

Antioxidant Effects in PVC Plasticized with DIDA

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Synopsis

Antioxidants such as bisphenol A (BPA) have long been recommended for retention of physical properties on oven-aging of PVC plasticized with certain plasticizers. We have shown how BPA inhibits oxidative fragmentation of plasticizers such as diisodecyl adipate (DIDA) and thus decreases apparent volatility, and how it improves retention of modulus, elongation, and low temperature flexibility. Low concentrations are more beneficial than either zero or high concentrations, especially on longer aging. At higher concentrations, although the plasticizer is retained in the PVC, it becomes less efficient at low temperature, and low-temperature flex is impaired while elongation is preserved. DIDA exudes during oven-aging unless oxidation occurs to prevent it. When BPA is present, exudation is worst at the most efficient concentrations of antioxidant. This appears to be the normal incompatibility of DIDA at 105°C which is permitted by the antioxidant. On oxidation, the dielectric constant of DIDA rises into the 4-8 range, signifying compatibility with PVC, and the DIDA does not exude.

INTRODUCTION

Antioxidants have frequently been added to plasticized poly(vinyl chloride) (PVC) for improved retention of physical properties on oven-aging, especially since Fischer and Vanderbilt¹ reported their value with plasticizers prepared from oxo-alcohols. The ASTM test method D 2288-64T² recommends use of 0.1% bisphenol A (BPA) in case of weight gain instead of a weight loss during volatility testing of plasticizers per se. Yet, there are problems that have remained unanswered. Our observations of PVC plasticized with diisodecyl adipate (DIDA) and of the plasticizer per se—with and without bisphenol A—have helped clarify a number of phenomena connected with the use of antioxidants. Among these are improved retention of elongation and low-temperature flex, reduced apparent volatility, but a reduction in apparent compatibility.

Plasticizers such as DIDA or diisodecyl phthalate with many methyl branches in the alcohol moieties have numerous tertiary hydrogens as points of attack for oxidation. The adipates to some extent, and the azelates and sebacates even more so, may also be oxidized in the acid portion of the molecule, probably on the beta carbon atoms.³ Antioxidants such as BPA inhibit this oxidation, protect the plasticizer and resin from deterioration, and help in the retention of physical properties of the plasti-

cized PVC when it is aged at elevated temperatures. For this study we chose DIDA not only because of its ease of oxidation but because of its borderline compatibility. It is near the lower end of the polarity and solubility parameter scales. Its dielectric constant ϵ is 3.74, and its solubility parameter δ is 8.4, whereas $\epsilon = 4-8$ and $\delta = 8.4-11.4$ are the preferred ranges for good compatibility of plasticizers for PVC.⁴

EXPERIMENTAL

Aging of Plasticizer per se

For measurement of weight loss of DIDA per se, with and without BPA, we used a forced-air oven with rotating shelf equipped for weighing samples while still in the oven. Samples of 5 g of DIDA with 0%–1% BPA were exposed uncovered in 5-cm diameter petri dishes. We checked the apparatus for any relationship between rate of vaporization and rate of air flow by use of a volatile, oxidation-resistant 18-carbon hydrocarbon. At 105°C its weight loss was linear with time at air rates of 0.66–5.8 cu ft/hr. No higher rates were attempted. For DIDA tests we maintained the air flow at about the midpoint of this range. For evaporation in a nitrogen atmosphere we used 99.5% pure nitrogen bubbled through two gas scrubbers filled with alkaline pyrogallol to remove the residual oxygen before it was blown through the gas-tight oven. DIDA is sensitive enough to oxidation that appreciable amounts of peroxide could be found in it when the test in nitrogen was continued a day or so after the pyrogallol had been exhausted in the scrubbers.

