

Diffusion of Stabilizers in Polymers. II. 2-Hydroxy-4-Octoxybenzophenone in Polyolefins

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Synopsis

The migration of radioactively labeled 2-hydroxy-4-octoxybenzophenone in a number of polyolefins was investigated over the temperature range 36–75°C. The rates of diffusion in the polymers studied were found to decrease in the order low-density polyethylene > high-density polyethylene ~ isotactic polypropylene, the activation energies being approximately 17, 36, and 24 kcal/mole, respectively. The results of the present study were found to be in qualitative agreement with those previously determined for the same stabilizer/polymer systems, quantitative differences being attributed to the different methods of sample preparation and the resulting differences in the morphological structures of the test specimens. The calculated solubilities of the substituted 2-hydroxybenzophenone in the various polymers were substantially higher, at a particular temperature, than the corresponding values previously determined for 2,4-dihydroxybenzophenone, being 1.4, 0.4, and 0.8 wt-% for low-density polyethylene, high-density polyethylene, and polypropylene, respectively at 75°C. Studies to determine the rate of loss of the stabilizer from polymer samples immersed in water resulted in extremely low rates of extraction, in contrast to those found for 2,4-dihydroxybenzophenone, as a result of the octoxy substituent and the resulting increase in compatibility between the stabilizer and polymer.

INTRODUCTION

The measurement of the rates of diffusion of additives through and/or their rates of loss from various polymeric materials has been the subject of a number of recent publications. These studies have dealt with a variety of additive/polymer systems and may be exemplified by those concerning accelerators, antioxidants, and extender oils in natural and synthetic rubbers,¹⁻⁷ plasticizers in poly(vinyl chloride),⁸ and antioxidants and ultraviolet stabilizers in polyolefins.⁹⁻¹⁶ Migration through and/or loss of additives from polymers, together with an understanding of the factors affecting these processes, is of practical value in that detrimental effects may often be incurred should the concentration of incorporated additives become sufficiently redistributed or depleted. For example, studies with unstabilized thin films of polypropylene have shown that photo-oxidative degradation of this polymer occurs essentially at the surface layers.¹⁷⁻¹⁹ The addition of ultraviolet stabilizing additives was found to substantially inhibit degradation until their depletion from the film became exces-

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sive, after which point failure of the film rapidly occurred.²⁰ In the case of substituted 2-hydroxybenzophenones, this was attributed to sublimation from the surface of the film. For thicker specimens, however, it is conceivable that the interior of the sample could act as a reservoir for the stabilizer, permitting replenishment of the surface region, at least to some extent, and thus enhancing the useful lifetime of the article.

In view of the above considerations it was decided that a series of studies with respect to the compatibility, mobility, and rate of loss of ultraviolet stabilizers from various polymers would provide useful information regarding the overall effectiveness of these stabilizers under conditions of usage. In a previous publication by the authors the results obtained from such studies for the UV stabilizer 2,4-dihydroxybenzophenone in high- and low-density polyethylenes and isotactic polypropylene over the temperature range 36–75°C were reported.²¹ The present paper reports the results of analogous studies obtained with the ultraviolet stabilizer 2-hydroxy-4-octoxybenzophenone.

EXPERIMENTAL

Materials

Ultraviolet Stabilizer

The preparation of radioactive 2-hydroxy-4-octoxybenzophenone was accomplished by conversion of previously prepared²¹ radioactive 2,4-dihydroxybenzophenone to the desired product by reaction with *n*-octylbromide. The reaction mixture, consisting of 0.75 g of ¹⁴C-labeled 2,4-dihydroxybenzophenone, 0.75 g of *n*-octylbromide, 4.75 g of acetone, and 0.49 g of potassium carbonate was placed in a 25-ml flask and refluxed for a period of 2 days. The contents of the flask were allowed to cool and filtered to remove potassium carbonate. The filtrate was poured into 50 ml of cold water and the resulting precipitate filtered and dried overnight in a vacuum oven at room temperature. The crude product was recrystallized from aqueous acetone and dried to constant weight. The final product (84.7% yield) was pale yellow and had a melting point of 47.5–48.5°C.

