Stabilization of Poly(vinyl Chloride). III. Synergism Between Metal Soaps and Masking Agents on the Stabilization of Poly(vinyl Chloride)

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Synopsis

The stabilization mechanism by synergetic metal soaps containing complementary colors was previously reported. With increased heating times, the color of heated poly(vinyl chloride) (PVC) films containing Cd/Ba and Zn/Ca synergetic soaps markedly deviated from the polyene color. These color deviations usually decreased the thermal stability of PVC. Discoloration from polyene color to blue appeared especially on PVC films containing Zn/Ca synergetic soap and was concomitant with a marked decrease in thermal stability. The stabilization of PVC containing synergetic metal soaps can be improved by masking or removing the excessive color. In this work, the addition of various masking agents, such as ethylenediaminetetraacetic acid, o-phenanthroline, triethanolamine, urea, N,N'-dimethylolurea, melamine, stearylamide, and lactams, to PVC containing synergetic metal soaps was investigated. It was shown that these masking agents do markedly slow down the discoloration of PVC.

INTRODUCTION

The color difference observed in heated poly(vinyl chloride) (PVC) film containing various metal soaps depends on the formation of π-complex of double bonds in the polyene chains with metal chloride which are produced by the corresponding metal soap.[1] From the fact that synergetic metal soaps are a mixture of warm color- and cool color-producing soaps, it has also been shown that the stabilization mechanism of synergetic metal soaps is based on the effect of complementary colors.[2]

The possibility of stabilizing PVC on the basis of complementary colors was developed from the following:[3,4] (1) An examination of the combination of two or more metal salts, based on colorimetry, in order to discover new synergetic combinations which set up complementary color relationships in PVC; (2) the addition of pigments or dyes which resulted in colors complementary with the polyene color; (3) the addition of chromophores and developers to synthesize the pigment or dye which set up complementary colors with the polyene color in PVC film by using liberated hydrogen chloride from dehydrochlorination of PVC. These methods employed colorimetry in order to keep PVC colorless during the addition of colors or various chromophores and developers which set up complementary colors in PVC; some of them have been put to practical use.

The color of heated PVC containing Cd/Ba and Zn/Ca synergetic soaps changed from a polyene color to Cd-complex and Zn-complex colors with increased heat treatment; this was due to the marked formation rate, or coloration rate, of Cd complex and Zn complex, respectively.[2] Discoloration from a polyene color to Zn-complex color (blue), observed especially on PVC films containing Zn/Ca synergetic soap in the early heating stage, markedly inhibits the stabilization of PVC.[2] This phenomenon in the PVC–Zn/Ca system has been called "zinc burning." The thermal stability of PVC containing metal soaps may be improved by the addition of some substance which masks the available metal chloride, which is produced from the corresponding metal soap, in order to inhibit the excessive formation of metal π-complex.

As the π-complex was broken down in the presence of tetrahydrofuran, N,N'-dimethylformamide, acetone, and ammonia,[1] the color of the complex markedly disappears. Longer heat efficiencies of synergetic metal soaps would be expected following the addition of some compounds containing nitrogen or oxygen atoms.

In the present work; the effects of adding various nitrogen-containing substances to PVC containing synergetic metal soaps are studied. The heat efficiencies of the synergetic soaps were improved by the addition of these substances, owing to their masking effects.

EXPERIMENTAL

Materials

PVC used in this work was Geon 103 EP; commercially available di(2-ethylhexyl) phthalate (DOP), metal stearates, and various nitrogen-containing compounds were used.

Preparation of PVC Film

PVC, DOP, metal stearate, and masking agent were milled, respectively, on an open roll (4 × 8 in.) at 150°C for 5 min. Each PVC film contained 20 phr DOP and 3 phr synergetic metal soaps. The compounded PVC films, about 0.5 mm in thickness, were heated at 160° ± 2°C in a gear oven. During compression of the roll films, the process time was minimized in order to avoid a heat history.

Colorimetry

PVC films were investigated by colorimetry at room temperature by using a Suga Shikenki Model AU-SCH-2 differential colorimeter.

