Stabilization of Poly(vinyl Chloride). VI. Synergetic Effects of Aminopolycarboxylates or Nitrogen-Containing Agents with Zinc Stearate/Calcium Stearate Soap

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Synopsis

Discoloration such as zinc burning was observed in aged poly(vinyl chloride) (PVC) compounded with synergetic soaps. This discoloration was caused by excessive formation of cool color-producing π complexes formed between double bonds in polyene chain and zinc chloride or cadmium chloride produced from the corresponding metal soap. The appearance of excessive color of the π complexes was reduced by adding some masking agents into PVC admixed with synergetic soaps. In the present study differences in masking effects results by adding solid or an aqueous solution of aminopolycarboxylates such as glycine, ethylenediaminetetraacetates, and nitrilotriacetates to PVC stabilized with zinc stearate/calcium stearate synergetic soap. The mechanism of synergetic effect between nitrogen-containing agents and synergetic soaps upon the stabilization of PVC is also investigated by colorimetry. The aqueous solution of aminopolycarboxylates exhibits a greater masking effect than the solid. The masking effect of aminopolycarboxylates depends on the ease with which they are finely dispersed into PVC. Colorimetry indicated that the masking effect of aminopolycarboxylates and other nitrogen-containing agents depends on forming the colorless complex compound with the excessive cool color-producing metal chlorides.

INTRODUCTION

The different colorations observed in aged poly(vinyl chloride) (PVC) compounded with various metal salts were caused by the coloration of π complex of double bonds in a polyene chain with metal chloride converted from the added metal salt.[1] The abrupt discolorations of aging PVC compounded with synergetic metal soap are caused by the excessive coloration of cool color-producing π complexes formed between double bonds and zinc chloride or cadmium chloride converted from the corresponding metal soap.[2]

The combined use of synergetic metal soaps and some masking agents resulted in a reduced effect on the discoloration of PVC, owing to the masking ability of the agents to form the colorless complex compound with cool color-producing metal chloride.[3–5] In particular, nitrogen-containing agents exhibited a marked effect involving some decrease in initial color.[3,4]

Although the masking effect of ethylenediaminetetraacetate has been reported in a previous article,[3] the influence of glycine, ethylenediaminetetraacetates, and nitrilotriacetates dispersions upon the stabilization of PVC are investigated in the present work.

The masking effect of these agents is markedly improved by adding them as an aqueous solution, owing to their fine dispersion into PVC. It is also confirmed from various colorimetries that the masking effect of aminopolycarboxylates

Journal of Applied Polymer Science, Vol. 25, 1407–1417 (1980)

0021-8995/80/0025-1407$01.10

and other nitrogen-containing agents is due to their abilities to form the colorless complex compound with excessive or harmful cool color-producing metal chloride.

EXPERIMENTAL

Materials

PVC used in this work was Geon 103 EP. Commercially available di(2-ethylhexyl)phthalate (DOP), metal stearates, and aminopolycarboxylates were also used.

Preparation of Film Specimens

Mixtures of PVC and 20 phr DOP, with or without additives, were milled in an open roll (4 × 8 in.) at 150°C for 5 min. The synergetic metal soap used in this work was a mixture of zinc stearate and calcium stearate, which was mixed with 2:1 composition by weight [Zn/Ca(2/1)-st].

The compounded PVC film specimens (0.5 mm in thickness, 50 mm in width and 50 mm in length) were heated at 160 ± 2°C up to 120 min in a circulating air oven.

This study was made with granules of less than 60-mesh particle size or an aqueous solution of glycine, ethylenediaminetetraacetic acid (EDTA), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), ethylenediaminetetraacetic acid tetrasodium salt (EDTA-4Na), nitrilotriacetic acid (NTA), nitrilotriacetic acid disodium salt (NTA-2Na), and nitrilotriacetic acid trisodium salt (NTA-3Na). Each aqueous solution was prepared in accordance with the amounts of aminopolycarboxylate dissolved in 10 ml distilled water. The aqueous solution was mixed with the undissolved part, even when the dissolving agent exhibited poor solubility in water.