Figure 1 shows weight loss in air of DIDA with varying amounts of BPA and weight loss in nitrogen of uninhibited DIDA at 105°C. The early slight increase in weight is shown best by the sample with no BPA, but the fact that all curves for DIDA with BPA at first lie above that for

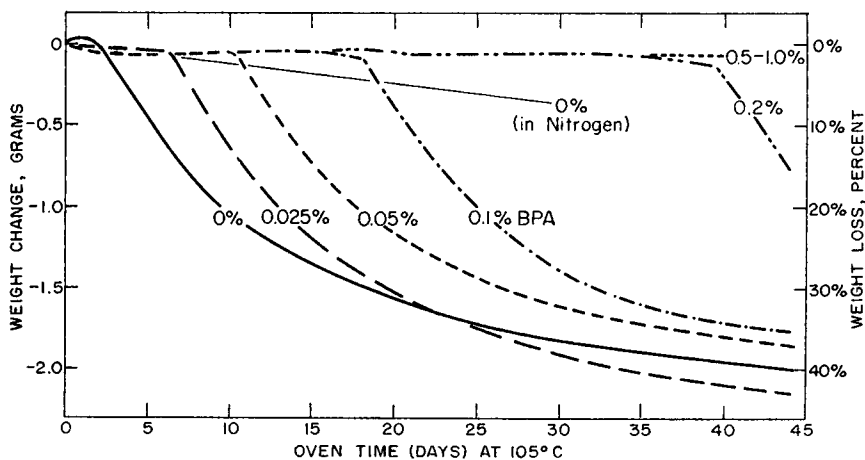


Fig. 1. Effect of BPA at various concentrations on pseudovolatility of DIDA per se.

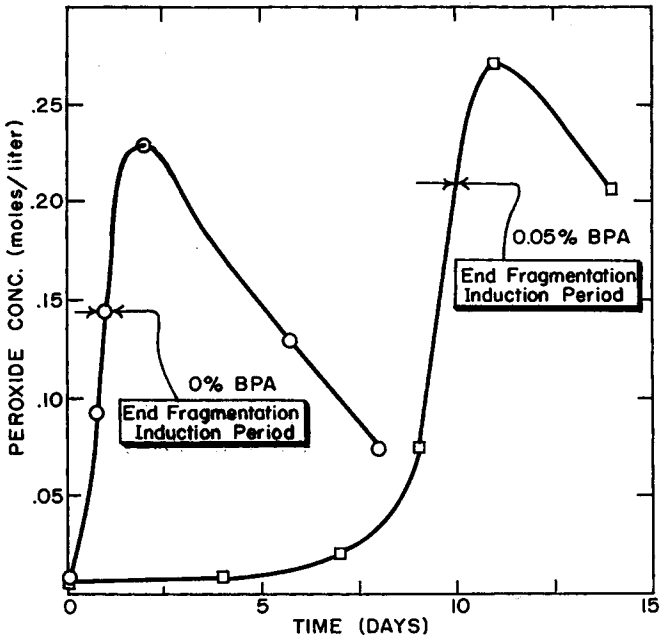


Fig. 2. Position of fragmentation induction period in the oxidation pattern of DIDA at 105°C.

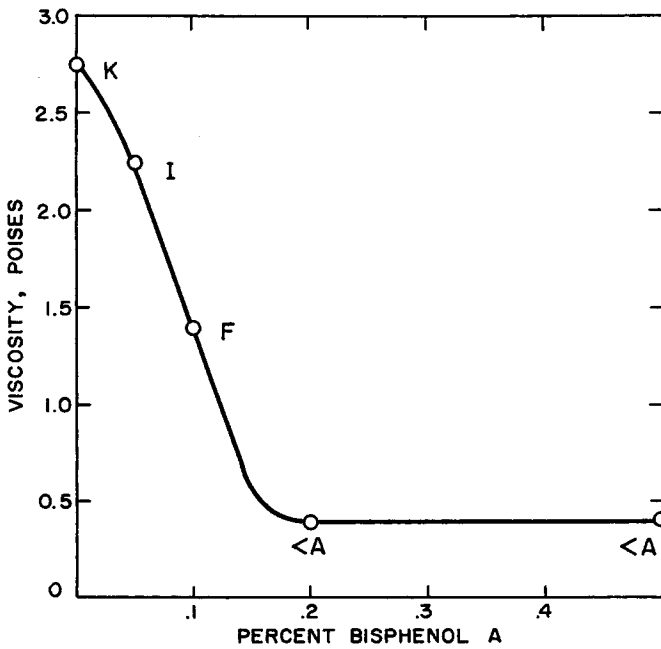


Fig. 3. Viscosity of residual plasticizer after 37 days at 105°C. Letters refer to Gardner viscosities.

