

INVESTIGATION OF SOME FACTORS WHICH EFFECT ON RATE OF EVAPORATION OF ANTIOXIDANTS AND ULTRAVIOLET STABILIZERS

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ABSTRACT

Volatility is a physical property which effect the retention of antioxidants during processing and use of polymeric products. The volatility data obtained for such compounds are very useful in choosing an antioxidant for particular application. In this study measurement of volatilities of some phenolic antioxidants and UV stabilizers were done by using an apparatus specially designed for this purpose.

It is apparent that the molecular weight and the molecular structure have a significant effect on the evaporation rate of the antioxidants as well as UV stabilizers. The polarity of the compounds also reduces the volatility while the environmental conditions such as vacuum enhances the volatility by a factor of 10^2 .

Key words: antioxidants, ultra-violet stabilizers, volatility

INTRODUCTION

In recent years, developments in polymer stabilizer technology have been concerned with the persistence of the stabilizer in the polymer under a wide range of environmental conditions. Volatility is one of the most important properties of a stabilizer that may affect its performance. It is a kinetic property but is expected to be proportional to the vapour pressure of the material which is an equilibrium property.

In this work volatilities of ultra violet absorbers using a new apparatus which has been constructed for this purpose, were measured. The evaporation of a stabilizer brings about a decrease in its concentration in the polymer, thereby reducing the stability of the polymeric material. Subsequently the concentration of the stabilizer in the surroundings increases. Equipment can be devised to measure volatility by one of the following:

- a) Determination of the amount of stabilizer vapourised.
- b) Determination of the weight loss of pure stabilizer or stabilized polymer.
- c) Determination of the content of stabilizer in the polymer.
- d) Stability decrease of the polymer

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Volatility of stabilizers

We have employed the method of weight loss measurement in this study. Temchin and coworkers (Temchin *et al.*; 1967a), (Temchin *et al.*; 1967b) have used a cell containing stabilizer, hanging on a torsion balance in a temperature controlled bath with or without gas flow to measure the volatility of pure stabilizers and stabilizers from polyethylene using different experimental conditions.

Volatility of antioxidants have also been determined by measuring their vapour pressures (Spacht *et al.*; 1964), (Spacht *et al.*; 1965). The evaporation of stabilizer in high vacuum has also been investigated by Schmit & Hirtt (1960) in order to determine their effectiveness in cosmic space of temperatures in the range 0-230 °C. In this work volatilities of ultra violet absorbers and some phenolic antioxidants were measured using a new apparatus which has been constructed for this purpose. Measurement of the loss of stabilizers at high temperatures provides data on the behavior of stabilizers during processing where some loss does occur. However, considerable loss can also occur at lower temperatures when the final product is used outside or under certain conditions (vacuum, washing).

MATERIALS AND METHODS

The names and the chemical structures of UV stabilisers are given in the Table 1.

Table 1. *The chemical structures and names of UV stabilizers*

Common name	Chemical name	Structure
cyasorb UV9	2-hydroxy-4-methoxy benzophenone	R-OCH ₃
Cyasorb UV531	2-hydroxy-4-octoxy benzophenone	R-OC ₈ H ₁₇
Aduvex 2412	2-hydroxy-4-dodecoxy benzophenone	R-OC ₁₂ H ₂₅

The chemical and trade names of the antioxidants are tabulated in the Table 2.

Determination of volatility

The method employed is similar to the method described by Schmitt & Hirt (1960). The apparatus used is shown in figure 1. It consists of a thermostatically controlled copper sample holder (cylindrical shape) which is covered with a ceramic insulator to minimise heat loss. The top part of the apparatus is filled with dry ice to cool the concave collecting surface where the vapours of the compound is condensed. The whole apparatus is attached to the vacuum system via a liquid nitrogen trap. Aluminum sample pans of surface area

Table 2. *Chemical and trade names of antioxidants*

Antioxidant	Chemical name	Melting point/°C
BHT	4-methyl-2,6-di-t-butyl phenol	71
BHEB	4-ethyl-2, 6-di-t-butyl phenol	49
AO754	4-hydroxy methyl-2, 6-di-t-butyl phenol	143
PWSP	2,2'-methylenebis-(4-methyl-6-(1-methylcyclohexyl) phenol	138
PL2246	2,2'-methylenebis-(4-methyl-6-t-butyl) phenol	13

3.46 cm² were used. The sample temperature was controlled to $\pm 0.1^\circ\text{C}$ by a Eurotherm controller, using a thermo couple sensor. Because of the cooling effect of the dry ice, the apparatus had to be calibrated using a series of compounds of known melting points. A temperature correction was made by plotting the set temperature versus actual temperature of the pure compounds. The experiments consisted of exposing each of the additives to vacuum at a series of temperatures for measured times. The evaporated additive condensed on the concave collecting surface was rinsed off with chloroform. The amount of weight loss was determined by weighing. All the measurements were taken above the melting points of the compounds to obtain smooth surface of known surface area.

Volatility measurements in circulating air

In the case of highly volatile antioxidants such as BHT, BHEB and AO754 weight loss measurements were carried out in an air circulating oven. The use of volatility apparatus was not possible as the compounds evaporate within too short a time when heated under vacuum. Samples (10 g) were kept in glass sample holders and placed in the ovens at different temperatures. Weight loss measurements were taken at certain time intervals. The loss in weight was calculated from the difference between initial and reweighed weights.

