An Investigation of Mechanisms of Synergistic Interactions in PVC Stabilization

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Synopsis

Synergism in poly(vinyl chloride) stabilization has been studied by measuring rates of hydrogen chloride evolution from samples of polymer in the presence of stabilizers in di-(2-ethylhexyl) phthalate solution in an inert atmosphere. Barium, cadmium, calcium, and zinc laurates, when used alone, allow escape of hydrogen chloride well before stoichiometric uptake is achieved, whereas synergistic mixtures of calcium–zinc and barium–cadmium laurates absorb almost the theoretical quantity of hydrogen chloride. Cadmium and zinc laurates replace labile chlorine atoms in the polymer backbone by ester groups, reducing formation of long polyene sequences: barium and calcium laurates delay the formation of cadmium and zinc chlorides, apparently by reconverting them into their respective laurates. Polyols function by forming complexes with the prodegradant cadmium and zinc chlorides, but contrary to popular belief phosphites possess little activity in this respect. Instead, they slow down the rate of polymer degradation by removal of labile chlorine atoms, by reaction with hydrogen chloride, and by peroxide decomposition.

INTRODUCTION

Although many workers have examined the mechanism of action of poly(vinyl chloride) stabilizers,[1] comparatively few have investigated the mechanism of synergistic stabilizer interactions. Synergism between metal laurates has been studied by several authors,[2–8] but only superficially in most cases. Nagatomi and Saeki[3] were able to measure the rates of formation of barium and cadmium chlorides individually in a barium–cadmium stearate-stabilized polymer, and found that cadmium chloride was not formed until nearly all of the barium stearate had reacted with hydrogen chloride. They assumed that barium stearate reacted more readily with hydrogen chloride than did cadmium stearate. Recently, Onozuka[5] has produced evidence which suggests that zinc chloride is formed first by action of hydrogen chloride upon a synergistic calcium–zinc stearate mixture, but that this is rapidly reconverted into its stearate by carboxylate interchange with calcium stearate.

Phosphite synergism received little fundamental study until two years ago, when Russian workers[9,10] discovered that phosphites improved the efficiency of metal stearates and proposed mechanisms to account for this observation.

In the present study, a detailed quantitative examination has been made of the rate of degradation in nitrogen at 180°C of poly(vinyl chloride) in the presence of phosphites, polyols, and phosphines, both alone and with metal laurates, and of calcium–zinc and barium–cadmium laurate blends. These studies provide results which enable a more comprehensive explanation of the mechanism of stabilizer interaction to be made.

EXPERIMENTAL

Materials

The poly(vinyl chloride) used in these studies was Corvic D50/16 suspension polymer (ICI Ltd., Plastics Division). No purification was attempted.

Triphenyl phosphite, tris(nonylphenyl) phosphite, diphenyl isodecyl phosphite, diisodecyl pentaerythrityl diphosphite, trilauryl phosphite, and trilauryl trithiophosphite, were commercially available stabilizers and were used without purification.

Di-(2-ethylhexyl) phthalate, mannitol, sorbitol, pentaerythritol, zinc chloride, cadmium chloride, and triphenyl phosphine were reagent-grade chemicals.

Cadmium, calcium, zinc, and barium laurates were prepared from 99% lauric acid by precipitation and gave the correct elemental analyses.

Trioctyl phosphite and trioctyl phosphine were synthesized by standard literature methods, and no impurities were detected by elemental analysis and infrared spectroscopy.

Degradation Measurements

Poly(vinyl chloride) (0.5 g) was weighed into a degradation tube (130 × 18 mm) and the appropriate additive and di-(2-ethylhexyl) phthalate (15 ml) were introduced. The tube was placed in a vapor heating jacket, and a stream of dried, white spot nitrogen was bubbled through the solution. The gas outlet of the degradation tube led via a sintered glass disc into an enclosed titration cell (250 ml) containing 1% potassium chloride solution.

The degradation tube was swept with nitrogen using a flow rate of 50 ml/min until all atmospheric carbon dioxide had been removed from the apparatus and the pH of the solution in the titration cell was constant. Degradation was commenced by heating the contents of the tube to 180°C using o-dichlorobenzene vapor. The hydrogen chloride evolved was monitored over the first 3–5 hr of degradation by means of a Radiometer automatic recording titration apparatus. (This apparatus is manufactured by Radiometer Ltd., 72, Emdrupvej, Copenhagen NV, Denmark (U.K. agents, V. A. Howe Ltd., London), and is fully described in their technical literature.) All experiments were repeated until duplicate determinations agreed to within 5%. Blank determinations on un-

stabilized polymer were carried out at regular intervals, since values obtained could vary slightly, particularly when different solvent batches were used.