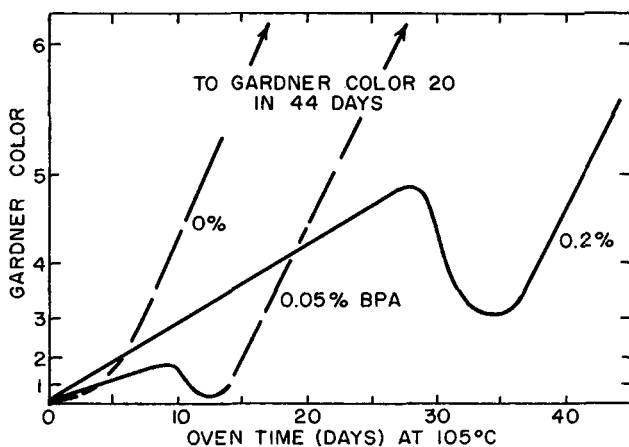


Fig. 4. Pattern of color development on oxidation of DIDA with and without BPA

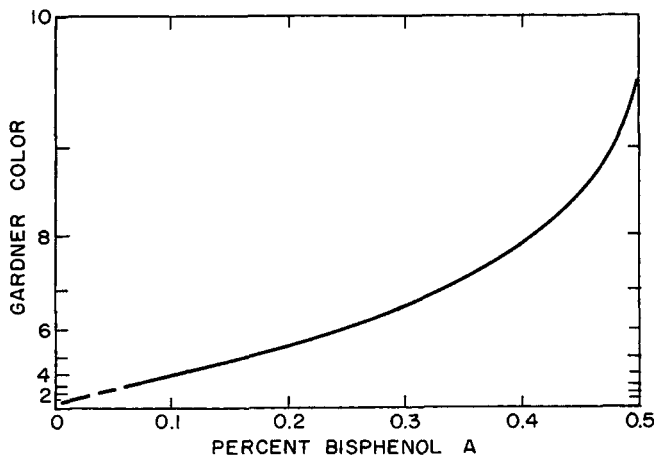


Fig. 5. Maximum color developed during induction period as a function of BPA concentration.

evaporation in nitrogen shows oxygen uptake even in these. After an induction period the samples began to lose weight rapidly. Weight loss then gradually tapered off. The residual liquid was dark brown and viscous.

This induction period before rapid weight loss ("fragmentation induction period") is not the same as the induction period for autocatalytic formation of peroxides but is longer, as shown by Figure 2. It corresponds to the induction period for latent degradation or the obvious deterioration of the plasticizer.⁵ We determined peroxide content by the simple iodometric method of Wagner and his co-workers.⁶ After 37 days at 105°C, the samples of DIDA had increased in viscosity as shown in Figure 3. The viscous residues were quite acidic and were no longer completely soluble in *n*-hexane. The hexane-insoluble matter consisted of a white solid, perhaps adipic acid, and an acidic gummy, yellow liquid.

Although BPA in very small amounts helps inhibit color formation in plasticized PVC,¹ it is not free of color problems itself. During the induction period, the color builds up to a maximum, with the maximum being a function of the concentration of BPA (Figs. 4 and 5). The exact height and time of the color maximum were difficult to determine, since bleaching began at or slightly before the end of the fragmentation induction period, while peroxide content was high. After appreciable bleaching, the color rose again even more sharply.