RESULTS AND DISCUSSION

Volatility of UV absorbers

All the experiments were conducted above the melting points so that the complication due to the non uniformity of the surface area of the powdered additive does not arise. Included in Table 3 are the volatilities of UV absorbers, measured using the volatility apparatus.

Volatility of stabilizers

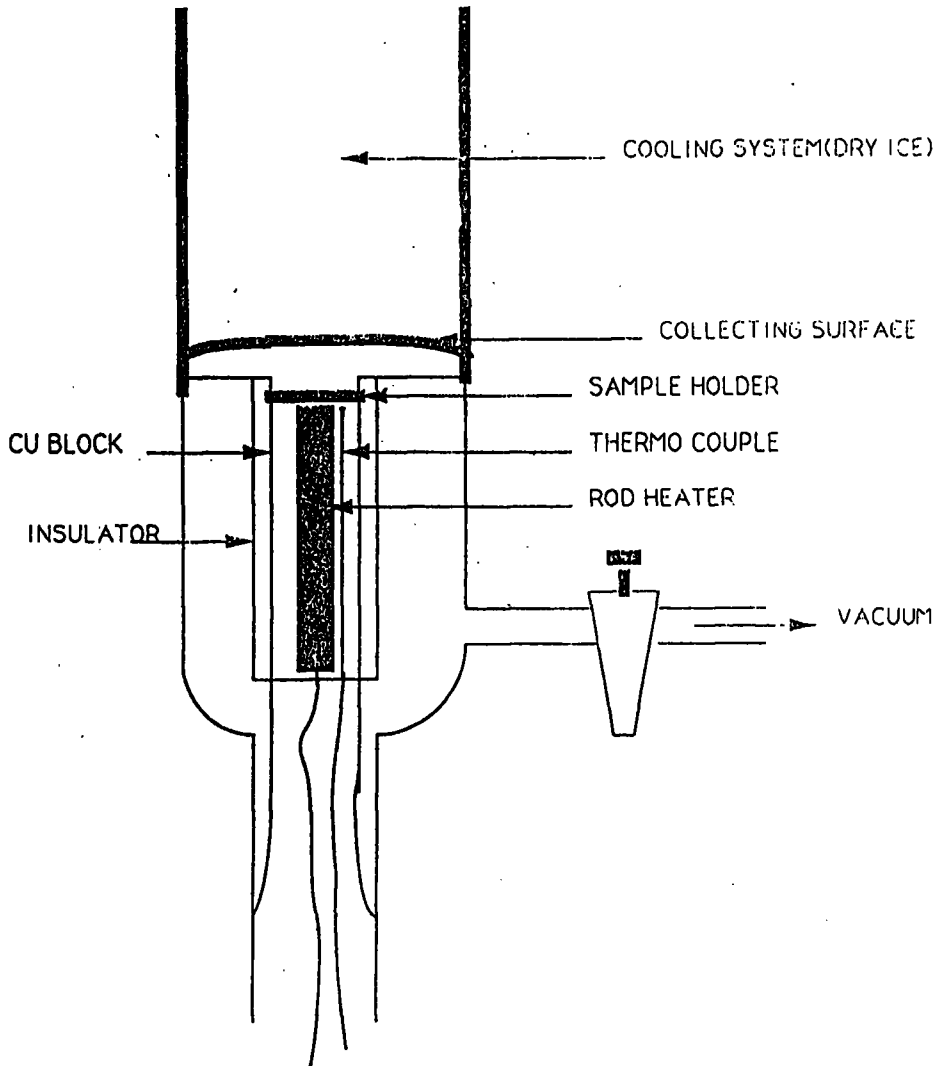


Fig. 1. Volatility apparatus

Table 3. *Volatilities of UV absorbers in vacuum*
gcm⁻²s⁻¹

T/°C	UV9	UV531	AD2412
65	1.75x10 ⁻⁶	-	-
70	2.55x10 ⁻⁶	-	-
76	3.66x10 ⁻⁶	3.57x10 ⁻⁸	-
86	-	9.10x10 ⁻⁸	-
96.5	-	1.71x10 ⁻⁷	-
107	-	3.25x10 ⁻⁷	5.17x10 ⁻⁸
133	-	-	3.94x10 ⁻⁷
138	-	-	7.93x10 ⁻⁷
148	-	-	1.23x10 ⁻⁶

Measurements of volatility under vacuum was difficult for antioxidants BHT and AO754 as they are highly volatile. AO754 starts giving fumes at high temperatures. Such experimental difficulties were encountered with several compounds at temperatures high enough for volatility measurements. Table.4 gives the volatilities of the stabilizers measured in hot air ovens.

