Loss of Additives from Polymers: A Theoretical Model

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Synopsis

The rate at which an additive is lost from the surface of its solution in a polymer is considered to depend upon three factors—the solubility of the additive, the rate at which it volatilizes from the polymer surface, and its diffusion coefficient within the bulk of the polymer. By adapting the mathematics of heat flow in a solid, the loss of additive from a polymer is mathematically modeled in terms of these three variables for bulk polymer and for film and fiber samples. Two cases are considered—loss of additive by volatilization or dissolution from the polymer surface and loss by precipitation on the surface from a supersaturated solution of the additive. The results are applied to a discussion of the relative importance of the three parameters under various conditions occurring or expected in practical application of additives as oxidation stabilizers for polyethylene and polypropylene.

INTRODUCTION

Additives of several types are commonly incorporated into polymers at concentrations of 0.01 to 1.0 wt. % to minimize the effects of oxidative degradation, both during processing and in the subsequent service life of the polymer. The effectiveness of a stabilizer mixture depends primarily on its ability to interfere with the oxidation chemistry either by virtue of chemical reaction (radical trapping or peroxide decomposition) or by physical processes (ultraviolet absorption or excited state quenching). The inherent efficiency of many modern stabilizing systems measured in accelerated tests on liquid hydrocarbon substrates is often very high, and predicted polymer lifetimes are correspondingly long. However, a secondary factor of great importance is that an effective stabilizer must be capable of being introduced into the polymer in a form in which it is active and must remain in the polymer long enough for its potential stabilizing effect to be realized. It has long been recognized that the loss of additives by volatilization from the polymer surface may be a very important factor in determining service lifetimes. For example, Hawkins et al.,[1] Temchin et al.,[2] and Bair[3] have shown that typical stabilizing additives are lost from polyethylene films, both above and below the melting point of the polymer, at rates which are significant relative to the lifetime of the polymer. Similar conclusions have been demonstrated by Spacht et al.[4] and by Angert et al.[5] for loss of phenolic and amine antioxidants from rubbers.

Assuming that a compatible stabilizer can loosely be defined as a system which can be put into the polymer in a form in which it is effective and which will remain in the polymer long enough to be able to exert its stabilizing influence, then it is useful to examine the factors that are important in determining additive compatibility. Clearly, one very important factor is the solubility of the additive,

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since a completely insoluble additive is unlikely to be particularly effective and the solubility determines the amount of material which can be present in the polymer as an equilibrium homogeneous solution. Ambrovic and Mikovic[6] and Nechitailo and Sanin[7] have used melting point depression methods to study interaction of stabilizers with polyethylene and polypropylene, and Feldshtein and Kuzminskii[8] have made similar measurements by vapor pressure methods; all three groups appear to consider that solubility is the most important factor in additive compatibility.

Assuming an additive that is present in the polymer as a homogeneous solution, Angert et al.[5] have pointed out that the rate of loss of additive is determined by two extra factors. Initially, the loss rate is determined by the rate of volatilization of material from the polymer surface, which will act to create a concentration gradient at the surface. Subsequently, material depleted from the surface must be replaced by diffusion from the bulk so that the overall loss process depends upon both the rate of mass transfer across the sample surface and the rate of diffusion within the sample. By comparison of theoretical and experimental data, Angert et al. concluded that the loss of phenyl-β-naphthylamine from thick samples of rubber is dominated by the rate of removal of the additive from the surface, although they did not correlate this rate with the additive volatility. Unfortunately, despite this early work subsequent investigators have largely considered compatibility in terms of only one of the important factors.

As part of a study of additive migration, Westlake and Johnson[9] examined the extraction of 2,4-dihydroxybenzophenone from thin films of polymer into water and interpreted their results in terms of a diffusion coefficient model. Similarly, Cicchetti et al.[10,11] consider that diffusion is the most important property of an antioxidant.