Polymers

The polymer samples used in this (and the previous) study were commercial samples in the form of 1.5-mm thick sheets. Data concerning the composition of the polymers, the presence of additives, and conditions utilized in the molding of the sheets have been reported previously.²¹ Some of the physical properties of the polymers are presented in Table I.

Procedure

The experimental apparatus and procedure utilized for both the diffusion and the extraction studies have been described in detail elsewhere.²¹ In summary, the rate of diffusion of the radioactive stabilizer through the polymers was determined by application of a thin layer of stabilizer from solution to one surface of a disc of the material under investigation and measurement of the increase in the counting rate on the initially stabilizer-free surface by means of a Geiger-

TABLE I
Physical Properties of the Polymers

Property	Polypropylene	Low-density polyethylene	High-density polyethylene (A)	High-density polyethylene (B)
Density, g/cm ³	0.90 ^a 0.8985 ^b	0.920 ^a 0.9190 ^b	0.955 ^a 0.9588 ^b	0.960 ^a 0.9535 ^b
Crystallinity, %	~65 ^a ~56 ^c	~40-46 ^d	~72 ^d	~80 ^a ~68 ^d
\bar{M}_n	91,700 ^b	25,600 ^b	14,000 ^b	5,500 ^a
\bar{M}_w	266,500 ^b	679,400 ^b	188,500 ^b	120,000 ^a
Intrinsic viscosity, dl/g	~2 ^a	~1.5 ^a	~2 ^a	

^a Data of supplier.

^b Data provided by RAPRA.

^c Calculated from density measurements.²⁴

^d Calculated from density measurements.²⁵⁻²⁷

Müller tube. The experiments were carried out in brass cells between 36 and 75°C, the temperature being maintained within $\pm 0.05^\circ\text{C}$ of the desired value by placing the cell assembly in a water bath (approximately 70% immersed). Calculation of values for the diffusion coefficients was accomplished by comparison of experimentally determined data with theoretically generated curves obtained for the diffusion process under conditions corresponding to those of the experiment.

Extraction experiments were performed by immersion of polymer discs (into which radioactive stabilizer had been diffused) in water in a glass tube which was placed in a temperature-control bath maintained at 44°C. The water in which the disc was immersed was changed at periodic intervals and the activity of the sample containing the extracted stabilizer was measured by liquid-scintillation counting. Calibration of the counting unit with a standard solution of stabilizer of concentration comparable to those encountered during the extraction experiments permitted the calculation of the weight of stabilizer lost from the disc as a function of time. From this data the value of the diffusion coefficient may be obtained as outlined above utilizing the appropriate equation.

THEORETICAL TREATMENT

The equations used to calculate values of the diffusion coefficients are those which apply to diffusion in a plane sheet.²² In the case of the diffusion experiments, equations were selected for conditions corresponding to an initially stabilizer-free sheet with a thin, uniform layer of the diffusing substance applied to one surface. In the extraction experiments, the equation applicable to desorption by a membrane was used. The assumption involved in the use of these equations and their conversion (where applicable) to a convenient form for analysis of the experimental data have been reported in a previous paper.²¹ The final forms of the appropriate equations are given in the next section.

Diffusion Experiments

Saturation conditions. This situation corresponds to the case in which the stabilizer is applied in sufficient quantity to maintain the surface concentration

constant throughout the duration of the experiment. The initially stabilizer-free surface is considered impermeable.

$$\frac{R_0}{R_E} = 1 - \frac{4\mu}{(\pi l - e^{-\mu l})} \times \left\{ \sum_{n=0}^{\infty} \frac{1}{2n+1} \cdot \frac{(-1)^n \mu + \frac{(2n+1)\pi}{2l} e^{-\mu l}}{(\mu^2 + (2n+1)^2 \pi^2 / 4l^2)} \cdot e^{-D(2n+1)^2 \pi^2 t / 4l^2} \right\} \quad (1)$$

Nonsaturation conditions. In this case both surfaces are impermeable in nature and diffusion takes place under conditions approaching zero concentration relative to the saturation value.

$$\frac{R_1}{R_E} = 1 + 2 \sum_{n=1}^{\infty} \frac{\mu^2}{\mu^2 + n^2 \pi^2 / l^2} \cdot \frac{\cos(n\pi) - e^{-\mu l}}{1 - e^{-\mu l}} \cdot e^{-Dn^2 \pi^2 t / l^2} \quad (2)$$

In the above equations, R_0 and R_1 are the counting rates at the surfaces $x = 0$ and $x = l$, respectively, at time t , and R_E is the corresponding equilibrium value. D is the diffusion coefficient (cm^2/sec), l is the thickness of the disc (cm), μ is the absorption coefficient of the polymer (cm^{-1}), and t is the time (sec).