Paralleling the study of the effects of BPA in DIDA per se, we examined some of the effects in the more complicated environment of a complete PVC system. Results were not always straightforward.

Retention of Physical Properties

We prepared six compounds of PVC designed essentially as electrical formulations with the following compositions: PVC, 100; DIDA, 50;

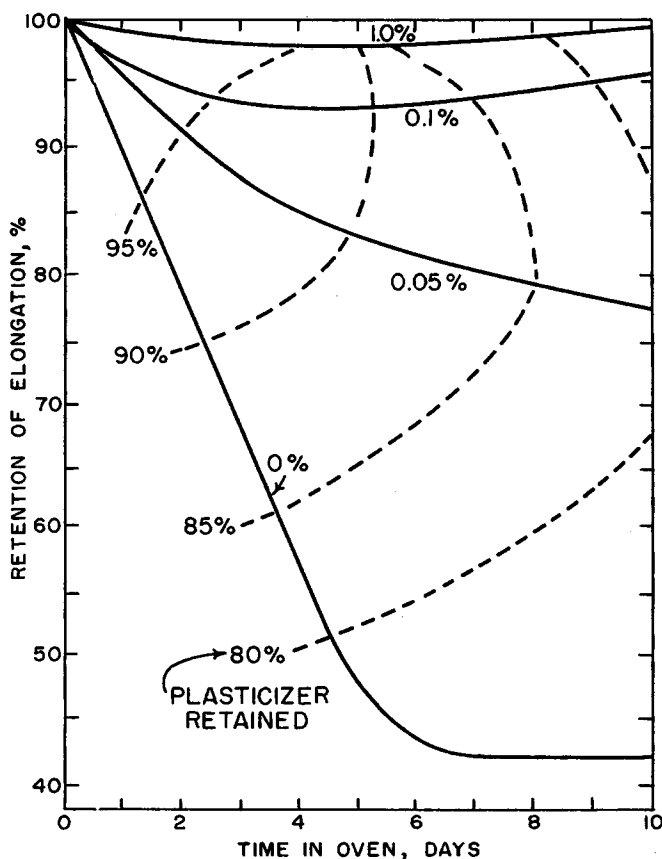


Fig. 6. Effect of BPA at various concentrations on retention of elongation after aging at 105°C (solid lines). Dashed lines designate equal amounts of plasticizer retained.

#33 clay, 18; Tribase E, 5; stearic acid, 0.5; bisphenol A, 0.0–0.5 (or 0%–1% of the plasticizer).

The BPA and the stearic acid were dissolved in the DIDA in each case and these solutions were added to the other components. Each formulation was milled at 165°C for 5 min, sheeted off, and molded under pressure. Molded sheets were aged at 105°C in a rotating-shelf, forced-air oven for 0–10 days, with samples removed periodically for study.

Modulus of 0.075-in.-(1.9-mm)-thick specimens at 100% elongation and ultimate tensile strength increased very slightly in all specimens during aging, as would be expected. Elongation at break, the most common and perhaps most sensitive measure of deterioration during heat

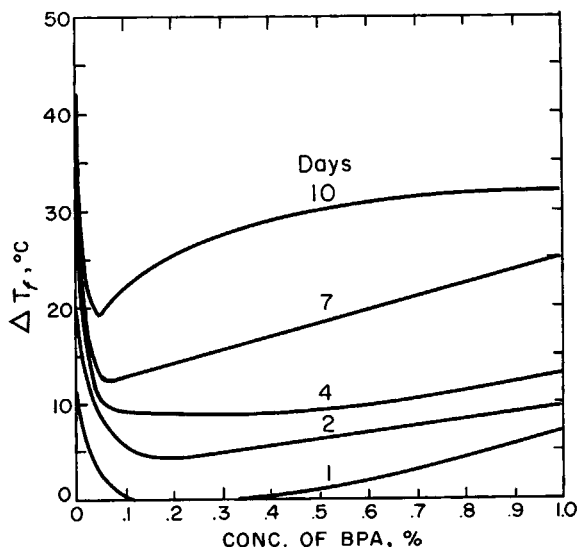


Fig. 7. Effect of BPA at various concentrations on change in low-temperature flex (ΔT_f) after aging at 105°C.