In contrast, most other authors have attempted to consider antioxidant loss in terms of volatilization, ignoring the role of diffusion. For example, Spacht et al.[4,12] correlated antioxidant loss from slabs of rubber with measurements of bulk volatility, and similar correlations have been attempted for polyolefins.[13–16]

Loss of additive from the polymer surface by a dissolution mechanism, such as volatilization into air or solution into a flowing liquid (usually water), has been widely studied. An alternative process can occur when the additive is present in the polymer at concentration above its saturation solubility. For the most common case where the melting point of the additive is below that of the polymer, it appears that supersaturated solutions are readily formed so that the additive may then precipitate either within the polymer or on the surface. The latter process is termed "blooming," and it has been observed by Bair,[3] Roe,[17] and Haward[18] although no attempt has been made to quantify the process. In contrast, as far as we are aware there is no case of loss of an additive by crystallization within the polymer, although Clark et al.[19] have shown that crystalline precipitates of vulcanization accelerators can be observed in rubber. Using x-ray analysis, thermal analysis, and ultraviolet microscopy, we have so far been unable to detect precipitation of additives in polypropylene[20] although we have indirect evidence that it may occur in some situations.

In view of the lack of any quantitative model to describe loss of additives and because of the importance of the problem in industrial practice, we have at-

tempted to establish a basic model which will take into account the involvement of solubility, volatility, and mobility in both volatilization loss and blooming mechanisms.

In addition, a complete model would also need to take into account the consumption of additives by oxidation reactions and the variations of ultraviolet intensity with depth in the sample during stabilizer loss. For the present, both of these factors are neglected since they make the mathematics of the model excessively complex. It is however essential to have some criterion for failure of an antioxidant system, and appropriate criteria are discussed below.

CASE 1: ADDITIVE LOSS BY SURFACE REMOVAL

Basic Model—Definition of Terms

We consider first the situation in which a polymer sample contains a single additive, present as a homogeneously dissolved component, which is lost by dissolution into a flowing medium in contact with the polymer surface. This causes the additive concentration immediately above the polymer surface continuously to be maintained at zero. The flowing medium may be a gas, in which case we are considering the simple surface evaporation case; alternatively, it may be a liquid.

The process of removal of any soluble additive must involve two distinct processes; (1) the removal of material from the surface by evaporation or dissolution and (2) its replacement in the surface layer by diffusion from the bulk polymer. Clearly, a mathematical model requires two parameters: a mass transfer constant characterizing transfer across the boundary and a constant characterizing mass transfer within the bulk polymer. In this sense additive loss is precisely analogous to radiative heat loss, where the two parameters are surface emissivity and thermal conductivity, respectively. In the context of additive loss, the bulk parameter is clearly the diffusion coefficient D, but the surface loss parameter is less immediately obvious.

Consider the interface between a polymer and air and imagine a crystal of additive in contact with the polymer surface. At equilibrium this crystal is simultaneously in equilibrium with the vapor space above the polymer and with its saturated solution in the polymer. It thus follows that the vapor pressure of additive above its saturated solution in the polymer must be equal to the vapor pressure of the pure additive at the same temperature. As a reasonable approximation we assume that the solution of additive in polymer behaves in a near-ideal way so that the vapor pressure above an unsaturated solution is the value for saturation multiplied by the fraction of saturation solubility. If we further assume that the rate of volatilization of the additive is proportional to its vapor pressure in any given set of conditions, then the rate of volatilization V of additive from the polymer is related to the rate of volatilization V_0 of pure additive per unit surface area by

$$V = V_0 C_s / S = H C_s \tag{1}$$

where C_s is the concentration of additive at the polymer surface and S is the saturation solubility; the parameter H is then the required mass transfer constant and can be evaluated by measurements of V_0 and S.

Mathematically, additive loss into a flowing liquid is exactly the same situation, but it is much more difficult to assign values to H since V_0 now becomes the rate of dissolution of pure additive in the liquid medium. Although this quantity is expected to be proportional to additive solubility in the liquid, we are not aware of any attempts to measure these quantities, and accordingly for the remainder of this section we restrict ourselves to the surface evaporation case.