Table 4. *Volatility of pure stabilizers in air*

AO	T/°C (+1)	Volatility/gcm ⁻² s ⁻¹
BHT	99	3.74x10 ⁻⁶
	90	2.17x10 ⁻⁶
	70	2.89x10 ⁻⁷
	60	5.70x10 ⁻⁸
BHEB	90	1.52x10 ⁻⁶
	70	2.26x10 ⁻⁷
	60	5.20x10 ⁻⁷
AO754	110	8.34x10 ⁻⁷
	90	5.10x10 ⁻⁸
UV9	110	4.60x10 ⁻⁷
	90	3.79x10 ⁻⁸

Volatility of stabilizers

The volatilities of the antioxidants PWSP and PL2246 which are moderately volatile and stable at temperatures above T_m , were measured. The experiments were confined to short periods of time at higher temperatures. The measurements were taken within 15 min time periods at 150 °C for PL2246.

The temperature dependence of Volatility was determined by applying the Clausius-Clapyron equation,

$$\frac{\delta \ln V}{(1/T)} = \frac{\delta \ln P}{(1/T)} = \frac{\Delta H_v}{R}$$

Where V, P and T are volatility, pressure and temperature and ΔH_v is the latent heat of vaporization. This assures that the volatility, which is a kinetic quantity, will be proportional to the vapour pressure, a thermodynamic quantity, for any given set of evaporation conditions. Figures 2-6 show the typical weight loss versus time plots for the two antioxidants, PWSP and PL2246 and three uv absorbers measured in vacuum.

The weight loss versus time plots are given in figures 7-10. The data were found to fit the Clausius-Clapyron equation for all the compounds within the temperature range studied as the plots of $\ln V$ versus $1/T$ are linear. The heats of vaporization was evaluated from the slope. Figures 11,12 and 13 show the typical plots for the temperature dependence of volatility of antioxidants and UV stabilizers. This is in agreement with the data published by Schmit & Hirtt (1960). Figure 14 shows the temperature dependence of volatility of BHT, measured above and below the melting temperature. In this case where the data were obtained above and below T_m , there is a break at the T_m , within the experimental temperature error of few degrees. This kind of behavior has been observed by Schmitt et al. for some stabilizers including UV9. They have observed that the change in slope at the break point is equal to heat of fusion of the compound. Infact, we find a much larger change in slope but the errors involved are very large since only two points are available in each range.

Table 5 compares the volatilities of some stabilisers measured at 90 °C in hot air.

Table 5. *Volatility of pure stabilisers at 90°C in circulating air*

Antioxidant	Volatility $\text{gcm}^{-2}\text{s}^{-1}$	MWt.	Melting pt. °C	H_f KJmol ⁻¹
BHT	2.17×10^{-6}	220	74	19.5
BHEB	1.52×10^{-6}	234	49	18.4
AO754	5.10×10^{-6}	236	143	28.8
UV9	3.79×10^{-8}	228	60	22.1

