine whether the color change for PVC with dyes was caused by the chemical behavior or thermal decomposition of the dyes and accelerating dehydrochlorination of PVC.

The PVC films containing 0.01 phr TB, CB, OV, MLV, MLG, or MLR were heated at 160°C for t min $[(PVC–dye)_t]$. PVC film without dye was also heated under the same conditions $[(PVC)_t]$. The heated PVC film without dye was put on the unheated film containing 0.01 phr dye $[(PVC)_t/(PVC–dye)_0]$. The color of each layered film of $(PVC)_t/(PVC–dye)_0$ was the same as the color of film containing 0.01 phr of the corresponding dye with heating at 160°C for t min: $(PVC–dye)_t$. Similar phenomena were observed for all systems and heating times, except the system containing CB.

The results of colorimetry of PVC with MLV are shown in Figures 4–6. No color differences are observed between the single film $[(PVC–dye)_t]$ and the layered ones $[(PVC)_t/(PVC–dye)_0]$. Although a marked difference of hue is observed at 45 min, the difference between the −484 nm of $(PVC)_{45}/(PVC–MLV)_0$ and the 630 nm of $(PVC–MLV)_{45}$ is negligible. Moreover, this difference of hue between $(PVC)_{45}/(PVC–MLV)_0$ and $(PVC–MLV)_{45}$ could not be distinguished with the naked eye.

The values of substances which layer up two transparent films containing different color (Yc) can be calculated from the following equation based on the Lambert-Beer's law:

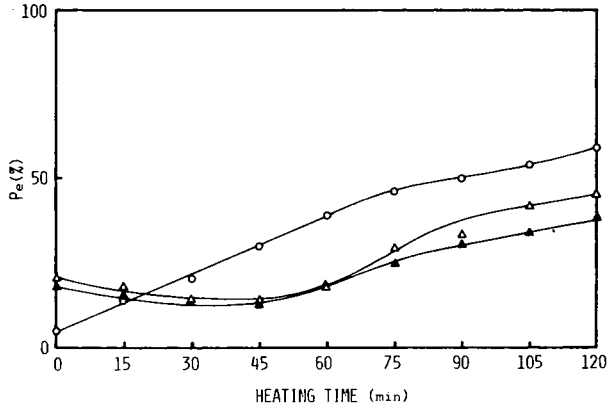

Fig. 5. Appreciation of color-mixing phenomenon evaluated by *Pe* in PVCs without (○) and with various dyes: 0.01 phr MLV (△) and the layered system of $(PVC)_t/(PVC\text{–}MLV)_0$ (▲). Each PVC film contained 20 phr DOP. Films heated at 160°C.

$$Yct = 100(Ypt/100) \times (Yd/100) \tag{2}$$

where *Ypt* and *Yd* represent *Y* of $(PVC)_t$ and $(PVC\text{–dye})_0$, respectively.

The color change involving the heated PVC with each dye should satisfy the following equation, where α and β must be 1 and 0, respectively, if the dyes have not decomposed in PVC by heating:

$$Yot = \alpha Yct + \beta \tag{3}$$

where *Yot* represents the *Y* of $(PVC\text{–dye})_t$. The calculated *Yct*, therefore, should be identical with *Yft*, which is the experimental *Y* of $(PVC)_t/(PVC\text{–dye})_0$. Accordingly, the following relationship may also be valid:

$$Yot = \alpha Yft + \beta \tag{4}$$

The calculated *Yct* in the system PVC–MLV, for example, is shown in Figure 6. The relationships of *Yot* and *Yct* or *Yft* are shown in Figure 7. A linear re-

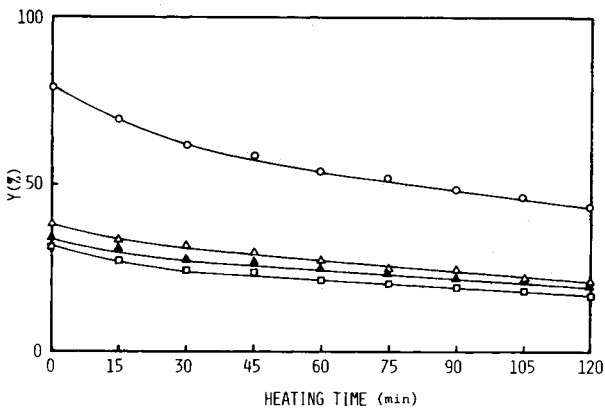

Fig. 6. Appreciation of color-mixing phenomenon evaluated by *Y* in PVCs without (○) and with various dyes: 0.01 phr MLV (△), layered system of $(PVC)_t/(PVC\text{–}MLV)_0$ (▲), and the calculated system of $100(Ypt/100) \times (Yd/100)$ (□). Each PVC film contained 20 phr DOP. Films heated at 160°C.

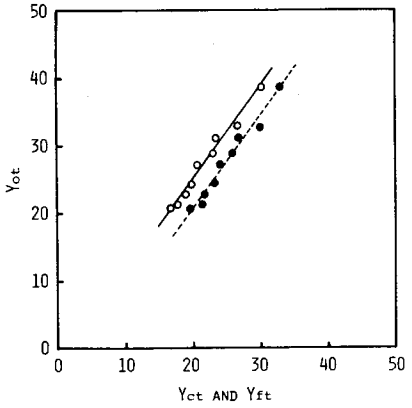

Fig. 7. Examination of color-mixing phenomenon for the calculated system of $Yot = \alpha Yct + \beta$ (○) and the layered system of $Yot = \alpha Yft + \beta$ (●). Each film contained 20 phr DOP. Films heated at 160°C.

lationship exists in both systems. Additionally, the α and β [eqs. (3) and (4)], which are calculated by the least-squares method, are summarized in Table I. α and β for all systems, except PVC–CB system, are equal to unity within colorimetric error. The differences in β may be due to the light scattering which occurs in surfaces of a layered film.

The thermal color changes which appear in PVC containing dyes depend on the color-mixing phenomenon of polyenes and dyes. The color change which appeared in heated PVC with CB depends on the presence of salts of alkali metal or alkali earth metal in the dye; and the color of PVC containing CB turns to red at 60 min or more (Fig. 1).

The results fully support the previous deductions[2–6] that stabilization of PVC is due to the compensation of the polyene color by adding chromophores or developers to produce cool colors. These, in turn, set up complementary colors with the polyene color.

The authors wish to thank Sanyo Kako Co., Ltd. for the various dyes and color-mixing technology and Mr. M. Sasama for his assistance in the experimental work.

TABLE I
Evaluation of Color Mixing[a]

Dye	System	α	β
TB	Calculated	1.11	8.76
	Layered	1.00	8.55
CB	Calculated	2.05	−24.1
	Layered	1.69	−19.0
OV	Calculated	1.27	−1.01
	Layered	1.23	−3.79
MLV	Calculated	1.31	−1.29
	Layered	1.31	−5.47
MLG	Calculated	1.39	−5.94
	Layered	1.21	−4.30
MLR	Calculated	1.20	2.14
	Layered	1.40	−7.70

[a] Values of calculated system were obtained from $Yot = \alpha Yct + \beta$. Values of layered system were obtained from $Yot = \alpha Yft + \beta$.

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