aging, dropped off. This decrease in distensibility without an antioxidant is normal and represents the combined results of volatility and oxidation. The less severe decrease when 0.05% BPA is used shows the value of even a trace of antioxidant in stopping deterioration; 0.1% is even better, but beyond that there is no additional value in these tests, just as Fischer and Vanderbilt¹ observed in their work. It seems that 0.1% BPA was enough for ten days at 105°C. A plot of the retention of elongation with time (Fig. 6) shows nothing unusual unless it be that the 0% BPA curve levels off at about seven days and that retention at ten days appears slightly better than at four to seven days when higher concentrations are used.

Figure 7 shows changes in low-temperature flex, ΔT_f , of the same samples. The initial T_f averaged -53°C . Without antioxidant, T_f deteriorated rapidly, so that after ten days at 105°C it was 42°C above

(poorer than) its original good, low value. With only 0.05% BPA, it rose only 19°C; but 0.1%–1.0% BPA was less effective than the lower concentrations. This special effectiveness of 0.05% BPA toward T_f must be related to its ability to reduce apparent volatility of the plasticizer as

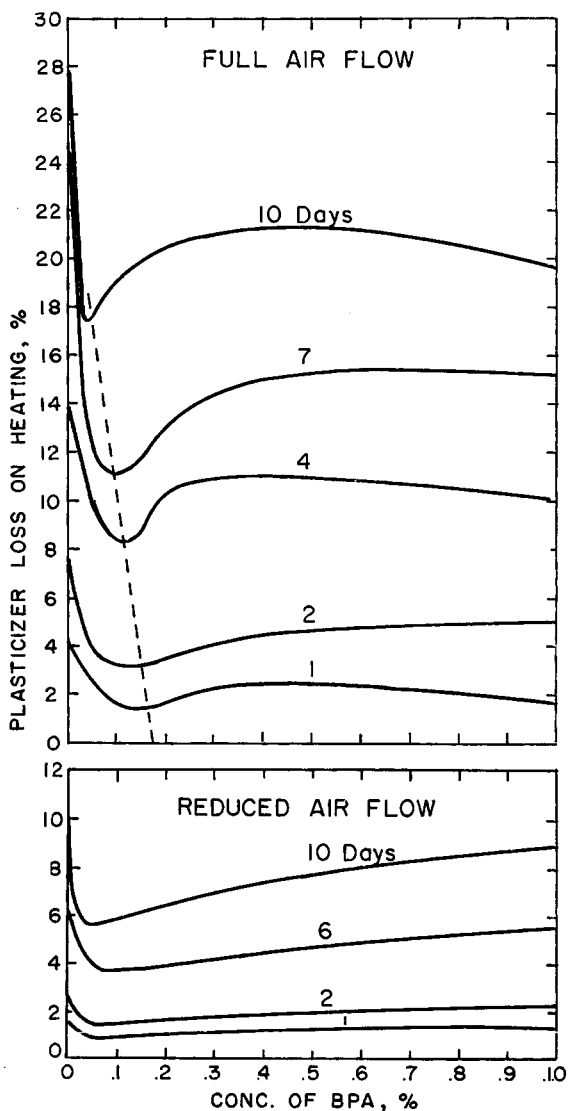


Fig. 8. Plasticizer loss from plasticized PVC at 105°C influenced by BPA.

shown in Figure 8, where again 0.05% BPA is more effective than the higher concentrations. Volatility tests were run at 105°C, first with full air flow through the oven. They were then repeated at reduced air flow with fresh samples to permit more careful examination of the surface.