The analogy between evaporative loss of an additive and radiative loss of heat has already been mentioned, and the mathematical approach to both problems is identical. Solutions to the heat flow problem are presented by Carslaw and Jaeger[21] and have been recast into diffusion terms by Crank.[22] It is thus possible to obtain solutions for many cases of practical interest and to compute the time dependent additive concentration profiles. By combining this data with an appropriate failure criterion we may estimate the critical time to failure in terms of the parameters D and H and the sample geometry. Several cases of interest are presented below.

Surface Evaporation with Finite Boundary Conditions—Loss from Films and Fibers

We consider first a film of polymer of thickness $2l$ from which additive is lost by surface evaporation at a rate determined by the surface concentration and the parameter H, the lost additive being replaced by diffusion from the bulk with a diffusion coefficient D. For simplicity we assume in this and all other calculations that D is independent of the additive concentration. Crank[22] has shown that under these conditions the total amount of additive M_t leaving the polymer up to time t is expressible as a fraction of the corresponding amount M_∞ at infinite time by

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp(-\beta_n{}^2 T)}{\beta_n^2(\beta_n^2 + L^2 + L)} \qquad (2)$$

where $T\ (= Dt/l^2)$ and $L\ (= lH/D)$ are dimensionless variables and the β_n values are the positive roots of

$$\beta \tan \beta = L \qquad (3)$$

and are tabulated by Carslaw and Jaeger.[21]

In order to apply eq. (2) it is necessary to define some criterion for failure of the antioxidant system, and we consider it reasonable for a first approximation to assume that degradation will proceed rapidly to sample failure when the average concentration of additive falls to 10% of its initial value, i.e., when M_t/M_∞ = 0.9

Numerical evaluation of eq. (2) quickly reveals that no significant error is introduced by ignoring terms other than $n = 1$. The failure criterion can thus be written

$$\frac{2L^2 \exp(-\beta^2 T)}{\beta^2(\beta^2 + L^2 + L)} = 0.1 \qquad (4)$$

Figure 1 shows a plot of eq. (4) for a variation of L over a range of six orders of magnitude. For high values of L (thick film, rapid evaporation, and low diffusion rate), the equation approaches the asymptotic limiting form $\log T = -0.06$ so that high L values lead to a failure time given by
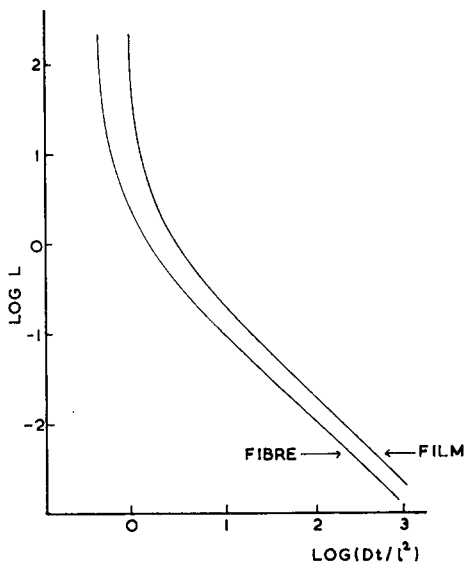
Fig. 1. Predicted times for loss of 90% of original additive from fibers and films expressed in dimensionless coordinates.

$$t = 0.87l^2/D \qquad L > 10 \tag{5}$$

and, as expected, the failure time is diffusion dominated and independent of H.

In contrast, at low values of L, eq. (4) becomes a line of unit slope obeying the equation $\log L + \log T = 0.383$, from which the time to failure is given by

$$t = 2.42l/H \qquad L < 0.6 \tag{6}$$

And, again as expected, the diffusion rate is unimportant under conditions where diffusion is very rapid compared to surface loss. The form of eq. (4) is such that either eq. (5) or eq. (6) will apply with little error except in the range $10 < L < 0.6$ where the equation is significantly curved.