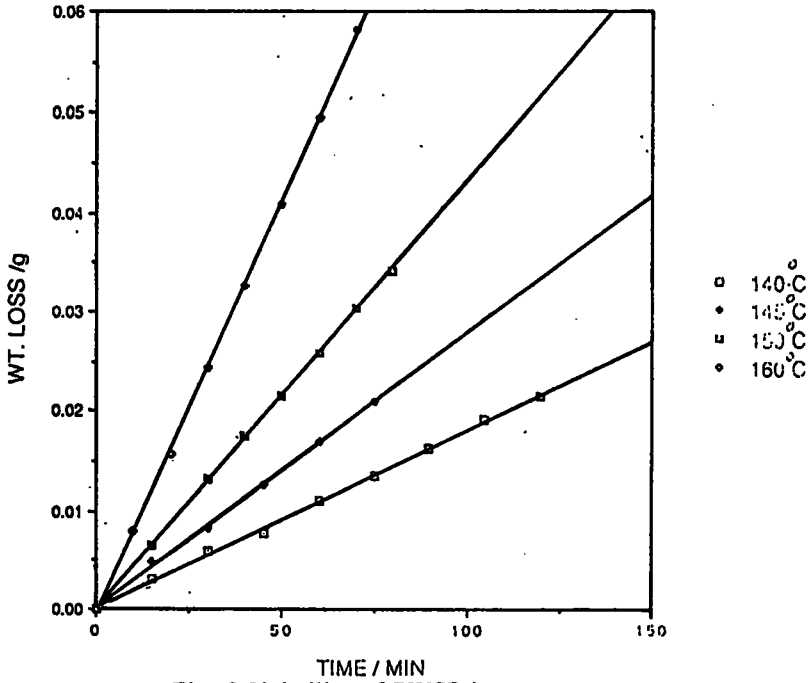


Fig. 2. Volatility of PWSP in vacuum

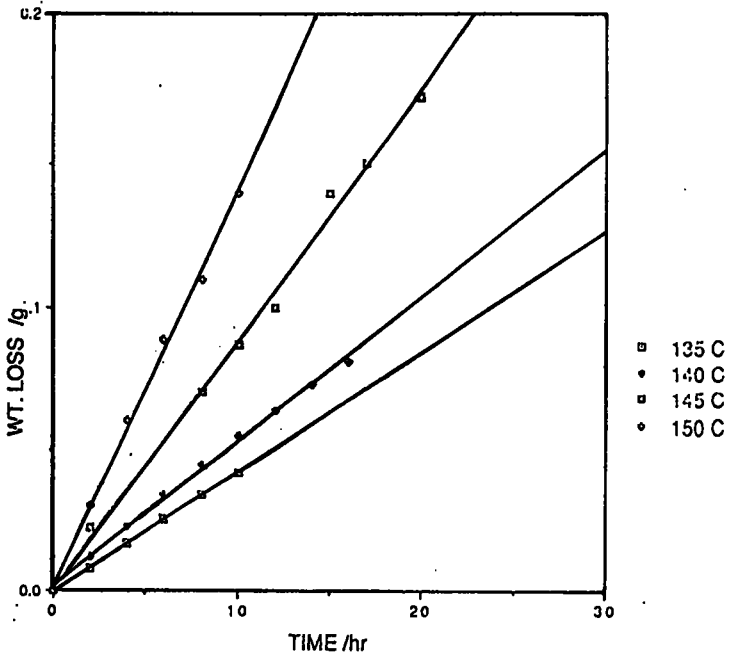


Fig. 3. Volatility of PL2246

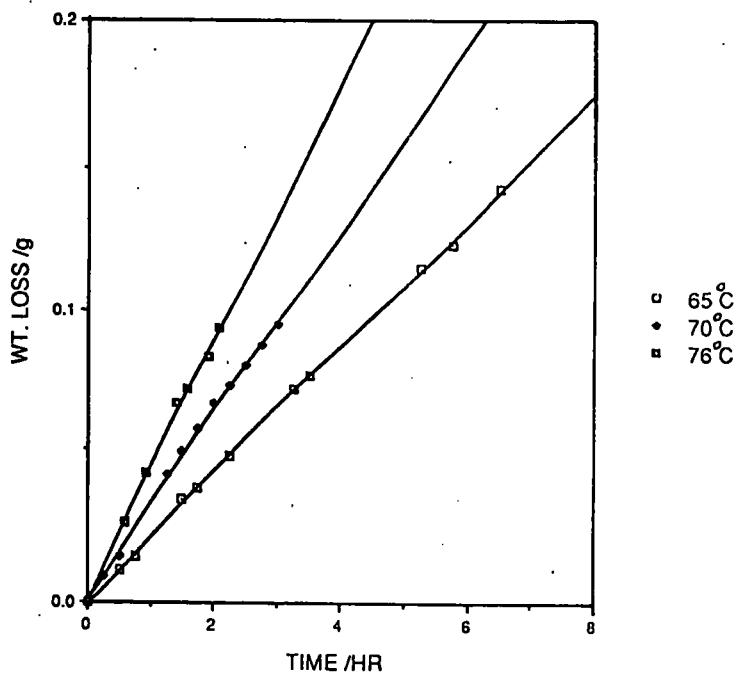


Fig. 4. Volatility of UV9 in vacuum

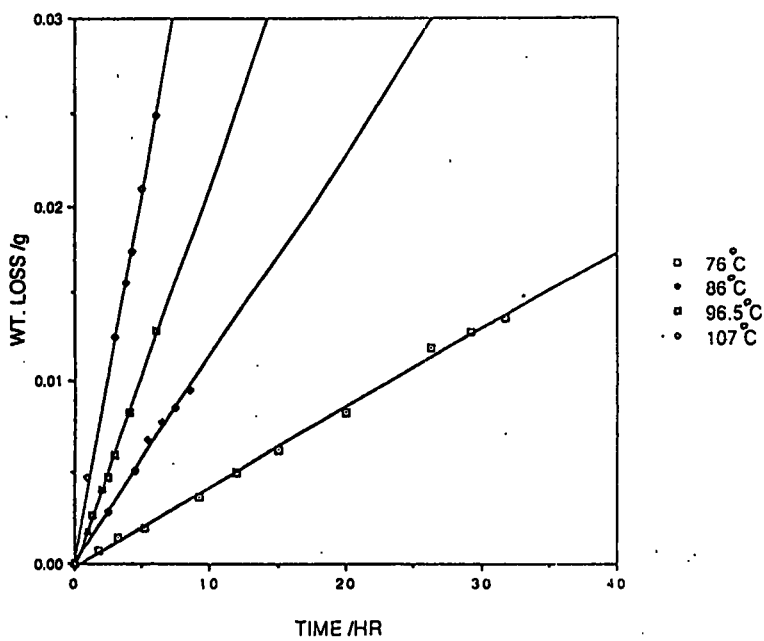