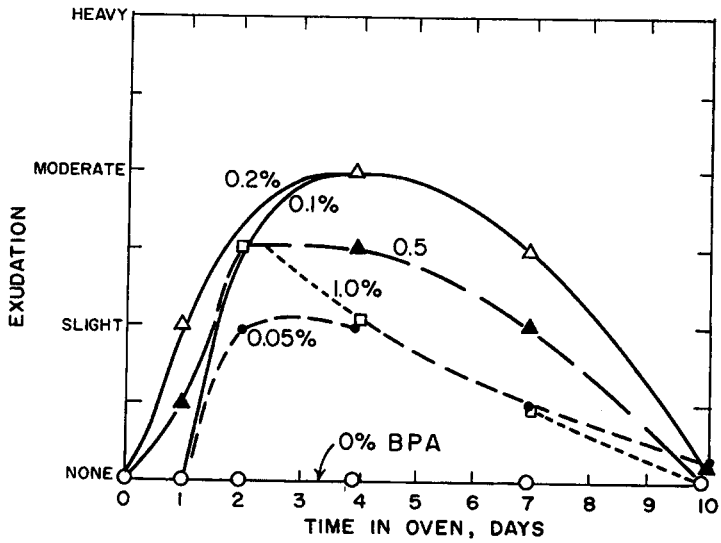


Fig. 9. Exudation as influenced by BPA content.

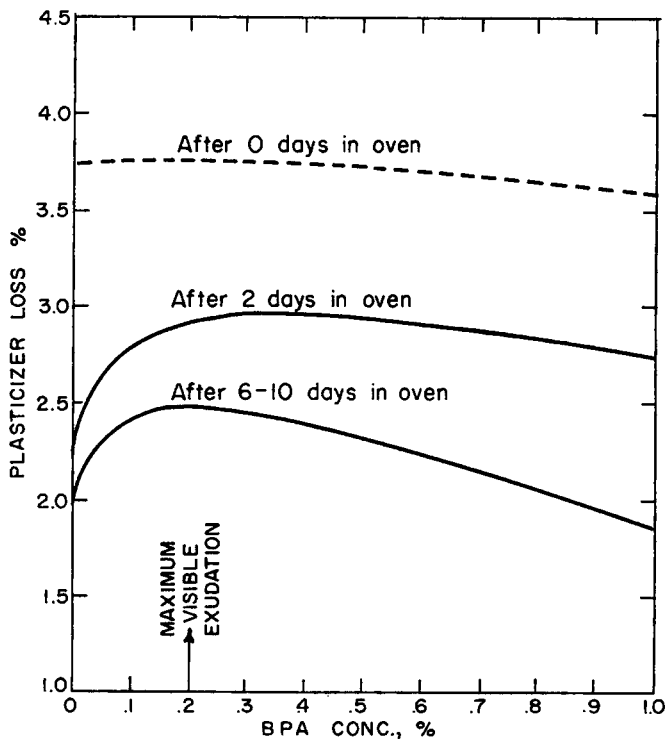


Fig. 10. Loss on washing as influenced by BPA content.

The retention of elongation which appeared simple in the solid lines of Figure 6 is seen to be more complex when the per cent plasticizer retained is considered in the dashed lines. At, for example, a loss of 15% of the original plasticizer (or 85% retained), the sample with no BPA has only 62% of its original distensibility, whereas with 0.05% BPA, again at 85% plasticizer retained, it has almost 80% of the original distensibility. Higher concentrations are even more effective. There are probably changes in the resin itself, chain scission and crosslinking, but it seems highly probable that the plasticizer that is retained differs in efficiency with different amounts of BPA: the more BPA, the more efficient the remaining plasticizer at room temperature.