RESULTS AND DISCUSSION

Mixed Metal Laurate Synergism

Results obtained on degrading poly(vinyl chloride) in the presence of barium and cadmium laurates alone and in admixture are shown in Figure 1; similar results for calcium and zinc laurates are given in Figure 2. The metal salts are completely soluble in the phthalate solvent. Table I shows the percentage of stabilizer consumed before evolution of hydrogen chloride, calculated by assuming that degradation during the induction period occurs at a rate identical to that in unstabilized polymer. All of the laurates, when used alone, permit escape of hydrogen chloride well before stoichiometric conversion to the respective chlorides occurs, behavior which has been noted previously in the solid phase for some of the salts.[4,11,12] After the induction period, as expected,[1] polymer degradation occurs at a rate identical to that of the control in the presence of calcium and barium laurates, respectively, and at a vastly increased rate in the presence of zinc laurate. Hydrogen chloride evolution from cadmium laurate-stabilized polymer was not as rapid as that observed in previous work,[13-15] and deg-
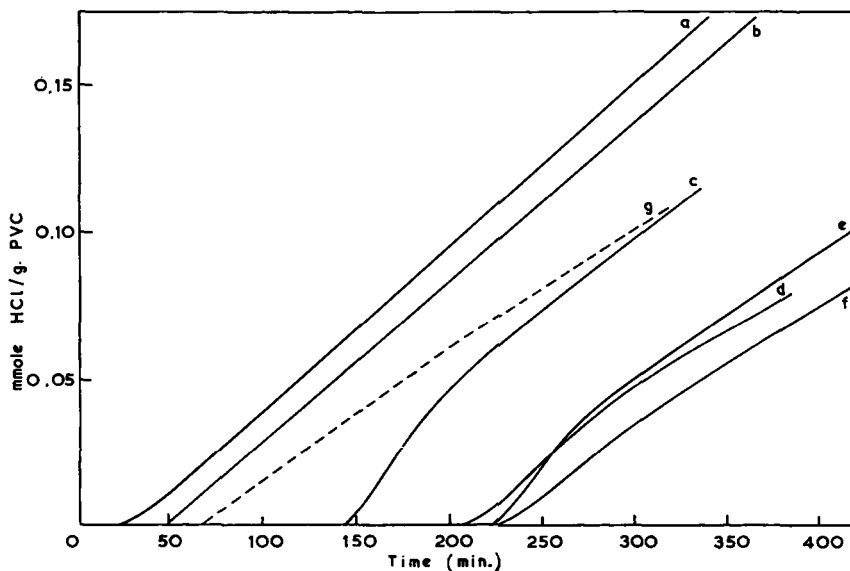

Fig. 1. Degradation of poly(vinyl chloride) at 180°C in the presence of barium laurate, cadmium laurate, and their synergistic mixtures: (a) unstabilized control; (b) 3% barium laurate; (c) 3% cadmium laurate; (d) 2.25% barium laurate + 0.75% cadmium laurate; (e) 1.5% barium laurate + 1.5% cadmium laurate; (f) 0.75% barium laurate + 2.25% cadmium laurate; (g) 3% barium laurate + 0.3% cadmium chloride.
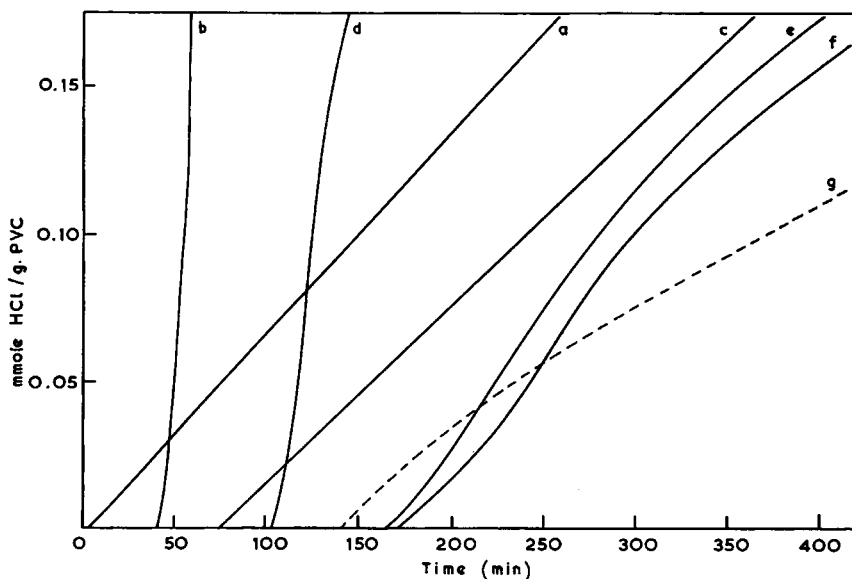
Fig. 2. Degradation of poly(vinyl chloride) at 180°C in the presence of calcium laurate, zinc laurate, and their synergistic mixtures: (a) unstabilized control; (b) 3% zinc laurate; (c) 3% calcium laurate; (d) 2.25% zinc laurate + 0.75% calcium laurate; (e) 1.5% zinc laurate + 1.5% calcium laurate; (f) 0.75% zinc laurate + 2.25% calcium laurate; (g) 0.1% zinc chloride + 3% calcium laurate.