Fig. 5. Volatility of UV531 in vacuum

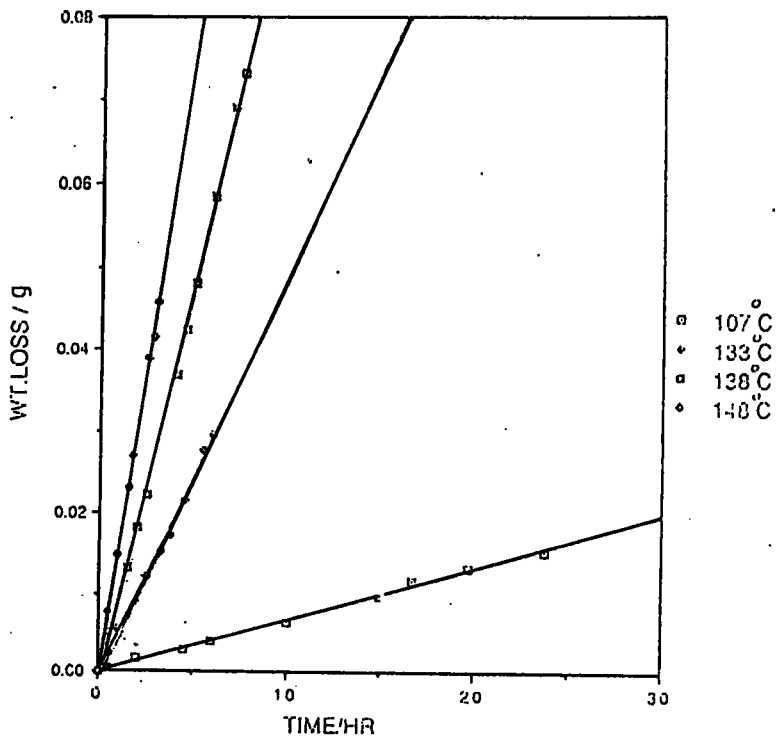


Fig.6. Volatility of AD2412 in vacuum

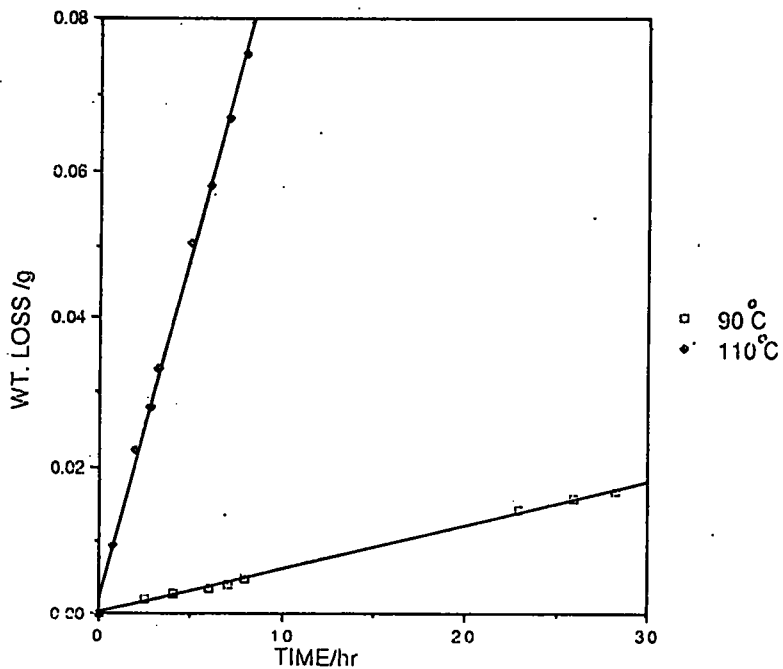


Fig. 7. Volatility of AO754 in air circulating oven

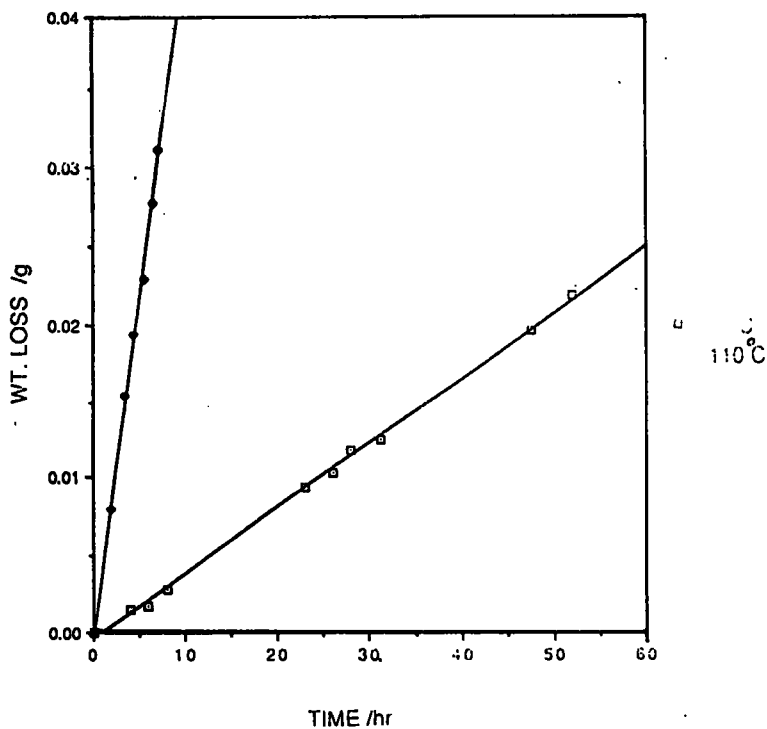


Fig. 8. Volatility of UV9 in air circulating oven