Colorimetry

PVC films were investigated by colorimetry at room temperature using a Suga Shikenki model AU-CH-1D differential colorimeter mounting a specimen holder window of 30 mm in diameter. Tristimulus values of each film were determined by averaging the values recorded from three different places on the film surface, using a white color standard plate ($Y = 84.5$, $X = 82.4$, and $Z = 93.7$) as a reflector.

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.

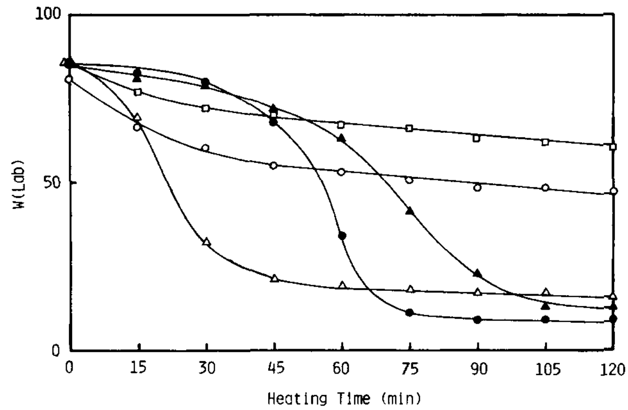

Fig. 1. Stabilization effect of aminopolycarboxylates. PVC 100 and DOP 20 (○); PVC 100, DOP 20, and Zn/Ca(2/1)-st 3.0 (●); PVC 100, DOP 20, and glycine 1.0 (△); PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and glycine 3.0 (▲); and PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and glycine(aq) 0.4 (□) were milled at 150°C for 5 min and heated at 160°C.

RESULTS AND DISCUSSION

Masking Effect of Aminopolycarboxylates

Various discolorations of PVC with or without additives are shown in Figures 1 and 2. These figures illustrate the relationship between the whiteness in *Lab* color system [*W*(*Lab*)] and heating time.[5]

Zinc burning, which is caused by excessive zinc chloride–polyene complex color, is observed at 45 min as for stabilized control. With regard to PVC alone, the polyene color (yellow–orange) is developed with increasing heat. In particular, PVC with glycine alone shows the characteristic reddish color which appears on aged PVC films containing excessive nitrogen-containing agent[3] and grows deeper with increasing heat. *W*(*Lab*) of PVC with glycine alone is much less than for PVC alone.

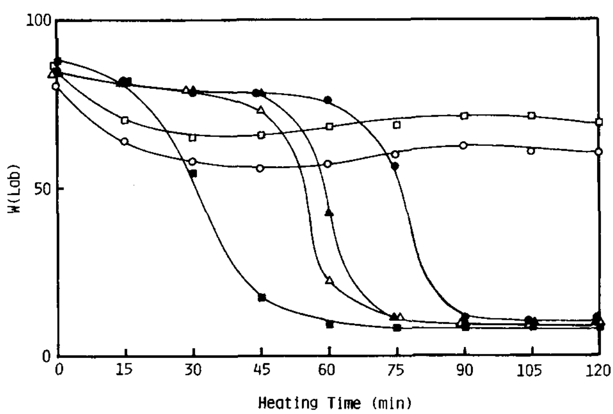

Fig. 2. Stabilization effect of aminopolycarboxylates. PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and EDTA-4Na 3.0 (●); PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and EDTA-4Na(aq) 1.0 (○); PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and NTA 3.0 (▲); PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and NTA(aq) 3.0 (△); PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and NTA-3Na 3.0 (■); and PVC 100, DOP 20, Zn/Ca(2/1)-st 3.0, and NTA-3Na(aq) 1.0 (□) were milled at 150°C for 5 min and heated at 160°C.

In the case of combined use with synergetic soap, a different effect is observed between aqueous solution and solid particles of glycine, NTA-2Na, NTA-3Na, and EDTA-4Na. On the other hand, no masking effect is observed in either of aqueous solution and granule of EDTA and NTA.