Absorbance of Ultraviolet Spectrum

Ultraviolet absorbances of heated PVC, dissolved in tetrahydrofuran (2 g/l.), were obtained by using a Shimadzu Seisakusho Model MPS-50L spectrophotometer at room temperature.
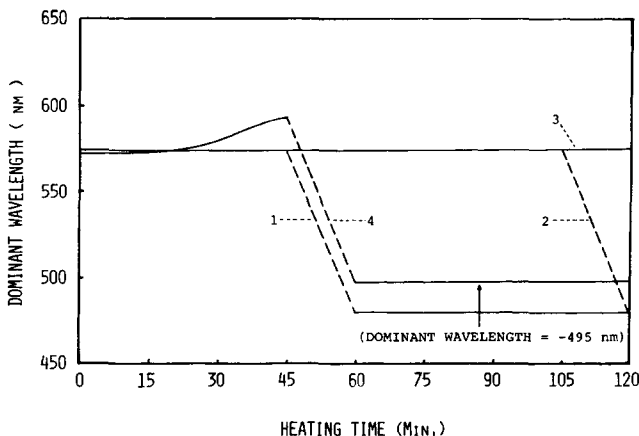
Fig. 1. Masking effect of TEA evaluated by dominant wavelength: (1) PVC 100, DOP 20, and Zn/Ca(2/1)-st 3.0; (2) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and TEA 0.2; (3) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and TEA 0.4–3.0; (4) PVC 100, DOP 20, and TEA 1.0; heated at 160°C.
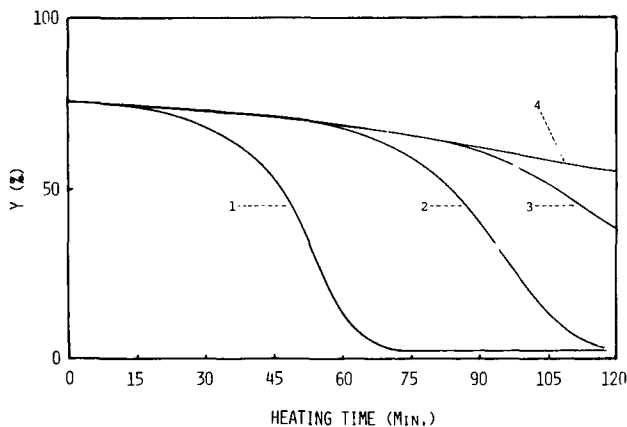

Fig. 2. Masking effect of TEA evaluated by Y: (1) PVC, 100 DOP 20, and Zn/Ca(2/1)-st 3.0; (2) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and TEA 0.2; (3) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and TEA 0.4; (4) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and TEA 0.6–3.0; heated at 160°C.
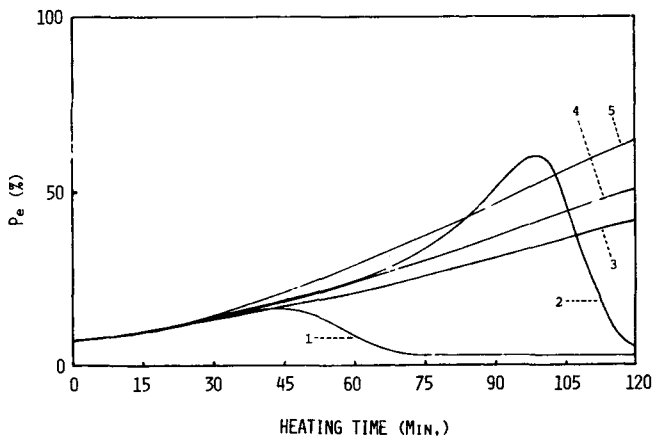