Extraction Experiments

The theoretical equation used for the determination of diffusion coefficients from the extraction studies is that corresponding to desorption by a membrane, initially at uniform concentration, with the concentration at both surfaces equal to zero during the course of the experiment.

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-D(2n+1)^2 \pi^2 t / 4l^2} \quad (3)$$

M_t is the total amount of stabilizer lost from the sample at time t , and M_{∞} is the corresponding value after infinite time. The remaining terms are defined as previously with the exception of l , which is the half-thickness of the disc.

Analysis of the experimental results using the above equations was performed using the computer facilities of the University of Lancaster.

RESULTS AND DISCUSSION

To evaluate the diffusion coefficients using the theoretical equations presented in the previous section, it is necessary that experimental conditions with respect to the concentration of stabilizer applied to the surface of the disc closely approximate those corresponding to either the nonsaturation or the saturation condition. The equilibrium counting rates for saturation conditions were therefore determined at 75°C by the method described previously²¹ and were found to be approximately 3400, 2500, and 2200 cpm for low-density polyethylene, high-density polyethylene, and polypropylene, respectively. The magnitude of these values indicated that, in order to carry out the proposed studies under saturation conditions, a considerable quantity of the radioactive stabilizer would be required. Consequently, it was decided to conduct the diffusion studies under nonsaturation conditions. This was achieved by using dilute stabilizer solutions for application of the stabilizer to the surface of the disc, the equilib-

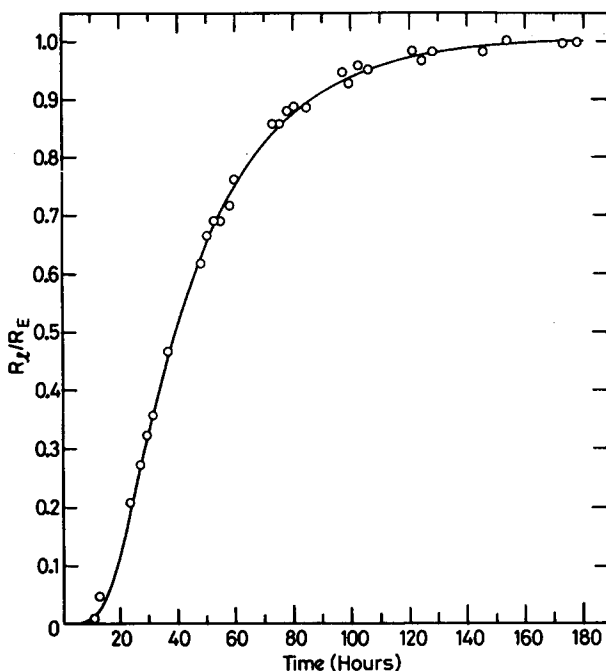


Fig. 1. Diffusion data. Plot of R_i/R_E versus time: polymer, low-density polyethylene; temperature, 60°C; disc thickness, 0.148 cm, (O) experimental points; (—) theoretical curve for $D = 2.15 \times 10^{-6}$ cm²/sec.

rium counting rates being 75 cpm or less for all experimental conditions investigated. Since studies conducted at the low end of the temperature range considered under saturation conditions indicated that the lowest equilibrium counting rate attained was 740 cpm, the per cent saturation encountered in the nonsaturation studies ranged between approximately 4 and 10%, depending upon the temperature and the particular polymer under consideration. The use of nonsaturation conditions was also found to be advantageous in that the experimental time required to attain the equilibrium counting rate was considerably less than for the corresponding saturation case.