Serious loss of plasticizer by volatility involves transport of plasticizer from inside the sheet to the surface and evaporation in the stream of hot air. Normally a compatible plasticizer would migrate from the inside only to attempt to restore equilibrium as plasticizer is lost from the surface. Examination of the surface of our DIDA-plasticized specimens during aging showed the DIDA exuding at the elevated temperature (Fig. 9). Exudation reached a maximum at 0.1%–0.2% BPA and after about four days in the oven. After four days it gradually disappeared from the surface, so that at seven to ten days the sheets were dry; a powder was left on the surface. Specimens with larger amounts of BPA had larger amounts of the powder on the surface. Aged and unaged sheets were then weighed, washed with 5 cc chloroform for 15 sec in a flat bottom dish, dried, and reweighed. The chloroform solutions, even those containing almost exclusively the powder, appeared by infrared analysis to be DIDA or some material of almost identical nature, perhaps a polymer produced from the plasticizer. No measurable amount of BPA was seen.

The plasticizer loss on washing (Fig. 10) repeated much the same pattern as that of visual exudation, with maximum plasticizer loss at 0.1%–0.5% BPA content. At zero days in the oven, washing only extracted DIDA and did that uniformly with little or no influence of BPA concentration. After at least two days in the oven, the effect of BPA showed up as exuding samples gave greater weight loss. The lower curves show less extraction from within the PVC sheets as they aged.

DISCUSSION OF RESULTS

During the induction period of Figure 1, oxygen is taken up slowly. There is a slight gain in weight, or at least the weight loss is less than would be expected from true volatility. The weight gain or loss during this induction period may not be uniform but may fluctuate, since several different chemical structures are involved in the oxidation and the peroxides formed differ in stability.³ As the peroxide content increases toward a maximum, the peroxides begin to break down into small fragments which are lost. The odor of formaldehyde as methyl groups are removed is strong above DIDA that is being oxidized.

The loss of these fragments results in a pseudovolatility much greater than the volatility that would be predicted after the manner of Quackenbos.⁷ He has shown that plasticizer loss from PVC film can generally be predicted from its vapor pressure. Poly[ethylene glycol di(2-ethylhexoate)] was an obvious exception in his work, as it was lost from the film at a rate 10–20 times too fast. He offered no explanation at the time, but the many ether groups in its structure should make it oxidize and fragment easily.

Color during the induction period probably results from production of quinoid structures from the BPA. With higher concentrations of BPA, more quinoid groups may be formed. It may also be expected that with higher concentrations of BPA the uptake of oxygen *during the induction period* will be greater as an increased number of short-chain reactions are started.⁸ Bleaching is probably caused by the peroxides that form, and there is at first a competition between color formed from decomposing peroxides and color bleached by the peroxides.

The increase in viscosity is the result of some type of oxypolymerization and, as such, the increase in viscosity should begin after the peroxide induction period.⁸ The residual viscous plasticizer should be less efficient than DIDA, so in PVC it should result in higher modulus and higher T_g than the starting DIDA. Elongation would not necessarily be much affected by this change in efficiency.

In these experiments on aging of DIDA per se there is little to indicate that higher concentrations of BPA behave in any unsuspected manner. They extend the induction period as would be predicted. Except for color it might seem that the more BPA, the better.

Weight loss from plasticized PVC (Fig. 8) showed this is not the case. At higher concentrations of BPA, an abnormal weight loss was again observed. This is probably a result of increased oxidation. At higher concentrations, various types of antioxidants have been found to be pro-oxidants,⁹ especially in the presence of metals.¹⁰ It seems highly probable, therefore, that the combination of antioxidant, stabilizers, etc., resulted in the pro-oxidant effect. Figure 8 also shows that at longer times the most efficient amount of BPA is actually found at lower and lower concentrations, in agreement with the idea that the antioxidant not only terminates free-radical chain reactions early, but also starts an even larger number. Figure 7 shows the same concentration effect but with less precision.

Oxidation, of course, is worse when no BPA is used. A comparison of results at 0.0% BPA and at 1% BPA seems to indicate that although oxidation and pseudovolatility have changed the DIDA, in both cases, there is a difference. T_g has been severely damaged in both cases, but elongation is retained in the presence of high BPA. The low extraction at high BPA content plus the presence of an apparently polymeric material on the surface suggest that at higher BPA concentrations in plasticized PVC, the DIDA was changed to a less efficient but compatible plasticizer mixture rather than being destroyed completely as a plasticizer.