radation of poly(vinyl chloride) in the presence of cadmium chloride (0.3%) did not appreciably increase the rate. Evidently the polymer used in these studies is not as susceptible to cadmium chloride-catalyzed degradation.

The use of synergistic mixtures markedly increases the period before evolution of hydrogen chloride, owing to greatly improved acceptance

TABLE I
Percentage of Stabilizer Consumed Before Evolution of Hydrogen Chloride

Stabilizer	% Consumed	Stabilizer	% Consumed
Barium laurate, 3%	10	Calcium laurate, 3%	35
Barium laurate, 2.25% Cadmium laurate, 0.75%	88	Calcium laurate, 2.25% Zinc laurate, 0.75%	86
Barium laurate, 1.5% Cadmium laurate, 1.5%	95	Calcium laurate, 1.5% Zinc laurate, 1.5%	82
Barium laurate, 0.75% Cadmium laurate, 2.25%	94	Calcium laurate, 0.75% Zinc laurate, 2.25%	50
Cadmium laurate, 3%	56	Zinc laurate, 3%	19

of hydrogen chloride. Apparently, calcium–zinc systems are slightly less efficient than barium–cadmium systems, presumably because zinc chloride is a much stronger prodegradant than cadmium chloride.

The theory proposed by Onozuka[5] offers a reasonable explanation of how this improved hydrogen chloride acceptance is achieved. Results to be described later in this paper show that if the effects of their prodegradant chlorides are removed, cadmium and zinc laurates are extremely efficient acceptors of hydrogen chloride.

They are also known to esterify labile chlorine atoms in the polymer backbone which act as sites for initiation of degradation,[16,17] thus inhibiting the formation of long, highly colored polyene sequences. If the zinc and cadmium chlorides formed during the stabilization process are reconverted into their laurates by carboxylate interchange with calcium and barium laurates, a prodegradant is removed and an effective stabilizer is reformed, e.g.:

$$ZnCl_2 + Ca(OOCC_{11}H_{23})_2 \rightarrow Zn(OOCC_{11}H_{23})_2 + CaCl_2.$$
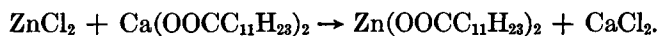
This theory was confirmed in calcium–zinc mixtures by degrading poly-(vinyl chloride) in the presence of 0.1% zinc chloride and 3% calcium laurate. A marked increase in induction period and stabilizer consumption is noted compared with calcium laurate alone (see Fig. 2). However, a much smaller increase in induction period is obtained when poly(vinyl chloride) is degraded in the presence of 0.3% cadmium chloride and 3% barium laurate (Fig. 1). Probably the low solubility of cadmium chloride in the reaction medium accounts for this, and it therefore seems likely that laurate interchange does not simply occur through cadmium chloride itself, but through some more compatible intermediate such as a cadmium laurate–chloride. The observation[3] that an almost stoichiometric amount of barium chloride is produced on degradation of a polymer stabilized by barium–cadmium stearate before any cadmium chloride is formed tends to support a carboxylate interchange mechanism.