The behavior of a finite cylinder (fiber case) is expected to be rather similar to a film, and such is found to be the case. For the case of a cylinder of radius l, the appropriate equation is[22]

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4L^2 \exp(-\beta_n^2 T)}{\beta_n^2(\beta_n^2 + L^2)} \tag{7}$$

where the β_n values are now roots of

$$\beta J_1(\beta) - L J_0(\beta) = 0 \tag{8}$$

$J_1(\beta)$ and $J_0(\beta)$ being the corresponding Bessel functions. Figure 1 shows the equivalent plot to eq. (2) for eq. (7). The corresponding limiting failure times are, for high values of L (diffusion dominated),

$$t = 0.35l^2/D \qquad L > 15 \tag{9}$$

and for low values (volatility dominated),

$$t = 1.21l/H \qquad L < 0.3 \tag{10}$$

Comparison of fiber and film results show that at high values of L, where surface evaporation is the rate-determining process, the time to failure of a film is predicted to be twice that of a fiber. In contrast, at low values of L, where diffusion is becoming the dominant process, the fiber is expected to fail 2.5 times faster than a film of the same thickness.

Surface Evaporation from a Semiinfinite Solid—Loss from Bulk Polymer

The evaporative loss of additive from a semiinfinite bulk solid is somewhat more difficult to characterize than is the case with fibers or films. If the initial concentration at the surface is C_0, then the concentration at a depth l at time t is given by[21]

$$\frac{C}{C_0} = \text{erf}\left(\frac{l}{(4Dt)^{1/2}}\right) + \exp\left(\frac{Hl}{D}\right) + \frac{H^2t}{D}\,\text{erfc}\left(\frac{l}{(4Dt)^{1/2}}\right) + \left(H\frac{t}{D}\right)^{1/2} \quad (11)$$

where erf is the Gaussian error function and $\text{erfc} = 1 - \text{erf}$. The failure criterion must be expressed in terms of both concentration and depth, and we have chosen to assume that failure occurs when the additive concentration is reduced to 10% of C_0 at a depth l. Appropriate dimensionless parameters are now L $(= Hl/D)$ and T' $(= Ht^{1/2}D^{-1/2})$, and Figure 2 shows the failure criterion calculated by numerical solution of eq. (11) in terms of these variables. For low values of L (<0.1), corresponding to high diffusion rate and low volatility, the asymptote is $\log T' = 0.74$ giving a failure time

$$t = 30D/H^2 \quad (12)$$

For high values of L (>3), equivalent to rapid evaporation and low diffusion rate, the relationship is given by $\log L = \log T' -0.75$, and the failure time is
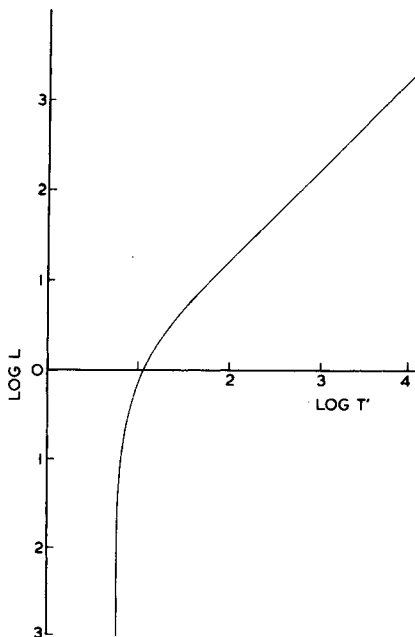

Fig. 2. Predicted times for loss of 90% of original additive at any specified depth of bulk polymer expressed in dimensionless coordinates.

$$t = 32l^2/D \tag{13}$$

As expected, this equation has a form similar to (5) and (9), the equivalent versions for fibers and films. The numerical coefficient is much higher partly because of the large reserve of additive provided by the bulk polymer and partly because the failure criterion is more severe involving reduction to 10% at depth l, rather than an average of 10% over the whole sample. In contrast, the failure time for low L is independent of l due to the fact that slow surface loss with high replacement rate leads to a very flat concentration profile extending into the bulk material.