The masking effect of various aminopolycarboxylates is summarized in Tables I and II based on Figures 1 and 2. The aminopolycarboxylates do not stabilize PVC without synergetic soap, and no masking effect is observed by adding them as a solid particle (Table I). On the other hand, aqueous solutions of aminopolycarboxylates, except EDTA and NTA, delay the appearance of zinc burning compared to stabilized control. This occurs because $\lambda d(f)$ is not shifted to a lower wavelength which corresponds to λd of zinc chloride–polyene complex color (λd = 475 nm).[2]

In particular, 0.4 or more phr glycine(aq) and 1.0 or more phr EDTA-4Na(aq) and NTA-3Na(aq) inhibit completely the appearance of zinc burning up to 120 min (Table II). No significant prolongation of good initial color for these systems was observed with increased additions.

The marked discoloration caused by the appearance of characteristic reddish colors (λd = 611 to −526 nm; red or red purple) observed on the PVC films with nitrogen-containing agents alone appeared on the PVC compounded with 3.0 phr Zn/Ca(2/1)-st and 0.8 or more phr glycine(aq). Hence, the appearance of characteristic reddish color is due to the excessive additions of glycine related to the amount of converted zinc chloride. Additionally, the decrease of the good initial color of PVC compounded with nitrogen-containing agent and synergetic soap is caused by the appearance of the reddish colors.

The color mixture of zinc chloride–polyene complex and the reddish color appears on aging PVC compounded with 3.0 phr Zn/Ca(2/1)-st and 1.0 or more phr NTA-2Na(aq) (Table II). Moreover, three-step changes of $W(Lab)$ are observed as for 1.0 or more phr EDTA-4Na(aq) and NTA-3Na(aq) systems (Fig. 2). $W(Lab)$ of these systems decreased markedly up to 15 min and then increased with increasing heat. A similar phenomenon was observed in Zn/Ca(2/1)-st–NTA-2Na(aq) system.

Although the details of the mechanism for the reddish color have not been resolved completely, it may be suggested that the coloration is due to the interaction between nitrogen atoms in the agents and oxygen or hydrogen chloride. The second-step decoloration for Zn/Ca(2/1)-st–NTA-2Na(aq), NTA-3Na(aq), or EDTA-4Na(aq) systems should be due to the disappearance of the reddish color. This is caused by dissociation of the nitrogen atoms and oxygen or hydrogen chloride interactions which are formed in the early heating stage. This resulted from the coordination of zinc chloride converted from zinc stearate to the nitrogen-containing agents.

Influence of Dispersion

Different effects are observed in the case of an aqueous solution and a solid particle of aminopolycarboxylates (Tables I and II).

Solubilities of glycine, NTA, NTA-2Na, and NTA-3Na in water at 25°C are 25.0, 0.15, 49, and 96, respectively, and those of EDTA, EDTA-2Na, and EDTA-4Na at 22°C are 0.2, 10.8, and 60, respectively. Ten milliliters of water, therefore, dissolve each amount of EDTA-4Na, NTA-2Na, and NTA-3Na to be added.

The effect of aminopolycarboxylates compounded as an aqueous solution depends on the solubility of each agent (Table II). When adding them as solids, undispersed granules were observed in all films. On the other hand, when employing the aqueous solution, aminopolycarboxylates, except NTA, EDTA, and EDTA-2Na, exhibited fine dispersion in PVC.

The blooming phenomenon was observed on films compounded with synergetic soap and granule aminopolycarboxylates, which were allowed to stand for one year at room temperature, while the phenomenon was not evident in films compounded with Zn/Ca(2/1)-st and glycine, NTA-2Na, NTA-3Na, EDTA-2Na, or EDTA-4Na as an aqueous solution.

In adding water-soluble agents as an aqueous solution, the masking effect is greater than with granules (Tables I and II). Additionally, the characteristic reddish color appearing in the PVC films that were compounded with a larger amount of nitrogen-containing agents is considerably reduced with smaller amount. This is due to fine dispersion of aminopolycarboxylates.

The amount of masking agents used can be decreased by dispersing them in PVC or in the vicinity of the compounded metal soaps.