Synergism of Polyols with Metal Laurates

In the presence of pentaerythritol, mannitol, and sorbitol (1%), poly-(vinyl chloride) degrades linearly at rates of 0.86, 0.92, and 0.85 relative to that of the control, and without any increase in induction period. Use of greater amounts of polyols does not alter the rate of degradation. These reductions in rate could be caused by complex formation with traces of iron (2 ppm) present in the polymer, or by mild antioxidant action similar to that observed with polyolefins.[18] Figures 3 and 4 show the effect of adding polyols (1%) to poly(vinyl chloride) in admixture with 1% zinc laurate and 1% cadmium laurate, respectively. In every case, the induction period prior to evolution of hydrogen chloride is markedly prolonged, and degradation does not take place until virtually the theoretical amount of metal laurate has been consumed. The rate of hydrogen chloride evolution is not diminished by the presence of polyols, and the use of
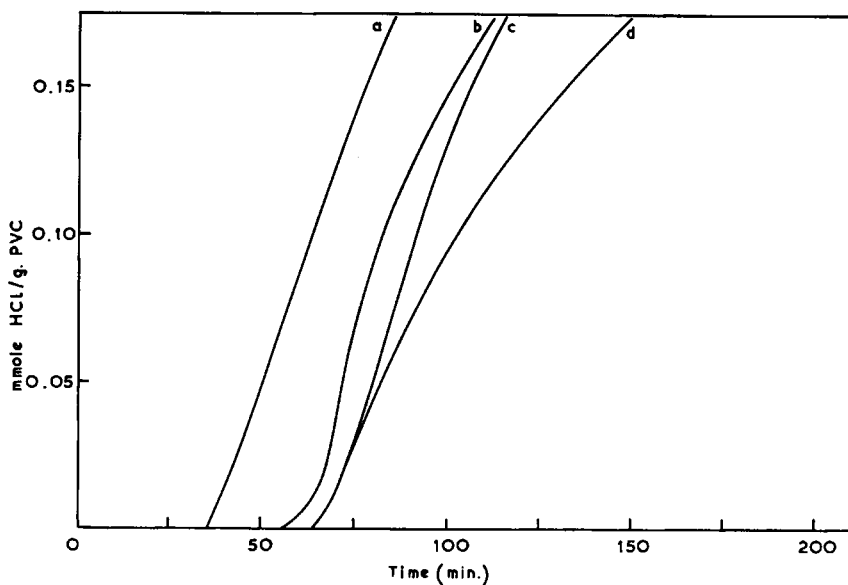
Fig. 3. Degradation of poly(vinyl chloride) at 180°C in the presence of zinc laurate and polyols: (a) 1% zinc laurate; (b) 1% zinc laurate + 1% pentaerythritol; (c) 1% zinc laurate + 1% sorbitol; (d) 1% zinc laurate + 1% mannitol.
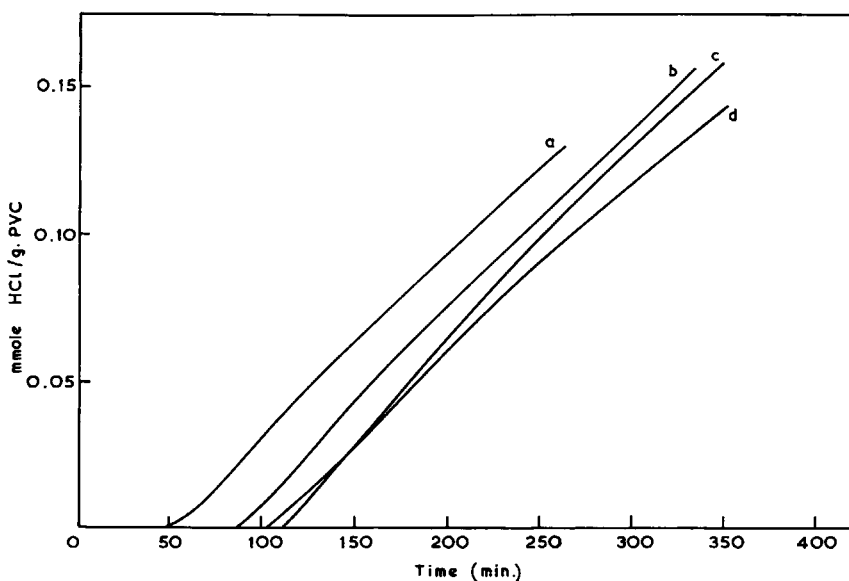
Fig. 4. Degradation of poly(vinyl chloride) at 180°C in the presence of cadmium laurate and polyols: (a) 1% cadmium laurate; (b) 1% cadmium laurate + 1% pentaerythritol; (c) 1% cadmium laurate + 1% mannitol; (d) 1% cadmium laurate + 1% sorbitol.

excess polyol does not alter the degradation characteristics. Polyols have the effect of prolonging the good early color obtained on aging poly(vinyl chloride) in the presence of cadmium- and zinc-containing stabilizers and delaying the onset of severe discoloration. It has been proposed[19] that they act by forming complexes with zinc and cadmium chlorides, thereby delaying their prodegradant effect. The results obtained here are entirely consistent with this theory, and the fact that severe degradation resumes when all hydrogen chloride-accepting stabilizers have been consumed agrees with observations in the literature that complex formation is more favored in nonacidic conditions.[20] Complex formation is not observed when only zinc chloride and a polyol are added to poly(vinyl chloride) and acidic conditions prevail.