CASE 2: ADDITIVE LOSS BY SURFACE PRECIPITATION

In the previous section we considered the case of additive loss under conditions where additive molecules crossing the surface of the sample are immediately removed by the flowing gas environment. This is the only valid model if the additive is present below its saturation solubility; it may also apply to an additive above its saturation value if it evaporates from the surface rapidly. However, a more probable mechanism for loss from supersaturated samples is the process of "blooming" to produce crystals upon the sample surface. The effect of blooming is to fix the concentration at the sample surface at a value S equal to the saturation solubility. This is also the limiting concentration throughout the sample at equilibrium, and the concentration can only fall below S at any point if the crystals are removed from the surface to change the loss mechanism to an evaporation case. Since the surface concentration is fixed at saturation, the loss process is essentially by diffusion through the concentration gradient in the sample. Only one parameter is required, D, and the mathematical model is the equivalent of heat loss from a sample at constant surface temperature.

For cases having finite boundary conditions (films and fibers), it is readily shown and intuitively obvious that the approach to saturation equilibrium is identical to the case of very high evaporation rate described in the previous section. Thus, eqs. (5) and (9) will describe the time taken to reduce the initial average concentration in film and fiber, respectively, to within one tenth of its final level S. Loss then continues until a uniform concentration S is present throughout the amorphous polymer and further loss to zero concentration can only occur when the crystalline material on the surface has been removed by evaporation.

Similar considerations apply to loss by surface blooming in the case of a semiinfinite solid. The phenomenon is mathematically equivalent to the previous case with infinite H so that only the first term of eq. (11) is significant. Since the equilibrium case is $C = S$ and not $C = 0$, eq. (11) then becomes

$$\frac{C - S}{C_0 - S} = \text{erf} \frac{l}{(4Dt)^{1/2}} \tag{14}$$

And for depletion to within 10% of the equilibrium concentration of a depth l, the time is given by

$$t = 32l^2/D \tag{15}$$

which is, as expected, identical with eq. (13). Again, loss to zero concentration can only occur when the bloomed crystalline material is removed either mechanically or by its own slow evaporation.

DISCUSSION

In principle, the model we have described should allow prediction of both the mechanism and the time scale of loss of an additive from a polymer. In order fully to exploit or to test the model, it is necessary to know three properties of the additive at the appropriate temperature—its solubility in the polymer, its diffusion coefficient in the polymer, and the volatility of the pure additive. (In the case where air is replaced by a liquid it is necessary to know the rate of dissolution of the additive.) Since polymers are usually used at room temperature or at only moderately elevated temperatures, it is desirable to know these quantities at room temperature. Unfortunately, where measurements have been made they are almost invariably at elevated temperatures. There are wide discrepancies between the results of different workers, and we are not aware of any case where all three parameters have been measured for the same compound by the same workers. Clearly, any attempt to use our model must be treated with caution.

The most widely studied group of additives in polyolefins are the UV stabilizers and particularly the derivatives of 2-hydroxybenzophenone. Westlake and Johnson[9,23] have measured the solubility of the 2,4-dihydroxy- and 2-hydroxy-4-octoxybenzophenones in low-density polyethylene (LDPE) and in polypropylene (PP) over a range of temperatures and also determined the appropriate diffusion coefficients. The same molecules have been studied by Cicchetti et al.[10,11] whose values for the diffusion coefficients agree at least in order of magnitude with those of Westlake and Johnson. Volatility values for these molecules are not available, although Schmitt and Wirk[13] quote a value of 6.2×10^{-10} g-cm^2/sec for the volatility of 2,2'-dihydroxy-4-methoxybenzophenone at 25°C. Roe et al.[24] have suggested that the solubility of a phenolic antioxidant in polyethylene can be estimated from the solubility on low molecular weight hydrocarbons, while Feldshtein and Kuzminskii[8] measured solubilities of phenolic antioxidants directly. Unfortunately, there is an order-of-magnitude difference between the values obtained by these two groups.