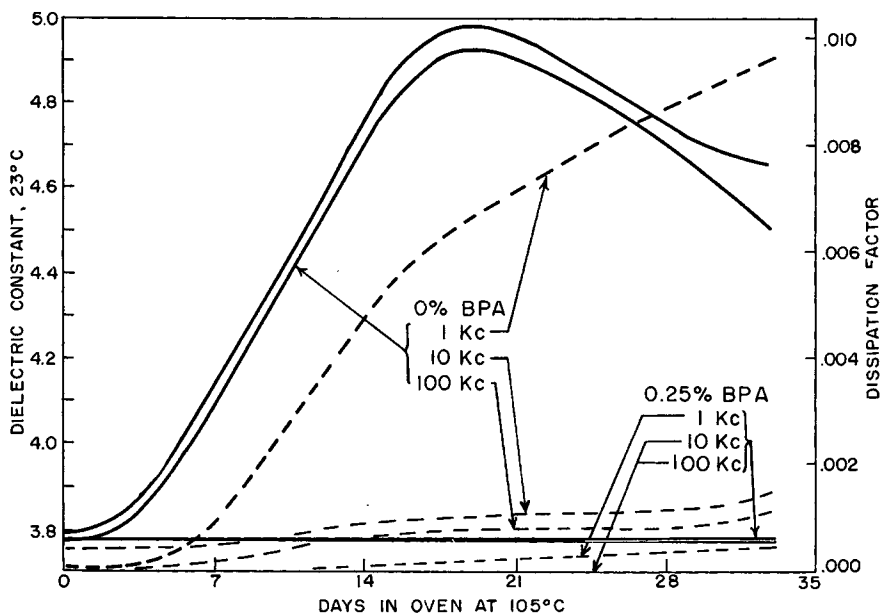


Fig. 11. Change in electrical properties during oxidation of DIDA with 0% and 0.25% BPA. Solid lines represent dielectric constants; dashed lines, dissipation factors at indicated frequencies.

Maximum exudation at intermediate concentrations of BPA is in keeping with the above concept. Probably the BPA does not cause or promote the exudation of DIDA, but simply permits it. Delmas and Patterson¹¹ have presented a theoretical explanation for an upper temperature region of resin insolubility as well as a lower temperature region. They speculate that the reason insolubility at elevated temperatures is not commonly observed is that it occurs above the boiling points of the solvents which might be used. Doolittle,^{12,13} on the other hand, has long pointed out that many plasticizers for cellulose are less compatible at elevated temperatures than at room temperature. This is particularly true with long, extended molecules with buried function groups. DIDA is such a compound. Salomon and Van Amerongen¹⁴ very early found in their study of solvent swelling of rubbers that with some solvents, swelling was greater at low temperatures than at higher temperatures. It seems likely, therefore, that the presence of exudate at intermediate concentrations of BPA is simply the result of normal incompatibility of DIDA at 105°C and that absence of liquid exudate at zero concentration and only slight exudation at high concentrations of BPA is a result of oxidation to more polar and more compatible products.

Figure 11 shows this increase in dielectric constant of DIDA from the low value of 3.74 to about 5.0, well inside the range which would indicate compatibility in keeping with the proposed theory. As might be expected from other latent degradation studies, the increase in dissipation factor

(accompanying more conductive impurities) lagged behind the change in dielectric constant. This is particularly true for measurements at higher frequencies. At higher frequencies the dissipation of energy (conductance, etc.) would require very mobile (small) molecules or segments of molecules and should come after severe fragmentation. BPA at 0.25% inhibited these changes for the duration of the test even though it developed a rather dark color.

Such effects as these are not restricted to DIDA but may be observed in any oxidizable plasticizer of borderline compatibility at the low end of the solubility parameter and dielectric constant scales.

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