The Influence of Phosphites and Phosphines upon Poly-(vinyl Chloride)Degradation

Most of the phosphites examined cause poly(vinyl chloride) degradation to proceed linearly without an increase in induction period. The relative rates of degradation observed are shown in Table II.

TABLE II
Rate of Degradation of Poly(vinyl Chloride) in the Presence of Phosphites

Phosphite	Relative rate of degradation
—	1.00
Triphenyl phosphite, 1%	1.04
Triphenyl phosphite, 5%	0.83
Tris(nonylphenyl) phosphite, 1%	0.91
Tris(nonylphenyl) phosphite, 5%	0.73
Diphenyl isodecyl phosphite, 1%	1.03
Diisodecyl pentaerythrityldi-phosphite, 1%	0.97[a]
Trioctyl phosphite, 1%	0.57[a]
Trioctyl phosphite, 5%	0.51[a]
Trilauryl phosphite, 1%	0.61[a]
Trilauryl trithiophosphite, 1%	0.85

[a] Slower rate in early stages of degradation. See Figure 5.

All of the trialkyl phosphites examined cause the polymer to lose hydrogen chloride at a markedly retarded rate in the early stages of degradation, and the degradation plots for these compounds are displayed in Figure 5 along with those for the two phosphines examined, which exhibited nonlinear behavior. These results may readily be explained on the basis of known reactions and reactivity of phosphites and phosphines. Many aliphatic chlorine-containing compounds readily undergo the Arbusov reaction with trialkyl phosphites,[21] and this reaction has been shown to occur in poly(vinyl chloride).[22]
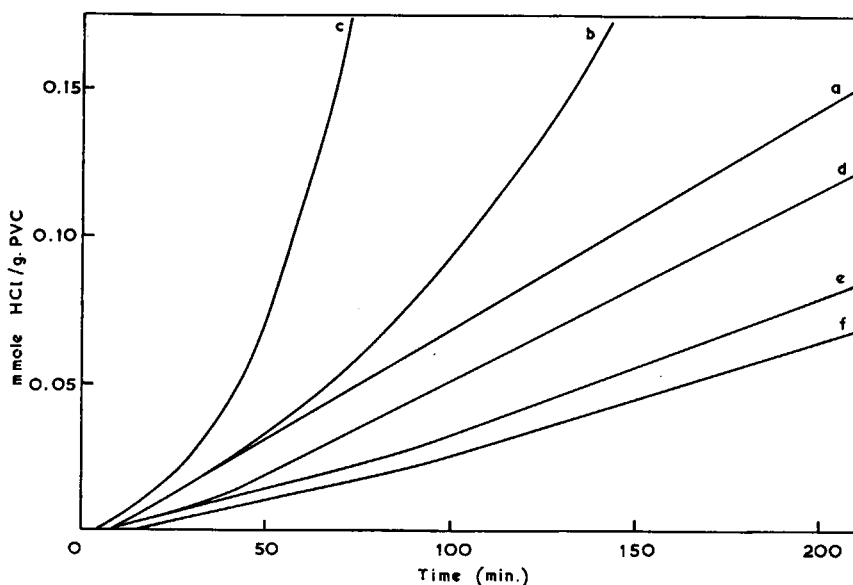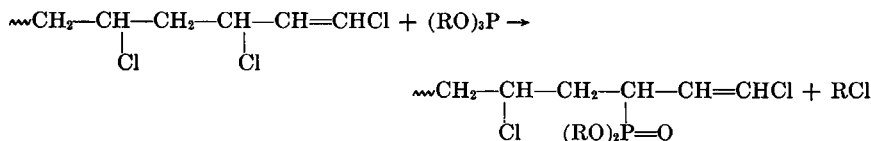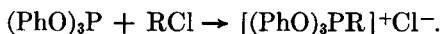
Fig. 5. Degradation of poly(vinyl chloride) at 180°C in the presence of phosphites and phosphines: (a) unstabilized control; (b) 1% triphenyl phosphine; (c) 1% triooctyl phosphine; (d) 1% diisodecyl pentaerythrityl diphosphite; (e) 1% trilauryl phosphite; (f) 1% trioctyl phosphite.