Stabilization Mechanism of Nitrogen-Containing Agents

Although the nitrogen-containing agents inhibited the appearance of zinc burning, they accelerated the dehydrochlorination of PVC with or without synergetic soap.[3,4]

The heat dependence of absorbance ratios between 274 and 363 nm is illustrated in Figure 3, as for nitrogen-containing agent alone. The absorbance at 363 nm indicates the formation of a longer polyene chain which causes discoloration of PVC.[6,7] The nitrogen-containing agents do not inhibit the formation of longer polyene chains.

From the fact that the stabilization effect of nitrogen-containing agents could not be observed in PVC without metal soap and that the stabilization of PVC was markedly improved by combined use of these agents and the synergetic metal soap, it is concluded that the stabilization effect of nitrogen-containing agents depends on the formation of the colorless complex compound.

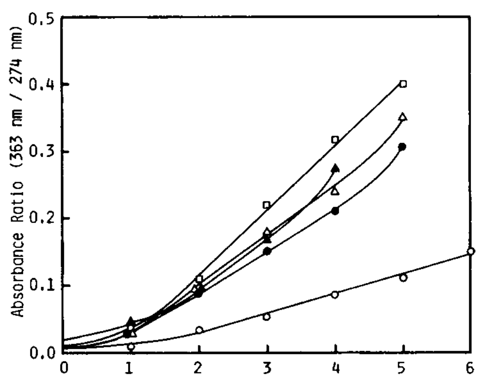

Fig. 3. Effects of nitrogen-containing agents upon the dehydrochlorination of PVC. PVC 100 and DOP 20 (○); PVC 100, DOP 20, and urea 1.0 (△); PVC 100, DOP 20, and stearylamide 1.0 (●); PVC 100, DOP 20, and N,N′-dimethylolurea 1.0 (▲); and PVC 100, DOP 20, and triethanolamine 1.0 (□) were milled at 150°C for 5 min and heated at 160°C.

TABLE I
Stabilization Effect of Aminopolycarboxylates (Solid)[a]

Additive[b]	phr	W_0	t_E, min	W_M	t_L, min	W_L	$W_0 - W_M$	$W_0 - W_L$	$\lambda d(i)$, nm	$\lambda d(f)$, nm
PVC	—	81	—	—	120	47	—	34	575	582
Glycine	1.0	86	—	—	120	16	—	70	574	−496
EDTA	1.0	87	—	—	120	48	—	39	574	582
EDTA-2Na	1.0	85	—	—	120	27	—	58	576	594
EDTA-4Na	1.0	86	—	—	120	29	—	57	574	595
NTA	1.0	88	—	—	120	47	—	41	575	583
NTA-2Na	1.0	85	—	—	120	40	—	45	576	586
NTA-3Na	1.0	87	—	—	120	42	—	45	577	587
Zn/Ca(2/1)-st	3.0	85	45	80	120	8	5	77	573	494
Glycine[c]	0.8	87	45	81	120	11	6	76	573	492
	1.0	85	45	76	120	8	9	77	572	493
	1.5	86	45	79	120	11	7	75	573	488
	3.0	85	45	79	120	13	6	72	573	487
EDTA[c]	0.4	85	45	76	120	6	9	79	575	493
	1.0	85	45	76	120	6	9	79	573	400
	2.0	87	45	77	120	6	10	81	573	477
	3.0	88	45	72	120	7	16	81	575	502
EDTA-2Na[c]	0.4	86	45	79	120	5	7	81	573	495
	1.0	86	45	79	120	5	7	81	573	494