Fig. 3. Masking effect of TEA evaluated by Pe: (1) PVC 100, DOP 20, and Zn/Ca(2/1)-st 3.0; (2) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and TEA 0.2; (3) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and TEA 0.4–0.8; (4) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and TEA 1.0–2.0; (5) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and TEA 3.0; heated at 160°C.
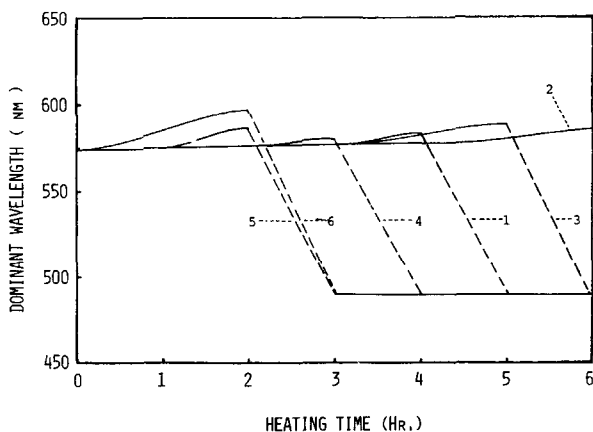
Fig. 4. Masking effect of TEA evaluated by dominant wavelength: (1) PVC 100, DOP 20, and Cd/Ba(2/1)-st 3.0; (2) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.2; (3) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.4; (4) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.6; (5) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.8–1.0; (6) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 2.0–3.0, heated at 160°C.
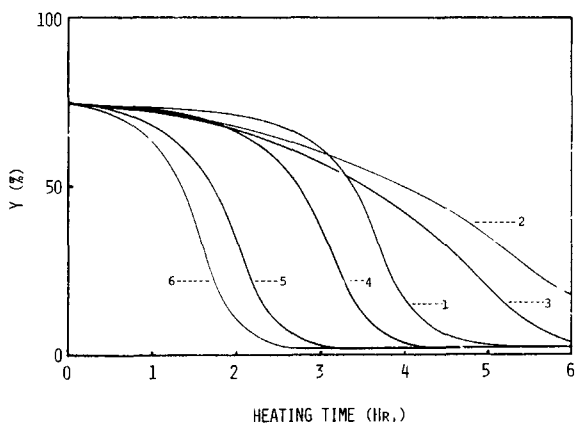

Fig. 5. Masking effect of TEA evaluated by Y: (1) PVC 100, DOP 20, and Cd/Ba(2/1)-st 3.0; (2) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.2; (3) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.4; (4) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.6; (5) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.8–1.0; (6) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 2.0–3.0; heated at 160°C.

RESULTS AND DISCUSSION

A study was made of the synergetic metal soaps and 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, and 3.0 phr ethylenediaminetetraacetic acid (EDTA), o-phenanthroline (OPH), triethanolamine (TEA), urea, N,N'-dimethylolurea (DMU), melamine, stearylamide, ε-caprolactam (CAL), and ω-laurolactam (LAL), respectively, and their synergistic effects on the thermal stabilization of PVC. These substances were found to retard the discoloration of PVC containing synergetic metal soaps.

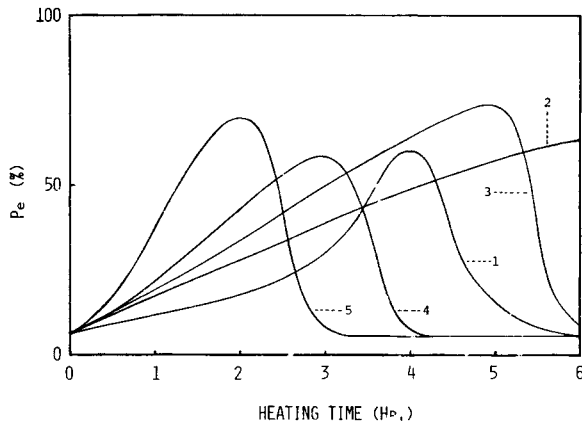The effects of TEA and DMU, for example, on color changes in heated PVC

Fig. 6. Masking effect of TEA evaluated by Pe: (1) PVC 100, DOP 20, and Cd/Ba(2/1)-st 3.0; (2) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.2; (3) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.4; (4) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.6; (5) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.8–3.0; heated at 160°C.
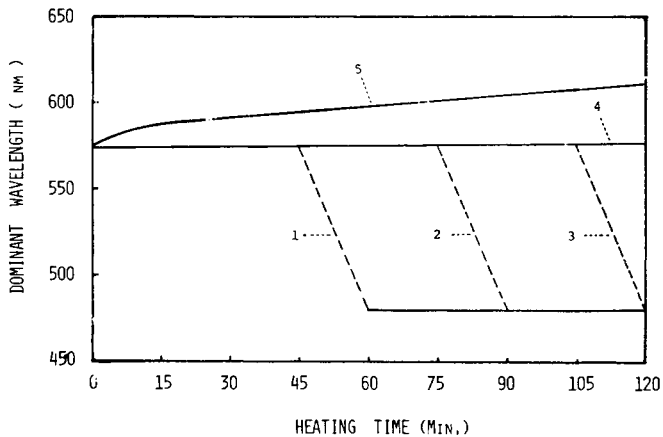