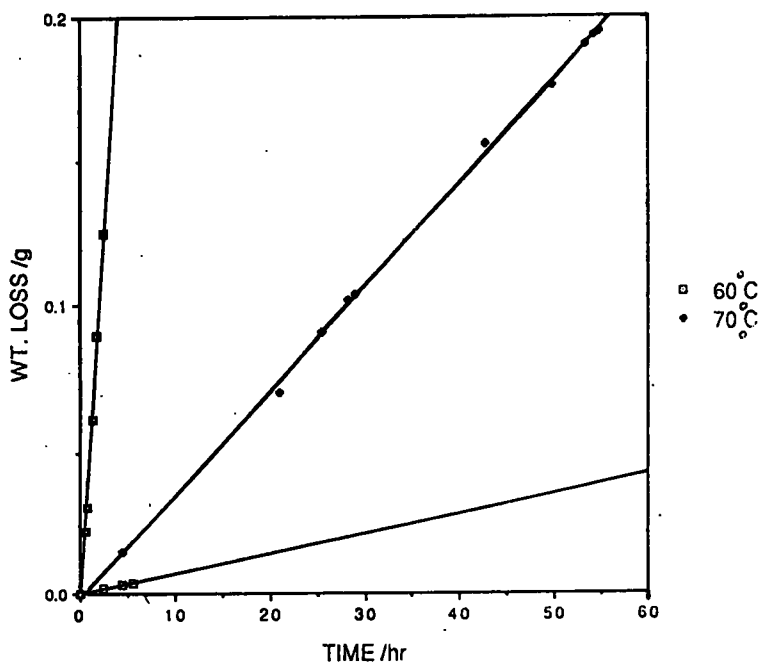


Fig. 9. Volatility of BHT in air circulating oven

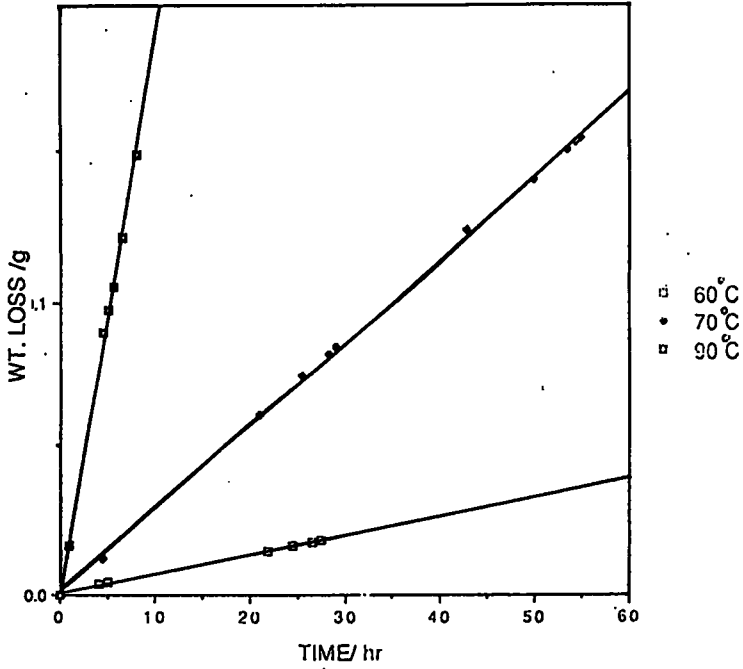


Fig. 10. Volatility of BHEB in air circulating oven

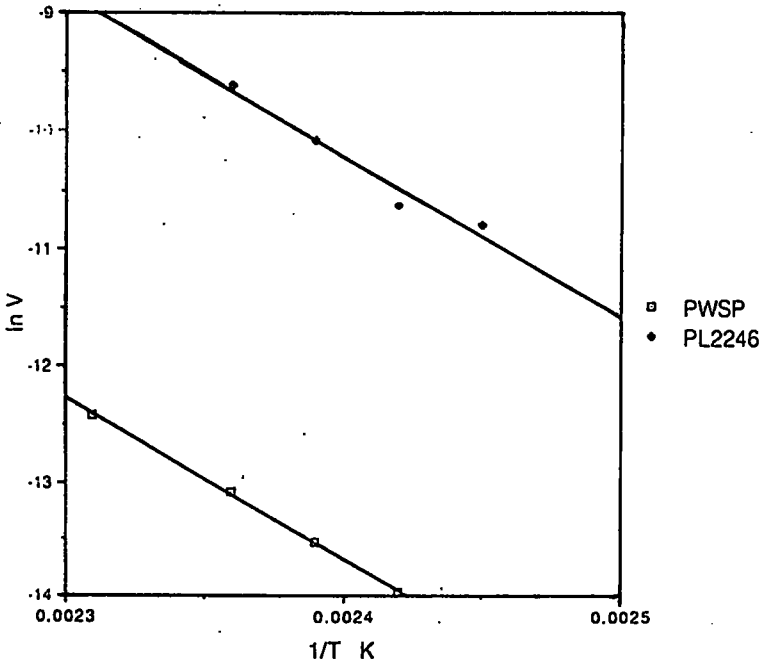


Fig. 11. Temperature dependence of volatility of antioxidants.