Trialkyl phosphites evidently undergo this type of reaction with the labile chlorine atoms which are sites for initiation of degradation, rendering the polymer more resistant to dehydrochlorination; e.g.:

$\sim$CH$_2$—CH—CH$_2$—CH—CH$=$CHCl $+$ (RO)$_3$P $\rightarrow$
                | |
                Cl   Cl

                        $\sim$CH$_2$—CH—CH$_2$—CH—CH$=$CHCl $+$ RCl
                                    | |
   Cl   (RO)$_2$P$=$O

Saturated secondary alkyl chlorides are virtually inactive in the Arbusov reaction, so it is likely that little substitution takes place other than at activated sites. Aryl phosphites do not undergo the Arbusov reaction readily; triphenyl phosphite forms a quaternary phosphonium salt rather than a phosphonate,[23] as follows:

$$(PhO)_3P + RCl \rightarrow [(PhO)_3PR]^+Cl^-.$$

Forcing conditions are needed to convert the salt into the phosphonate, and this lower activity of the aryl phosphites could explain why they have little effect on the rate of degradation of poly(vinyl chloride).

The extremely low initial rates observed with the trialkyl phosphites are undoubtedly due to their undergoing an Arbusov reaction with hydrogen chloride, a reaction that has previously been proposed to account for the action of phosphites in poly(vinyl chloride) stabilization:[24]

$$(RO)_3P + HCl \rightarrow (RO)_2P(O)H + RCl.$$
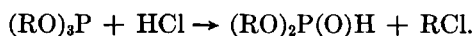
The participation of trialkyl phosphites in the above reactions has been proved by GLC examination of extracts of poly(vinyl chloride) treated at 180°C with trioctyl phosphite. Both dioctyl phosphite and octyl chloride were detected when 1% of the phosphite was used, while only the latter compound was found when the quantity of phosphite was increased to 10%.

Phosphites probably also act by decomposition of hydroperoxides in the polymer. Trilauryl trithiophosphite does not undergo the Arbusov reaction,[25] yet considerably retards the rate of polymer degradation. Furthermore, alkyl phosphites have been found to be more efficient decomposers of peroxides in model systems than are aryl phosphites.[26] Obviously, phosphites play a major part in preventing oxidative degradation, but the conditions used here were not designed to measure this effect.

Both of the phosphines examined catalyze the dehydrochlorination of poly(vinyl chloride), trioctyl phosphine being considerably more severe than triphenyl phosphine, whose prodegradant effect has previously been noted.[27]

Synergism of Phosphites and Phosphines with Metal Laurates

When used alone, phosphites do not prevent color formation in aged poly(vinyl chloride) samples, and in practice they are always used with metal carboxylates, when they improve the early color of aged polymer
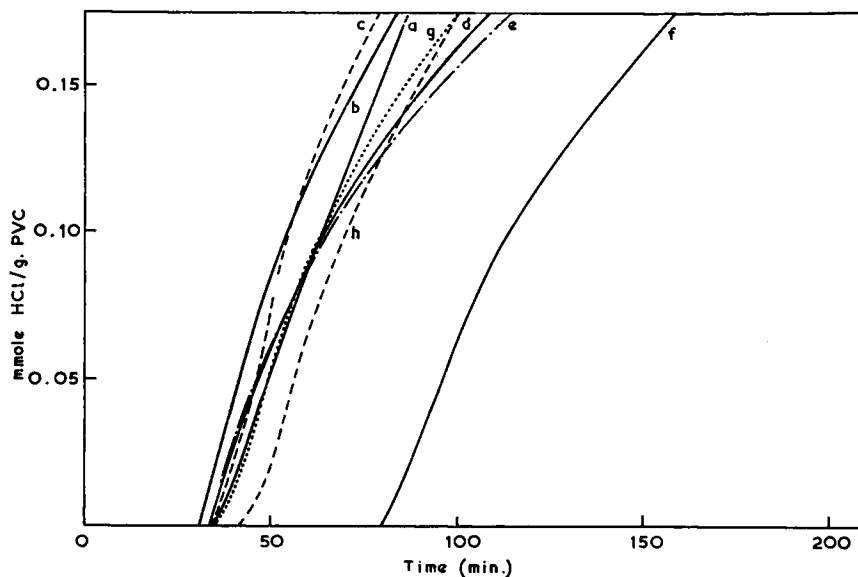