Fig. 7. Masking effect of DMU evaluated by dominant wavelength: (1) PVC 100, DOP 20, and Zn/Ca(2/1)-st 3.0; (2) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and DMU 0.2; (3) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and DMU 0.4; (4) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and DMU 0.6–3.0; (5) PVC 100, DOP 20, and DMU 1.0; heated at 160°C.

containing 3 phr of Cd/Ba (2/1) stearate (Cd/Ba-st) or Zn/Ca (2/1) stearate (Zn/Ca-st) synergetic soaps are shown in Figures 1 to 12. In these figures, dominant wavelength (λ_d), Pe, and Y correspond, respectively, to hue, chroma, and value based on colorimetry.

The Zn-complex and Cd-complex colors appear at 45 min and 3 hr in the PVC–Zn/Ca-st and PVC–Cd/Ba-st systems, respectively, while the polyene color is retained for longer heat treatment times when TEA or DMU is added, as shown
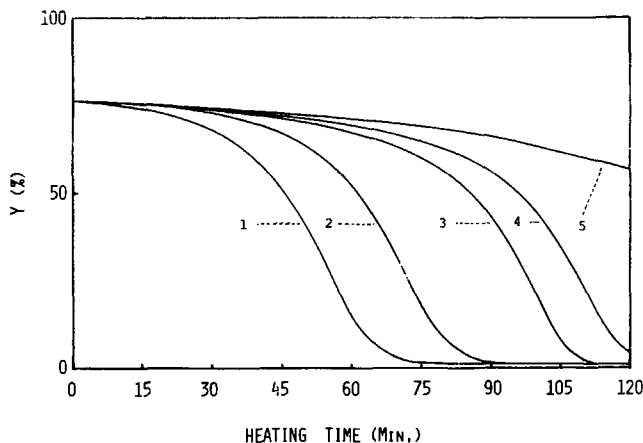
Fig. 8. Masking effect of DMU evaluated by Y: (1) PVC 100, DOP 20, and Zn/Ca(2/1)-st 3.0; (2) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and DMU 0.2; (3) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and DMU 0.4; (4) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and DMU 0.6–0.8; (5) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and DMU 1.0–3.0; heated at 160°C.
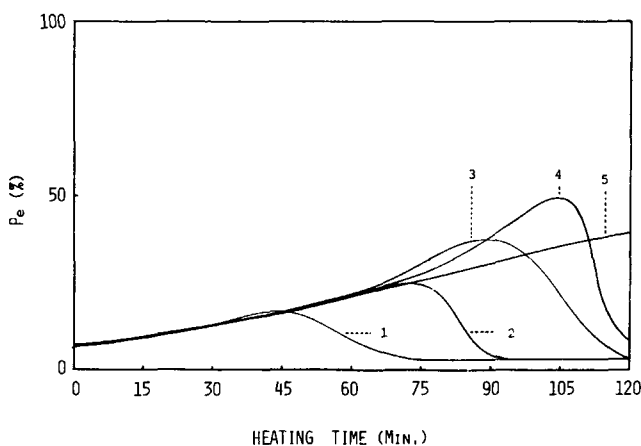

Fig. 9. Masking effect of DMU evaluated by Pe: (1) PVC 100, DOP 20, and Zn/Ca(2/1)-st 3.0; (2) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and DMU 0.2; (3) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and DMU 0.4; (4) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and DMU 0.6–0.8; (5) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and DMU 1.0–3.0; heated at 160°C.

in Figures 1, 4, 7, and 10. This means that the available $ZnCl_2$ or $CdCl_2$, produced by the corresponding soaps, is masked by the addition of TEA or DMU and that, subsequently, the Zn-complex color (λ_d = 470 nm) and Cd-complex color (λ_d = 485 nm) are removed.