Volatilities of typical polymer additives at elevated temperature have been determined by several authors,[13,15,16,25] but only Schmitt and Wirk[13] quote values for the latent heat of sublimation required for data extrapolation to room temperature.

Bearing in mind the limited range of data available, we have attempted to make some "guestimates" of the appropriate parameters for some interesting additive molecules, and our values are given in Table I. These values are derived from extrapolations of literature data plus intuitive guesses where data are not available.

It must be emphasized that these data are at best order-of-magntiude estimates and that they may be considerably worse. This is particularly true for PP since linear extrapolation from elevated temperatures to room temperature, which is close to the glass transition temperature, are of doubtful validity. Nevertheless, use of these figures gives us a useful basis for examining the likely importance of various factors in affecting antioxidant loss.

Using the data of Table I, it is possible to make some order-of-magnitude predictions of additive loss times, and these values are presented in Table II, being obtained by interpolation from Figures 1 and 2. For bulk polymers the critical depth is taken as 1 mm. Clearly, the most important parameter for any

TABLE I
Estimated Properties of Additives in Polymers

Additive	V_0, g-cm²/sec	LDPE			PP		
		$10^2 S$, g/g	D, cm²/sec	$10^{-2} H/D$, g	$10^2 S$, g/g	D, cm²/sec	$10^{-2} H/D$, g
2,6-Di-*tert*-butyl-4-methylphenol(BHT)	6×10^{-10}	1.5	1.5×10^{-9}	0.26	1.2	5×10^{-11}	10
2,4-Dihydroxybenzophenone (DHB)	5×10^{-10}	0.009	5×10^{-10}	111.0	0.007	5×10^{-12}	1.4×10^4
2-Hydroxy-4-octoxybenzophenone (HOB)	5×10^{-12}	1.0	1.5×10^{-9}	3×10^{-3}	0.5	1.5×10^{-11}	0.7

TABLE II
Predicted Loss Lifetimes for Additive Loss by Surface Evaporation

Additive	Polymer	Bulk solid	1 mm Film	100 μm Film	Critical Failure Time 10 μm Film	1 mm Fiber	100 μm Fiber	10 μm Fiber
BHT	LDPE	7 yr	50 day	3.5 day	8 hr	25 day	2 day	4 hr
BHT	PP	200 yr	1.4 yr	7 day	7 hr	200 day	3.5 day	3.5 hr
DHB	LDPE	20 yr	50 day	20 hr	3 hr	20 day	10 hr	100 min
DHB	PP	2000 yr	14 yr	50 day	12 hr	6 yr	25 day	6 hr
HOB	LDPE	6000 yr	7.6 yr	0.76 yr	28 day	3.8 yr	140 day	14 day
HOB	PP	700 yr	8 yr	140 day	14 day	3.5 yr	70 day	7 day

system is the quantity L $(= Hl/D)$ since this parameter determines whether additive loss is dominated by volatilization, diffusion, or the combination of both. For a simple low molecular weight additive such as BHT, the values of L are such that in both LDPE and PP loss from thick films and bulk solid is determined by diffusion while loss from thin films and fibers is controlled by the volatility of the additive; the lower diffusion coefficient on PP allows diffusion to dominate to lower sample thickness so that the lifetime is extended relative to LDPE for bulk solid and thick samples but not for thin samples.

For DHB in LDPE and PP the diffusion coefficient and volatility are expected to be comparable but the solubility is low. The value of H/D is very high so that for both polymers the diffusion rate dominates loss from even the thinnest samples. The effect of substituting an octoxy group into DHB is expected to alter the volatility much more than the diffusion coefficient for this rather flexible molecule. The result is to lower the value of L to the point where additive volatilization is the dominant process for all samples of LDPE; for PP the decrease in diffusion coefficient leads to diffusion limited loss from bulk solid and thick samples, with volatility dominating for thin samples.