Diffusion studies were conducted over the temperature range 36–75°C. Experimental results typical of those obtained for R_i/R_E versus time are illustrated in Figure 1 for the diffusion of 2-hydroxy-4-octoxybenzophenone in low-density polyethylene at 60°C. In most cases it was found that substitution of the appropriate value of D in the theoretical equation [eq. (2)] resulted in values that were in excellent agreement with those determined experimentally. In addition, duplicate studies indicated that good reproducibility in the calculated values of the diffusion coefficients was achieved in virtually all instances. Exceptions to this occurred for studies with low-density polyethylene at 36 and 44°C. The experimental data resulted in curves which exhibited a relatively large departure from those predicted by theory, yielding somewhat less reliable values for D at these temperatures. The temperature dependence of the calculated values of the diffusion coefficients is presented in Figure 2 for the four polymers investigated. In the case of the polypropylene and high-density polyethylene samples the results may be satisfactorily represented by an Arrhenius

TABLE II
Values of Diffusion Coefficients Calculated by Intercept and Curve-Fitting Approaches

Polymer	Temperature, °C	$D_{\text{intercept}}$, cm ² /sec	$D_{\text{curve fitting}}$, cm ² /sec
Low-density polyethylene	60	2.5×10^{-8}	2.2×10^{-8}
As above	68	5.0×10^{-8}	4.0×10^{-8}
High-density polyethylene	52	3.9×10^{-10}	2.5×10^{-10}
As above	75	7.8×10^{-9}	9.0×10^{-9}
Polypropylene	44	1.7×10^{-10}	1.2×10^{-10}
As above	75	4.7×10^{-9}	3.4×10^{-9}

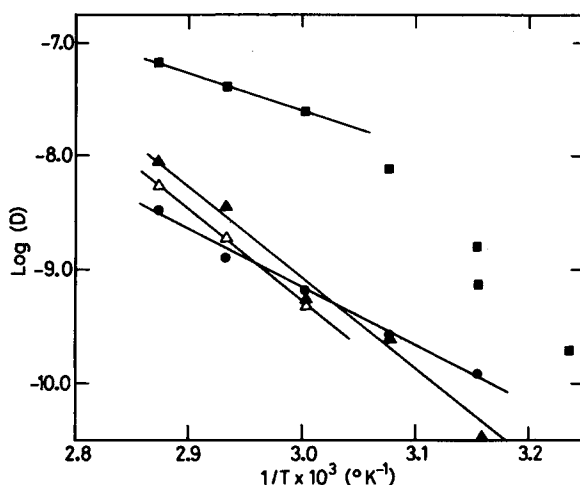


Fig. 2. Arrhenius plot of $\log(D)$ versus $1/T$: (■) low-density polyethylene; (▲) high density polyethylene (A); (△) high-density polyethylene (B); (●) isotactic polypropylene.

relationship over the temperature range considered. However, studies with low-density polyethylene indicated that a rather abrupt decrease in the value of D with decreasing temperature occurs at approximately 50°C. The activation energies for diffusion were calculated to be 16.8, 37.1, 35.6, and 23.6 kcal/mole for low-density polyethylene, high-density polyethylene (A), high-density polyethylene (B), and polypropylene, respectively. In addition to values of D calculated by curve fitting, the values were also determined by the intercept approach previously described.²¹ The data in Table II for samples chosen at random indicate that reasonably good agreement exists between values calculated by the two methods for the polymers and stabilizer under consideration.

The values of the diffusion coefficients obtained in the present study are in qualitative agreement with those previously determined for 2,4-dihydroxybenzophenone.²¹ On a quantitative basis, however, a number of differences are apparent. The diffusion experiments with polypropylene indicate that the rate of migration is somewhat higher and the activation energy considerably lower for 2-hydroxy-4-octoxybenzophenone over the temperature range investigated. In the case of high-density polyethylene samples, however, the opposite trend was observed. Comparison of the results obtained with low-density polyethylene is somewhat more difficult in view of the significant decrease in the values obtained for D in the present study below approximately 50°C. How-