As shown in Figures 2, 5, 8, and 11, TEA and DMU inhibit decrease in Y, due to masking of the Zn-complex and Cd-complex colors. Increase in Pe is also inhibited by TEA and DMU, as shown in Figures 3, 6, 9, and 12. Pe decreases after attaining a maximum caused by the decrease in Y.
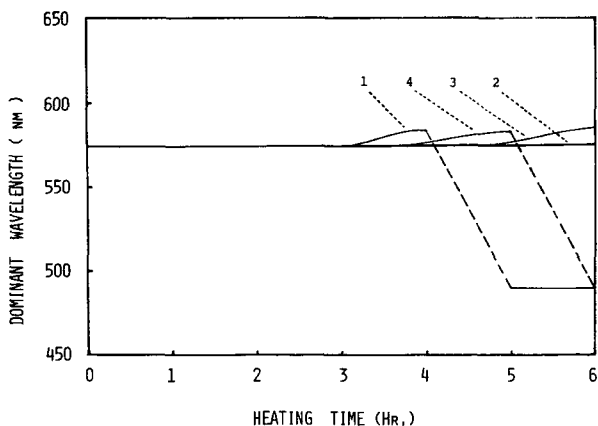
Fig. 10. Masking effect of DMU evaluated by dominant wavelength: (1) PVC 100, DOP 20, and Cd/Ba(2/1)-st 3.0; (2) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 0.2; (3) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 0.4–1.0; (4) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 2.0–3.0; heated at 160°C.
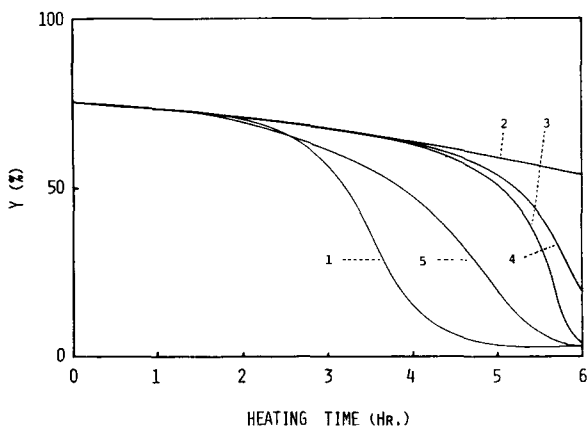

Fig. 11. Masking effect of DMU evaluated by Y: (1) PVC 100, DOP 20, and Cd/Ba(2/1)-st 3.0; (2) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 0.2; (3) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 0.4–0.6; (4) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 0.8–1.0; (5) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 2.0–3.0; heated at 160°C.

Further addition of masking agents, except OPH, CAL, and EDTA, resulted in greater slowing of the discoloration of PVC containing Zn/Ca-st. On the other hand, further addition of masking agents, except melamine, accelerates the discoloration of PVC containing Cd/Ba-st. The heated PVC–Zn/Ca-st system containing large amounts of OPH, CAL, and EDTA and the PVC–Cd/Ba-st system containing large amounts of masking agents, except melamine, show a characteristic reddish color which appeared on heated PVC films compounded with only nitrogen-containing substances. This means that the $ZnCl_2$ and $CdCl_2$
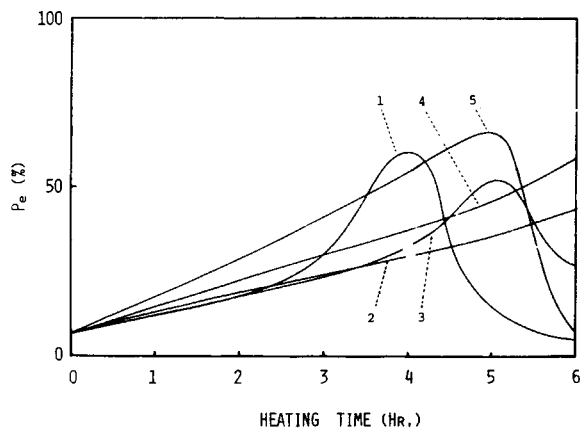
IIDA ET AL.