As described previously, the effect of either placing the polymer in contact with a solvent in which the additive dissolves rapidly or of supersaturating the solution to produce a "blooming" mechanism is to provide a mechanism for rapid transfer of the additive across the sample boundary. In all cases the kinetics of loss are expected to correspond to the high evaporation rate limits of the volatization model. Table III shows a selection of the data from Table II coupled with predicted values for "blooming" loss under the same conditions. For the simple phenolic BHT, the effect of transfer to a diffusion mechanism is a marked shortening of predicted life for conditions where volatility was important, i.e., thin samples. For thick samples the additive is still retained for long periods so that addition of excess over the saturation solubility may be beneficial. For thin films and fibers this advantage is completely lost since the time scale of blooming is so rapid. Similar conclusions are valid for polypropylene.

In both PP and LDPE, DHB is predicted to be lost by a pure diffusion mechanism for all realistic sample geometries, and under these conditions the lifetime is the same whether blooming or evaporation occurs. In particular, the rate of loss of additive is unaffected by supersaturation and excess may be used to advantage. The effect of the octoxy group in HOB is expected to produce a volatility dominated loss from LDPE under all conditions; transfer to a diffusion limited mechanism leads to rapid blooming of excess additive and there is no advantage in supersaturation. In PP the octoxy group produces a diffusion limited mechanism for bulk solid and thick samples. For such samples the failure time is still long because of the low diffusion coefficient and supersaturation is advantageous. For thin samples blooming is very rapid and supersaturation is not useful.

CONCLUSIONS

Both the mechanism and the kinetics of additive loss from a polymer are expected to depend upon the solubility, volatility, and diffusion coefficient for the additive. In this paper we have attempted to outline a model which combines these three parameters to predict both loss mechanism and loss rate, and the

TABLE III
Comparison of Predicted Loss Times for Evaporation and Blooming

Additive	Polymer	Loss by Volatilization			Loss by Blooming		
		Bulk	100 μm Film	10 μm Film	Bulk	100 μm Film	10 μm Film
BHT	LDPE	7 yr	3.5 day	8 hr	7 yr	4 hr	2.5 min
DHB	LDPE	20 yr	20 hr	3 hr	20 yr	12 hr	7 min
HOB	LDPE	6000 yr	280 day	28 day	7 yr	4 hr	2.5 min
HOB	PP	700 yr	140 day	14 day	700 yr	17 day	4 hr

approach used is readily adapted to other sample forms and to other failure critieria. In attempting to place the model in perspective, we have used what we believe to be realistic estimates of the parameters for some simple additives. In view of the difficulty of obtaining values at room temperature, these values and the conclusions drawn must be regarded as preliminary guesses. Nevertheless, we believe that useful conclusions can be drawn and that our approach will provide a useful basis for future studies of additive loss.

Given the conclusions outlined above, it is pertinent to summarize the important factors to be considered in designing an antioxidant for particular conditions. Clearly, the most important factor to be considered is the solubility of the additive in the polymer relative to the concentration at which it is used. If the additive is present below its saturation solubility, blooming cannot occur and the rate of loss into air is determined by the ratio H/D, that is, by whether volatilization or diffusion is dominant. Once the additive is soluble, the most important consideration is to reduce its volatility. The use of long flexible substituents is ideal since it increases solubility, reduces volatility, and has little effect on diffusion coefficient relative to the unsubstituted molecule. Thus, the stabilization of both PE and PP for air contact use is most effectively achievable by additives of high solubility and low volatility. If such an additive is supersaturated within the polymer, the situation is totally different since blooming becomes the main loss process and its rate is controlled by difffusion which is usually fast. Supersaturation of additives of low H/D ratio is likely to be of little advantage since the additive will bloom relatively rapidly back to saturation.

For polymers in contact with liquids, a different situation arises since, irrespective of the additive solubility in the polymer, the loss rate is determined by the rate of diffusion of the additive to the surface. Under these conditions the most important thing is to reduce the diffusion coefficient, which is most easily achieved by increasing the size of the molecule or by devising methods of bonding the additive to the polymer. Similarly, if the additive is supersaturated in an air contact situation, the most important factor is to lower the diffusion coefficient to prevent blooming.