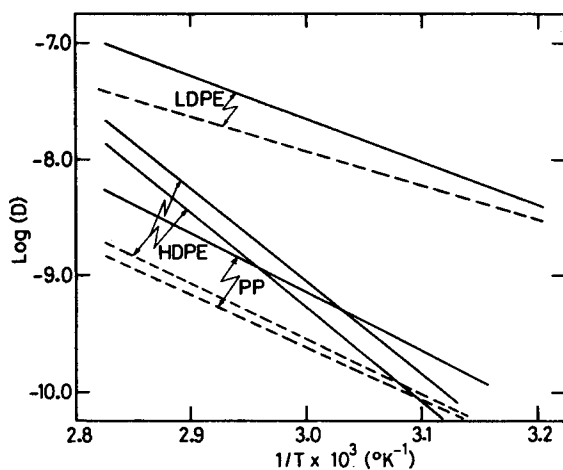


Fig. 3. Arrhenius plot of $\log(D)$ versus $1/T$: (—) data of present study; (---) data of Cicchetti.^{9,10}

ever, consideration of the results above this temperature indicates a trend similar to that found for polypropylene but to a lesser extent. The above observations may be interpreted in the following manner. In the case of 2-hydroxy-4-octoxybenzophenone, the alkoxy substituent results in an increase in the molecular volume of the stabilizer and also in an increase in the degree of compatibility of the stabilizer with the polyolefins, as evidenced by the substantial increase in the equilibrium counting rates observed. An increase in the molecular size of the diffusing species results in a decrease in the rate of diffusion, whereas an increase in compatibility between the penetrant and polymer would be expected to result in an increase in the rate of migration. Since these factors influence the value of the diffusion coefficient in opposing directions, the observed differences in the rates of migration for different stabilizers in a particular polymer depend upon the nature of the polymer itself. In the case of the highly crystalline high-density polyethylene samples, the results of the present work indicate that the size of the diffusing species is the determining factor, resulting in a decrease in the magnitude of the diffusion coefficients and an increase in the activation energy. For the more amorphous low-density polyethylene and polypropylene samples, however, the tendency towards a decrease in the rate of migration is more than compensated for by the increase in compatibility resulting in an enhanced rate of diffusion and a decrease in the activation energy. These results may be explained on the basis that diffusion in the more crystalline samples, even if occurring predominantly in the amorphous region, proceeds via a more tortuous path than in less crystalline polymers. In such instances the actual molecular size of the penetrant is the more significant factor with respect to the ease of migration. A comparison of the values obtained in the present study with those predicted by the extrapolation of results previously reported^{9,10} to the temperature range under consideration is presented in Figure 3. On a qualitative basis the results are in reasonably good agreement, particularly in the case of low-density polyethylene and polypropylene. However, it appears that the magnitude of the diffusion coefficients for migration in a given type of polymer varies depending upon the conditions of sample preparation and the

morphological nature of the polymer test specimen, as evidenced by the differences in the values of D obtained in the two studies and in the values determined for the different high-density polyethylene samples investigated in the present study.

Consideration of the equilibrium counting rates for saturation conditions permits the estimation of the solubilities of the stabilizer in the various polymers. Comparison of the saturation equilibrium values obtained in the present work at 75°C with the corresponding values previously obtained for 2,4-dihydroxybenzophenone indicates that the ultraviolet stabilizer 2-hydroxy-4-octoxybenzophenone is approximately 16, 39, and 11 times as soluble in low-density polyethylene, high-density polyethylene, and polypropylene, respectively, at this temperature. In addition, studies under conditions of saturation at lower temperatures with polyethylene samples indicated that the solubility increased by a factor of 3 over the temperature range 52–75°C, indicating a similar compatibility–temperature dependence for the two stabilizers in these polymers. Since determination of the solubilities of 2-hydroxy-4-octoxybenzophenone on a quantitative basis using the extraction technique previously employed was not feasible in the present study, estimates of the solubilities were made using the results previously obtained for 2,4-dihydroxybenzophenone and the relative solubilities determined above. At 75°C the calculated values for the solubilities of 2-hydroxy-4-octoxybenzophenone in low-density polyethylene, high-density polyethylene and polypropylene were found to be 1.4, 0.4, and 0.8 wt-%, respectively, compared with the corresponding values of 0.09, 0.01, and 0.07 wt-% for 2,4-dihydroxybenzophenone. In addition, comparison of the equilibrium counting rates obtained for low-density and high-density polyethylene samples under saturation conditions suggests that the distribution of stabilizer in these polymers may be somewhat different than that found for 2,4-dihydroxybenzophenone. In the previous study it was found that the ratio of the final saturation counting rates for low-density polyethylene and high-density polyethylene was 4–6:1, whereas the ratio of the corresponding amorphous regions was approximately 2:1, indicating that diffusion of 2,4-dihydroxybenzophenone was occurring essentially in the more accessible amorphous regions. In the present study, however, the ratio of the saturation equilibrium counting rates at 75°C was found to be 1.4:1. This result may be indicative of increased compatibility and diffusion of the substituted 2-hydroxybenzophenone in the less accessible semicrystalline regions of the polymer at this temperature. Results of a similar nature have recently been reported for the diffusion of 2-(2'-hydroxy-3',5'-di-*tert*-amyl phenyl)benzotriazole through isotactic polypropylene.²³ However, in view of the limited experimental data obtained under saturation conditions, this interpretation must be considered speculative at the present time.