Fig. 12. Masking effect of DMU evaluated by Pe: (1) PVC 100, DOP 20, and Cd/Ba(2/1)-st 3.0; (2) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 0.2; (3) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 0.4–0.6; (4) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 0.8–1.0; (5) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 2.0–3.0; heated at 160°C.
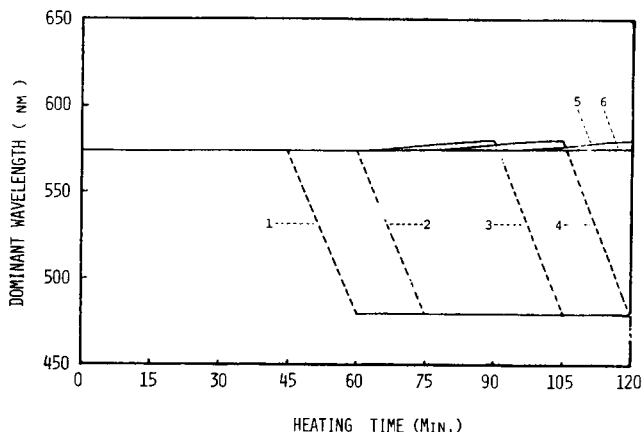

Fig. 13. Masking effects of various masking agents upon the stabilization of PVC: (1) PVC 100, DOP 20, and Zn/Ca(2/1)-st 3.0; (2) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and LAL 3.0, CAL 0.6, EDTA 0.6 or OPH 0.4; (3) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and stearylamide 3.0; (4) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and urea 3.0; (5) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and melamine 3.0; (6) PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and TEA 3.0 or DMU 3.0; heated at 160°C.

are completely masked by the addition of large amounts of OPH, CAL, and EDTA and all substances, except melamine. Accordingly, it is necessary, in order to stabilize PVC, that suitable amounts of masking agents must be combined to retain the efficient Zn-complex or Cd-complex colors which keep PVC colorless resulted in complementary colors with polyene color in PVC.

The masking effects of substances other than TEA and DMU are shown in Figures 13 and 14. Each substance slows down the discoloration of PVC containing Zn/Ca-st or Cd/Ba-st because of its masking effect.

The blue, which is observed in mixtures of zinc chloride and vitamin A, disappears upon the addition of masking agents; the disappearance is less for tetrahydrofuran, N,N'-dimethylformamide, acetone, and ammonia[1] due to the poor solubility of these masking agents in zinc chloride and vitamin A mixtures.
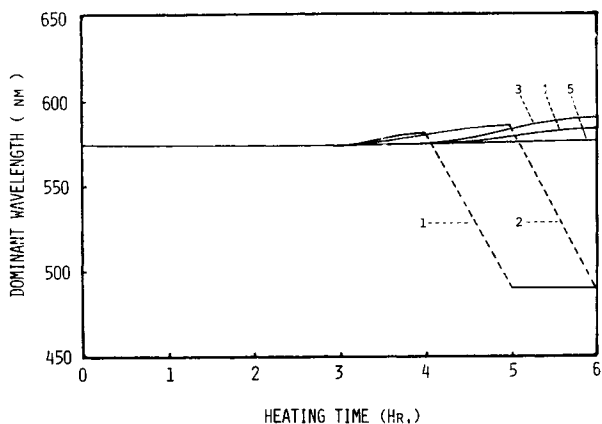
Fig. 14. Masking effects of various masking agents upon the stabilization of PVC: (1) PVC 100, DOP 20, and Cd/Ba(2/1)-st 3.0; (2) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and CAL 0.8, LAL 0.2, or EDTA 0.2; (3) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and melamine 3.0 or DMU 0.2; (4) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and stearylamide 1.0 or TEA 0.2; (5) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and urea 0.2; heated at 160°C.
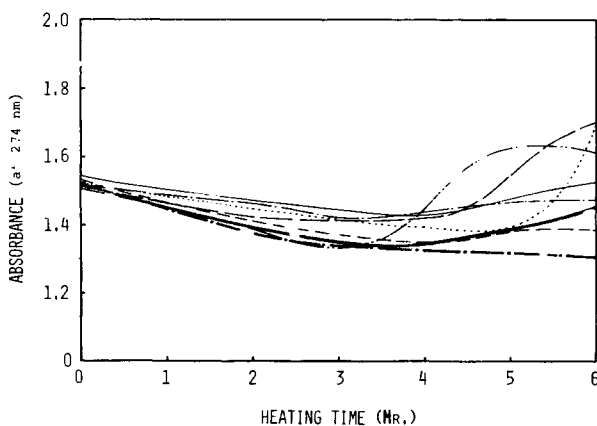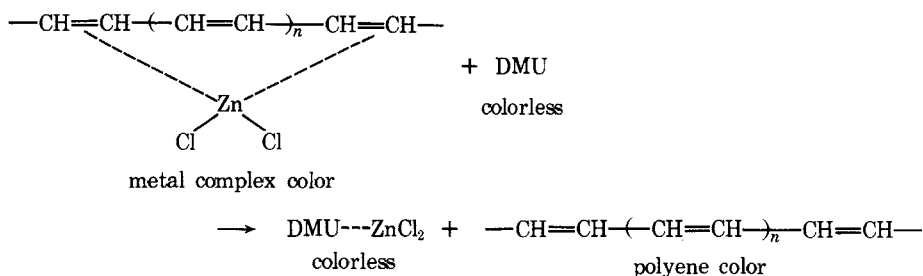