(a) UV9

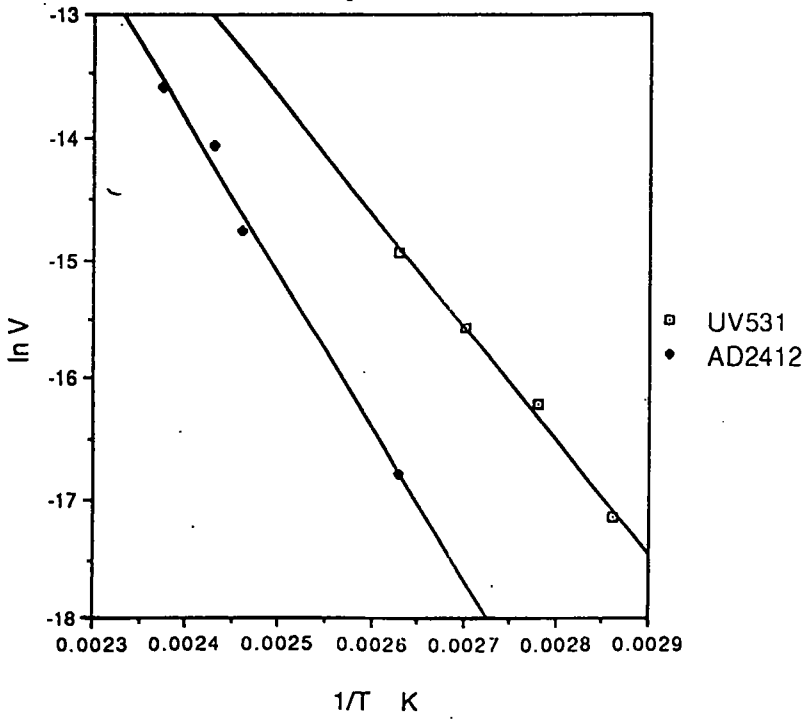
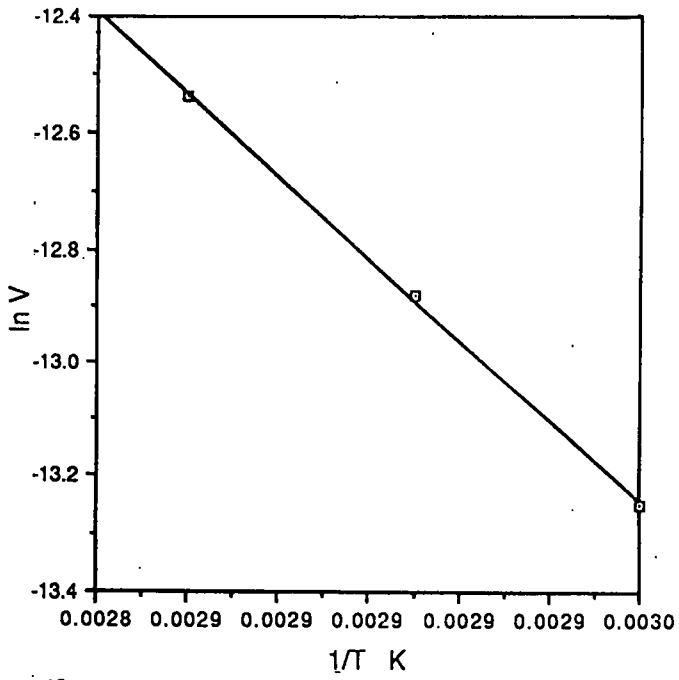


Fig. 12. Temperature dependence of volatility of UV absorbers

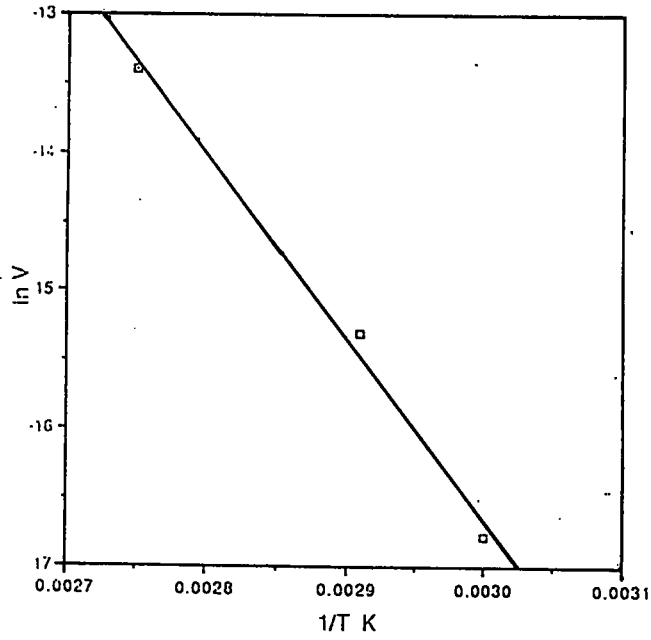


Fig. 13 Temperature dependence of volatility of BHEB

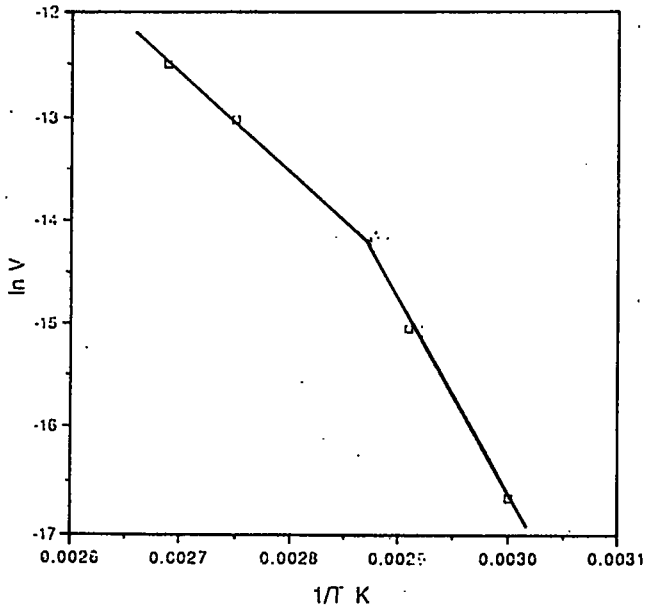


Fig. 14 Temperature dependence of volatility of BHT

Volatility of stabilizers

Table 6 summarizes the latent heats of sublimation, evaporation and fusion of additives measured under vacuum along with their volatilities at 25 °C, 76 °C and T_m of the additive.