Initial studies with respect to the rate of loss of stabilizer from the polymers immersed in water at 44°C were conducted with low-density polyethylene. In contrast to the results obtained for 2,4-dihydroxybenzophenone, the rate of extraction of 2-hydroxy-4-octoxybenzophenone was extremely slow, as evidenced by the results presented in Figure 4. After a period of 9 months it was estimated that less than 5% of the stabilizer initially present in the polymer disc had been extracted. This low rate of loss may be attributed to the substantial increase in compatibility between this stabilizer and the polymer as a result of the octoxy substituent. Consideration of these results, together with those

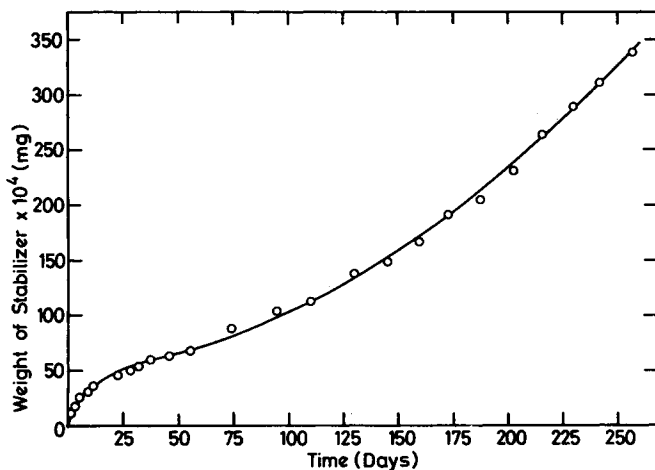


Fig. 4. Extraction data. Stabilizer loss versus time: polymer, low-density polyethylene; temperature, 44°C; disc thickness, 0.099 cm.

previously obtained for 2,4-dihydroxybenzophenone, indicate that the substituted 2-hydroxybenzophenone would be expected to be considerably more effective in applications where exposure to an aqueous or humid environment is anticipated.

In summary, the experimental results determined in the present study together with those previously obtained for 2,4-dihydroxybenzophenone indicate that significant differences exist between the two stabilizers with respect to the solubilities in, rates of diffusion through, and rates of extraction with water from the polyolefins investigated. For all polymers studied, the solubility of 2-hydroxy-4-octoxybenzophenone was found to be considerably higher than that of 2,4-dihydroxybenzophenone. The rates of diffusion of the substituted stabilizer were found to be higher and the activation energies lower in the case of isotactic polypropylene and low-density polyethylene, the opposite trend occurring for high-density polyethylene. Marked differences were noted for the rate of loss of stabilizer from polymers immersed in water, the rate of extraction of 2-hydroxy-4-octoxybenzophenone being considerably slower than that found for 2,4-dihydroxybenzophenone. In addition, comparison of the results of the present study with those calculated by the extrapolation of previously determined data for the same polymers to the temperature region under consideration indicates that the method of sample preparation and the morphological structure of the test specimen may influence the rates of diffusion to a considerable degree. From a practical viewpoint these results are of interest in that stabilizer compatibility with, rate of migration through, and rate of loss from commercially fabricated articles subjected to ultraviolet degradative processes under conditions of usage are undoubtedly important factors in determining the useful lifetime of the polymer in its intended application.

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