Fig. 6. Degradation of poly(vinyl chloride) at 180°C in the presence of 1% zinc laurate and phosphites or phosphines: (a) without phosphite; (b) 1% triphenyl phosphite; (c) 1% tris(nonylphenyl) phosphite; (d) 1% diisodecyl pentaerythrityl diphosphite; (e) 1% diphenyl isodecyl phosphite; (f) 1% trioctyl phosphine; (g) 1% trioctyl phosphite; (h) 1% triphenyl phosphine.
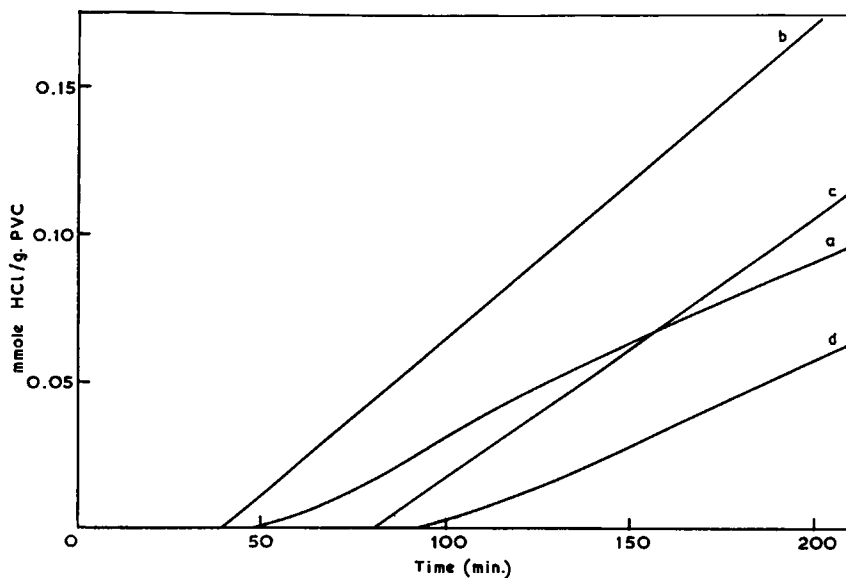
Fig. 7. Degradation of poly(vinyl chloride) at 180°C in the presence of 1% cadmium laurate and phosphites or phosphines: (a) without phosphite or phosphine; (b) 1% trioctyl phosphine; (c) 1% triphenyl phosphine; (d) 1% trioctyl phosphite.

samples. They are widely believed to act by rendering deleterious cadmium and zinc chlorides harmless through complex formation.[24,28] In experiments designed to test this theory, poly(vinyl chloride) was degraded in the presence of 1% cadmium or zinc laurate and 1% of a number of phosphites and phosphines.

Phosphites do not prolong the induction period prior to evolution of hydrogen chloride in the presence of zinc laurate (Fig. 6) and have little effect on subsequent rate of degradation, suggesting that complex formation is not occurring. Trioctyl phosphine and triphenyl phosphine, on the other hand, lengthen the induction period, the former compound being particularly effective despite the fact that alone it increased the rate of degradation by a factor of approximately 9. These effects can only be explained by complex formation between zinc chloride and the phosphines, the more nucleophilic trioctyl phosphine giving the stronger complex.

Rather different results are obtained when zinc laurate is replaced by cadmium laurate. Some phosphites prolong the induction period, although none has any effect on rate of hydrogen chloride evolution. The results are shown in Table III, and Figure 7 shows the degradation characteristics for a typical phosphite.

However, these increases in induction period are not apparently caused by complex formation, but are due to the fact that certain phosphites slow down the rate of polymer degradation (see Table I) and prolong the life of the cadmium laurate. Diphenyl isodecyl phosphite is exceptional in giving an increase in induction period which would not be expected from

TABLE III
Degradation of Poly(vinyl Chloride) in the Presence of Cadmium
Laurate (1%) and Various Phosphites (1%)

Phosphite	Induction period, min
—	48
Triphenyl phosphite	52
Diphenyl isodecyl phosphite	70
Tris(nonylphenyl) phosphite	60
Diisodecyl pentaerythrityl diphosphite	60
Trioctyl phosphite	90
Trilauryl phosphite	85
Trilauryl trithiophosphite	90

the above considerations, possibly because its reactivity with poly(vinyl chloride) is enhanced in the presence of the laurate.