Table 6. *The volatilities and latent heats of vaporization, sublimation and fusion of pure stabilizers in vacuum*

Additive	Volatility/gcm ⁻² s ⁻¹			KJmol ⁻¹		
	25 °C	T _m	76 °C	ΔH _s	ΔH _v	ΔH _f
UV9	4.3x10 ⁻⁸	1.37x10 ⁻⁶	3.56x10 ⁻⁶	81	59	22
UV531	1.5x10 ⁻¹⁰	2.30x10 ⁻⁹	3.57x10 ⁻⁸	116	78	37
AD2412	2.1x10 ⁻¹²	9.60x10 ⁻¹¹	2.78x10 ⁻¹⁰	143	104	39
PWSP	1.2x10 ⁻¹³	5.4x10 ⁻⁷	-	146	117	29
PL2246	4.4x10 ⁻¹²	1.35x10 ⁻⁵	-	141	113	27

Volatilities at 25 °C and at T_m were calculated taking into account the relationship,

$$\Delta H_s = \Delta H_f + \Delta H_v$$

where ΔH_s, ΔH_f and ΔH_v are the latent heats of sublimation, fusion and vapourisation respectively. Below the melting point of the additive the latent heat of sublimation is equal to latent heat of fusion.

Effect of branching on volatility: Branching of the substituents decreases the volatility as can be seen from the Table 6. It is reported that the branching of the substituents has a marked effect on their volatilities as shown by the volatilities of 2-hydroxybenzophenone, 2-(2'-hydroxy phenyl) benzotriazole and 2,6-ditert-butyl phenol while the replacement of the alkyls in these derivatives by cyclo-alkyl or aryl groups causes volatility decrease (Luston, 1980), (Holcik, 1976).

In our study, by increasing the length of the alkyl chain from 1-12 carbon atoms, the volatility decreases by a factor of 10⁴ at room temperature.

Effect of hydrogen bonding on volatility: The introduction into a molecule of functional groups which are capable of forming hydrogen bonds into a molecule usually reduces the volatility provided the steric effects do not inhibit the interaction between these groups (Durmis *et al.*; 1975). As can be seen from Table 5 volatilities of three phenolic antioxidants which differ only by having -CH₃, -C₂H₅ and -CH₂OH groups in the para position show that

the introduction of a hydroxyl group has reduced the volatility considerably. The formation of inter-molecular hydrogen bonds leads to an increase in intermolecular attraction forces which results in a decrease in volatility, provided that the steric effects do not prevent interaction between these groups.

Effect of molecular weight on volatility: It should be noted that the heats of both sublimation and vaporization of the uv absorbers increase in the same way as the decrease in volatility. This shows that more energy is required to vaporize the substance as the molecular weight increases. The two antioxidants PWSP and PL2246 have latent heat of vaporization values of 117 kJmol^{-1} and 113 kJmol^{-1} . At room temperature PL2246 which has a low molecular weight shows higher volatility than PWSP. The lower heat of fusion also accounts for the higher volatility of PL2246 when compared with PWSP and AD 2412.

Effect of environment on volatility: Table 7 shows the volatility of UV9 measured under two different environmental conditions. The data illustrate the great variation of the volatility of a substance under vacuum and in air. *i.e.* 10^7 fold increase in the vacuum. This emphasizes the fact that the vacuum encourages the loss of stabilizers. The practical significance of the volatility, particularly when protecting plastics in rockets, satellites and other space vehicles is well shown by this test.

Table 7. Volatility of UV9 under two different conditions

Experimental condition	Volatility/ $\text{gcm}^{-2}\text{s}^{-1}$	
	At 90 °C	At 100 °C
Under vacuum	7.99×10^{-6}	2.21×10^{-5}
In air	3.79×10^{-8}	4.60×10^{-7}

CONCLUSIONS

We can draw following conclusions.

- 1). Measurement of volatility for compounds typical of polymer stabilizers under use conditions is extremely difficult. At elevated temperature in air both thermal and oxidative degradation occur. More reproducible results are obtained under vacuum although thermal degradation is also a problem and the conditions are unrealistic.
- 2). Increasing molecular weight within a homologous series of additives markedly reduces volatility and increases the heat of vapourisation. The introduction of groups capable of H-bonding causes much larger reduction in volatility and a large increase in ΔH_f .

Volatility of stabilizers

- 3). The volatilities of commercially available UV absorbers are higher enough to cause appreciable loss in a relatively short time under conditions to be encountered in space applications.

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