Fig. 15. Effects of masking agents upon the dehydrochlorination of PVC: (——·——) PVC 100 and DOP 20; (———) PVC 100, DOP 20, and Cd/Ba(2/1)-st 3.0; (———) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and urea 0.6; (——·—)PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and DMU 0.6; (——··—) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and TEA 0.6; (— —) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and EDTA 0.6; (– – –) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and stearylamide 0.6; (- - - - - - - - -) PVC 100, DOP 20, Cd/Ba(2/1)-st 3.0, and melamine 0.6; heated at 160°C.

Ultraviolet absorbance at 274 nm observed in the heated PVC–BCd/Da-st system containing various masking agents is shown in Figure 15. The dehydrochlorination of PVC is accelerated by the addition of various masking agents. A similar tendency was observed with ultraviolet absorbance at other wavelengths. As shown in Figure 15, these masking agents stabilize PVC in spite of their great ability to accelerate the dehydrochlorination of PVC.

The above results indicate that the stabilization mechanism for masking agents can be illustrated, for example, as follows:

$$—CH{=}CH{-}({-}CH{=}CH{-})_{\overline{n}}{-}CH{=}CH{-}$$

+ DMU

colorless

(with Zn, Cl, Cl complex below)

metal complex color

$$\longrightarrow \quad DMU{-}{-}{-}ZnCl_2 \quad + \quad —CH{=}CH{-}({-}CH{=}CH{-})_{\overline{n}}{-}CH{=}CH{-}$$

colorless   polyene color

The structure of the metal π-complex has not been completely identified, since the isolation and analysis of this complex were difficult. The n may be presumed to be at least 3 or more, because the mixtures of zinc chloride and vitamin A[1] or β-carotene are blue in color.

The proposed stabilization mechanism for masking agents is well supported by the fact that the stabilization effect of these masking agents could not be observed on PVC films without metal soaps and that the stabilization of PVC was markedly affected by the combined use of these masking agents and the metal soaps. PVC films containing TEA or DMU alone showed a characteristic reddish color in the early heating stage, as shown in Figures 1 and 7.

CONCLUSIONS

The stabilization effect of masking agents does not depend on their influence on dehydrochlorination of PVC, but rather on their ability to mask the excessive π-complex color.

The stabilization mechanism for polyols and sulfur-containing compounds is probably based on their masking effects, since the blue which was observed in mixtures of zinc chloride and vitamin A was discolored by the addition of alcohols and sulfur-containing compounds.

Since the compatibility of some masking agents investigated in the present work was poor, modification of various amino acids, aminopolycarboxylates, acidic amides, urea, and other nitrogen-containing compounds should be carried out in order to improve their compatibility with PVC.

Moreover, the stability of PVC may be improved by the introduction into the PVC chains of groups having a masking ability and by blending PVC with polymers containing atoms or groups exhibiting masking effects.

References

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