The efficiency of antioxidant additives is often assessed by elevated-temperature oven-aging measurements, and it has often been pointed out that the relevance of such tests to room-temperature behavior is doubtful because the oxidation process is a complex reaction whose elementary steps have different activation energies. Precisely similar conditions apply to additive loss measurements since both S, V, and D are temperature-dependent quantities. In comparing a series of additives in the same polymer, oven-aging tests are likely to be extremely poor as indication of room-temperature loss behavior. In comparing one additive in a series of polymers, the situation is a little better since S and V are expected to have temperature coefficients more or less independent of the polymer, whereas D is expected to be more temperature dependent in PP than in PE. Thus, in cases where diffusion is important, the discrepancy between oven aging and reality will be bigger for PP than for PE.

References

1. W. L. Hawkins, W. Matryek, and M. A. Worthington, *J. Appl. Polym. Sci.,* **3,** 277 (1969).
2. Y. I. Temchin, Y. F. Burmustrov, A. I. Medvedar, Y. V. Kokhanov, M. A. Guschina, and M. A. Kisleva, *Polym. Sci. USSR* **12,** 2156 (1970).
3. H. E. Bair, *Polym. Eng. Sci.,* **13,** 435 (1973).

4. R. B. Spacht, W. S. Hollingshead, H. L. Bullard, and D. C. Wills, *Rubber Chem. Technol.,* **38,** 134 (1965).

5. L. G. Angert, A. I. Zenchenko, and A. S. Kuzminskii, *Rubber Chem. Technol.,* **34,** 897 (1961).

6. P. Ambrovic and J. Mikovic, *Eur. Polym. J. Suppl.,* 371 (1969).

7. N. A. Nechitailo and P. I. Sanin, *Sov. Plast.,* **11,** 11 (1967).

8. L. S. Feldshtein and A. S. Kuzminskii, *Polym. Sci. USSR* **A13,** 2618 (1971).

9. M. Johnson and J. F. Westlake, *J. Appl. Polym. Sci.,* **19,** 1745 (1975).

10. O. Cicchetti, M. Dubini, G. P. Vicario, and E. Bua, *Eur. Polym. J.,* **3,** 473 (1967).

11. O. Cicchetti, M. Dubini, P. Parrini, G. P. Vicario, and E. Bua, *Eur. Polym.,* **4,** 419 (1968).

12. R. B. Spacht, W. S. Hollingshead, H. L. Bullard, and D. C. Wills, *Rubber Chem. Technol.,* **37,** 210 (1964).

13. R. G. Schmitt and R. C. Wirk, *J. Polym. Sci.,* **45,** 35 (1960).

14. J. Durmis, M. Karvas, P. Caucik, and J. Holcik, *Eur. Polym. J.,* **11,** 219 (1975).

15. J. Holcik, M. Harvas, D. Kassovicova, and J. Durmis, *Eur. Polym. J.,* **12,** 173 (1976).

16. G. Scott and M. A. Plant, *Eur. Polym. J.,* **7,** 1173 (1971).

17. R. J. Roe, *ACS Coat. Plast. Prepr.,* **34,** 132 (1974).

18. R. N. Haward, *Chem. Ind. (London),* 1442 (1964).

19. G. L. Clark, R. L. Le Tourneau, and J. M. Ball, *Ind. Eng. Chem.,* **35,** 198 (1943).

20. N. C. Billingham and P. D. Calvert, unpublished results.

21. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids,* Clarendon, Oxford, 1959.

22. J. Crank, *The Mathematics of Diffusion,* 2nd ed., Clarendon, Oxford, 1975.

23. J. F. Westlake and M. Johnson, *J. Appl. Polym. Sci.,* **9,** 319 (1975).

24. R. J. Roe, H. E. Bair, and C. Gieniewski, *J. Appl. Polym. Sci.,* **18,** 843 (1974).

25. G. Scott, *Pure Appl. Chem.,* **30,** 267 (1972).