Trioctyl phosphite also prolongs considerably the induction periods of polymer stabilized with barium and calcium laurates, which do not give rise to prodegradant halides, demonstrating further that increases in induction period are not necessarily due to complex formation. Apparently the severe prodegradant effect of zinc chloride masks any increases in induction period when polymer is degraded in the presence of zinc laurate and phosphites. However, the induction period of a 1:1 synergistic mixture of calcium and zinc laurates is extended by 16 min by 1% trioctyl phosphite but unaltered by 1% triphenyl phosphite.
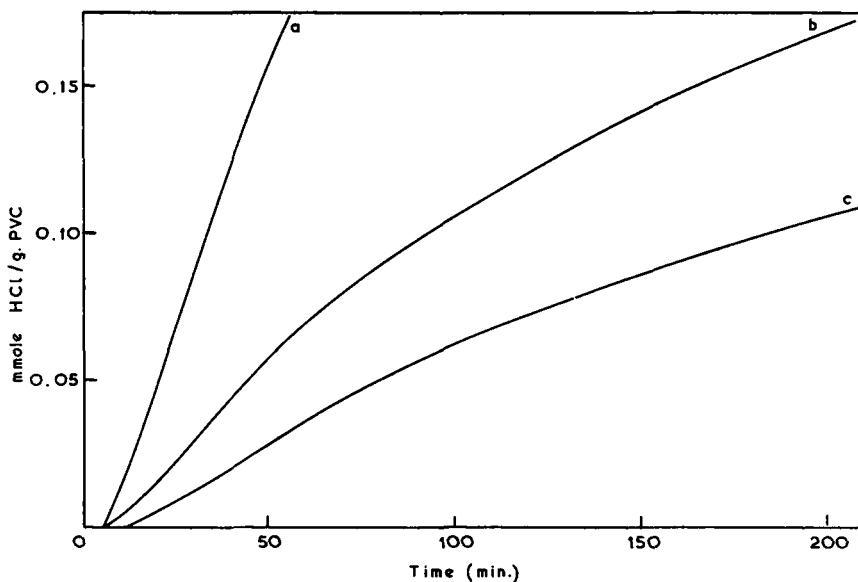

Fig. 8. Degradation of poly(vinyl chloride) at 180°C in the presence of 0.034% zinc chloride and phosphites: (a) without phosphites; (b) 1% triphenyl phosphite; (c) 1% trioctyl phosphite.

The action of the phosphines in the presence of cadmium laurate (see Fig. 7) is somewhat different from their action in the presence of zinc laurate. Trioctyl phosphine slightly shortens the induction period, and the ultimate rate of degradation is higher than that of cadmium laurate alone, but considerably less than that of the phosphine alone. This suggests only weak complex formation. Triphenyl phosphine, having less of a prodegradant effect, affords a longer induction period.

When poly(vinyl chloride) is degraded in the presence of zinc and cadmium chlorides and several phosphites, very little or no increase in induction period is noted, which indicates further that complex formation probably plays little part in the stabilization mechanism. Triphenyl phosphite, 1%, and 1% trioctyl phosphite scarcely alter the rate of dehydrochlorination in the presence of 0.3% cadmium chloride, but reduce the rate in the presence of 0.033% zinc chloride, as is shown in Figure 8.

These latter observations appear to be due to the ability of zinc chloride to react with phosphites as follows:

$$ZnCl_2 + 2(EtO)_3P \xrightarrow{150°C} (EtO)_2\overset{O}{\overset{\|}{P}}-Zn-\overset{O}{\overset{\|}{P}}(OEt)_2 + 2EtCl$$
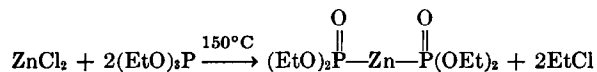
The above reaction was found to occur readily when anhydrous zinc chloride was heated with triethyl phosphite. Furthermore, the zinc phosphonate produced did not act as a prodegradant for PVC.

A similar reaction with cadmium chloride took place only under extremely forcing conditions (8 hr at 210°C), which explains the lack of influence of the phosphites examined upon cadmium chloride-catalyzed degradation. It is not known whether an identical reaction takes place with metal chlorides and aryl phosphites, since this was not examined. However, this type of reaction does not appear to contribute to poly(vinyl chloride) color stabilization and can have an adverse effect by destroying the phosphite.

These results on phosphite synergism agree reasonably well with those published during the course of this work by Russian workers,[9,10] who examined the effect of phosphites in aged polymer film containing metal stearates and proposed some additional mechanisms of phosphite action.

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