	2.0	86	45	80	120	8	6	78	572	493
	3.0	86	45	79	120	8	7	78	574	495
EDTA-4Na[c]	0.4	85	45	81	120	10	4	75	573	491
	1.0	85	45	80	120	8	5	77	575	496
	2.0	85	45	79	120	9	6	76	574	495
	3.0	85	45	78	120	10	7	75	574	495
NTA[c]	0.4	84	45	80	120	8	4	76	574	495
	1.0	84	45	82	120	7	2	77	574	496
	2.0	85	45	80	120	8	5	77	575	497
	3.0	86	45	79	120	10	7	76	575	496
NTA-2Na[c]	0.4	85	30	81	120	8	4	77	574	495
	1.0	85	30	81	120	7	4	78	574	495
	2.0	87	30	82	120	7	5	80	574	496
	3.0	87	30	82	120	6	5	81	574	494
NTA-3Na[c]	0.4	86	30	80	120	6	6	80	573	489
	1.0	87	30	82	120	8	5	79	573	489
	2.0	87	30	82	120	6	5	81	573	491
	3.0	88	30	82	120	8	6	80	573	493

[a] Heated at 160°C. W_0 represents $W(Lab)$ of unheated film. t_E is heating time for onset of zinc burning. W_M represents $W(Lab)$ at the heating time just before onset of zinc burning. t_L is the heating time attaining the lowest $W(Lab)$. W_L represents the lowest $W(Lab)$. $\lambda d(i)$ represents the dominant wavelength of unheated film. $\lambda d(f)$ represents the dominant wavelength of aged film which is heated for 120 min.

[b] Each film contained 20 phr DOP.

[c] 3.0 phr Zn/Ca(2/1)-st was compounded in each film.

TABLE II
Stabilization Effect of Aminopolycarboxylates (Aqueous Solution)[a]

Additive[b]	phr	W_0	t_E, min	W_M	t_L, min	W_L	$W_0 - W_M$	$W_0 - W_L$	$\lambda d(i)$, nm	$\lambda d(f)$, nm
Glycine(aq)	0.02	87	45	81	120	7	6	80	574	468
	0.1	86	90	74	120	7	12	79	574	492
	0.2	86	120	68	120	64	18	22	573	577
	0.4	86	—	—	120	60	—	26	574	578
	0.6	85	—	—	120	45	—	40	573	583
	0.8	79	90[c]	36	120	15	43	64	574	611
	1.0	83	75[c]	38	120	16	45	67	573	630
	1.5	83	60[c]	35	120	15	48	68	573	−526
	3.0	82	60[c]	28	120	16	54	66	574	−499
EDTA(aq)	0.4	85	45	73	120	5	12	80	572	495
	1.0	86	45	71	120	4	15	82	575	493
	2.0	86	45	54	120	9	32	77	572	494
	3.0	88	45	71	120	8	17	80	572	495
EDTA-2Na(aq)	0.4	86	45	82	120	6	4	80	573	487
	1.0	86	60	81	120	9	5	77	575	498
	2.0	86	75	76	120	12	10	74	575	491
	3.0	85	75	77	120	16	8	69	575	496
EDTA-4Na(aq)	0.4	82	105	66	120	60	16	22	575	576
	1.0	81	—	—	45	56	—	25	577	577

						(60)[d]		(21)		
	2.0	80	—	—	30	55	—	25	576	580
						(57)[d]		(23)		
	3.0	79	—	—	45	52	—	27	577	581
						(56)[d]		(23)		
NTA(aq)	0.4	85	45	79	120	11	6	74	573	493
	1.0	84	45	79	120	9	5	75	573	490
	2.0	84	45	78	120	9	6	75	573	494
	3.0	84	45	79	120	8	5	76	573	491
NTA-2Na(aq)	0.4	88	30	72	120	11	16	77	574	487
	1.0	85	75[e]	70	120	24	15	61	574	598
	2.0	87	90[e]	76	120	31	11	56	573	587
	3.0	87	105[e]	70	120	31	17	56	575	591
NTA-3Na(aq)	0.4	87	60	72	120	9	15	78	573	497
	1.0	87	—	—	30	65	—	22	573	576
						(69)[d]		(18)		
	2.0	87	—	—	75	55	—	32	575	581
						(58)[d]		(29)		
	3.0	86	—	—	120	53	—	33	573	582

[a] Heated at 160°C.
[b] Each film contained 20 phr DOP and 3.0 phr Zn/Ca(2/1)-st.
[c] The heating time when severe characteristic reddish color was observed.
[d] $W(Lab)$ at 120 min.
[e] The heating time when mixture of the reddish color and zinc chloride—polyene complex color was observed.

Identification of these colorless complexes in the PVC compounds was very difficult. We, therefore, carried out the colorimetry of various PVC films combined with the nitrogen-containing agent and metal soap which produces the metal chloride.

Coloration of aged PVC compound films is shown in Figure 4. In the *o*-phenanthroline–ferrous stearate system, a color change from red–orange to red–purple is observed with increasing heat. In *o*-phenanthroline–cupric stearate and melamine–cobalt stearate systems, a bluish color appeared even in roll mixing, and a greenish color appeared with increased heating. With urea–cobalt stearate and EDTA-2Na–cupric stearate systems, a greenish color appeared during roll mixing. The characteristic color that appeared in each system could not be observed in aged PVC films which were individually compounded with the same amount of corresponding nitrogen-containing agent alone or metal stearate alone. These nitrogen-containing agents exhibited marked masking effect with synergetic soaps.[3]

Thus, the characteristic color observed in each system is based on the formation of the complex compound of the agent with the metal chloride obtained from the corresponding metal stearate. The complex compounds are easily formed, even in compounded PVC. Different colorations are observed between EDTA-2Na–cupric stearate and *o*-phenanthroline–cupric stearate systems or between melamine–cobalt stearate and urea–cobalt stearate systems.

The colorless complex compound of nitrogen-containing agents with zinc chloride or cadmium chloride is formed in the presence of zinc stearate or cadmium stearate in aged PVC compounds.

CONCLUSIONS

The stabilization of PVC by nitrogen-containing agents does not depend on their influence in the dehydrochlorination of PVC, but rather on their ability to mask the excessive or injurious cool color-producing metal chlorides. But it is necessary to retain the efficient cool color-producing metal chlorides which keep PVC colorless in complementary colors relationship with polyenes.

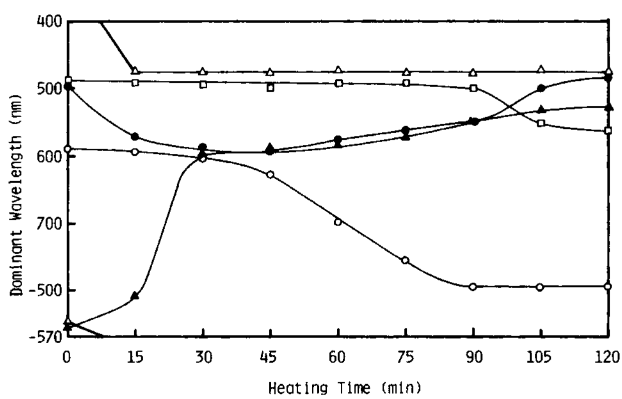

Fig. 4. Coloration of PVC compounded with various metal soaps and nitrogen-containing agents. PVC 100, DOP 20, ferrous stearate 0.1, and *o*-phenanthroline 0.1 (○); PVC 100, DOP 20, cupric stearate 3.0, and EDTA-2Na 3.0 (●); PVC 100, DOP 20, cupric stearate 0.1, and *o*-phenanthroline 0.1 (△); PVC 100, DOP 20, cobalt stearate 1.0, and melamine 3.0 (▲); and PVC 100, DOP 20, cobalt stearate 1.0, and urea 3.0 (□) were milled at 150°C for 5 min and heated at 160°C.

The discoloration of PVC should be inhibited by stopping the dehydrochlorination. But it is difficult to stop the dehydrochlorination of PVC, even by adding stabilizers such as metal soaps.[8,9] Moreover, the discoloration of PVC with synergetic metal soap was not necessarily dependent on the dehydrochlorination of PVC.[10]

The discoloration of PVC can be reduced even by adding masking agents which exhibit the effect of accelerating the dehydrochlorination of PVC containing synergetic soaps.

The authors wish to thank Miss A. Shitara and Mr. Y. Fujii for their assistance in the experimental work.

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Received October 31, 1979