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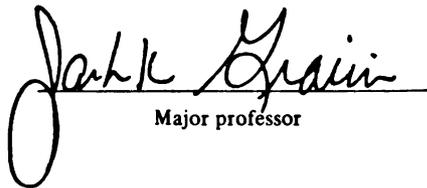
**MASS TRANSFER OF 3,5-DI-TERTIARY-BUTYL-4
-HYDROXYTOLUENE (BHT) FROM A MULTI-LAYER LAMINATION**

presented by

LYNNE BAILEY

has been accepted towards fulfillment
of the requirements for

MASTER degree in PACKAGING


Major professor

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MASS TRANSFER OF 3,5-DI-TERTIARY-BUTYL-4-HYDROXYTOLUENE (BHT)
FROM A MULTI-LAYER LAMINATION

By

Lynne Anne Bailey

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ABSTRACT

MASS TRANSFER OF 3,5-DI-TERTIARY-BUTYL-4-HYDROXYTOLUENE (BHT) FROM A MULTI-LAYER LAMINATION

By

Lynne Bailey

3,5-di-tertiary-butyl-4-hydroxytoluene (BHT), was incorporated into a multi-layer lamination consisting of a heat seal layer, a core layer of high density polyethylene (HDPE) impregnated with BHT, and an outer HDPE layer. The rate of loss of the antioxidant from the respective surfaces and the laminate film, was determined as a function of time and temperature, using UV spectrophotometric and high pressure liquid chromatographic (HPLC) procedures.

Graphical analysis indicated that a first order expression provided a good description of the rate of loss of BHT from the outer HDPE layer, the heat seal layer, and the laminate structure. The rate of loss of BHT from the heat seal layer was found to be significantly greater than that from the HDPE surface layer.

The mass transfer coefficient and the diffusion coefficient for BHT in the respective surface layers was estimated using an analytical model which assumed that surface evaporation was the rate limiting process.

DEDICATION

This thesis is dedicated to my friend Richard P. Ortiz, for his support, love and enduring patience throughout this work.

Also to my family for their support through all my academic endeavors.

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INTRODUCTION

Additives of various types are commonly incorporated into polymers at concentrations of 0.01 to 1.0 weight percent to minimize the effect of oxidative degradation, both during processing and in the subsequent service life of the polymer (Calvert and Billingham, 1979).

Antioxidants in the polymer are subject to chemical reactions (i.e., oxidation), which lead to the formation of complex mixtures of thermal and photochemical reaction products. Additional factors may contribute to antioxidant failure, including loss by evaporation from the polymer surface.

Phenolic antioxidants function by delaying the onset of oxidation by acting as free radical scavengers or metal chelating agents. Antioxidants may be classified as either synthetic or natural. Consumers are concerned with the use of synthetic chemicals in food processing. Thus, there is a move towards using natural ingredients for greater acceptance (Bailey, 1988).

3,5-Di-tertiary-butyl-4-hydroxytoluene (BHT), a synthetic antioxidant, has been used extensively for its antioxidant activity. The application of BHT for its antioxidant properties has been suggested for use in a variety of food products. Hoojjat et al. (1988) demonstrated the effectiveness of a BHT-impregnated film to retard lipid oxidation of a packaged oatmeal cereal, through the migration of antioxidant from the package to the product via the evaporation/sorption mechanism.

Due to the concentration of unsaturated fatty acids in cereal grain, there is potential for rancidity development. Two types of rancidity in cereal grain have been reported, namely: hydrolytic and oxidative (Dugan, 1976). Since oxygen first attacks food at the surface, impregnating packaging materials with an antioxidant may help to protect the product from oxidation. The proposed mechanism of antioxidant activity involves the following three step process: (i) antioxidant diffusion through the polymer bulk phase; (ii) evaporation of antioxidant from the surface of the packaging material; and (iii) subsequent antioxidant sorption onto and into the surface of the packaged product.

The present study thus focuses on determining the effect of temperature on the mass transfer of BHT from a multi-layer film. The lamination consists of an outer heat

seal layer (10.16 μ Surlyn-Ethylene Vinyl Acetate), a core layer of high density polyethylene (HDPE) impregnated with BHT (29.97 μ), and an outer HDPE layer (15.75 μ).

The specific objectives of the study include: (i) monitoring the rate of loss of BHT from a multi-layer film as a function of time and temperature; (ii) determining the rate of loss of BHT from the respective outer layers of the multi-layer laminate structure; and (iii) utilizing data obtained from the rate loss studies to develop a better understanding of the transfer mechanism(s) of BHT from the packaging film. Knowledge generated from these studies should enable better design and selection of packaging systems for controlled transfer of BHT.

Literature Review

Antioxidants

General Review

Lipid oxidation occurs by an autoxidation process involving a free radical chain reaction between lipids and oxygen (Hudson, 1990). Such oxidation processes can also occur with polymers. For example, when atmospheric oxygen spontaneously reacts with organic compounds such as synthetic polymers, it leads to a number of degradative reactions that result in the loss of physical and mechanical products of polymers. Such reactions may also result in lipid oxidation in foods. Antioxidants are substances with the ability to retard, delay or prevent oxidation processes and are commonly added to polymers and food products to provide this function (Hudson, 1990).

Loss of antioxidants may occur during the storage and processing of foods, as a result of their chemical and physical properties. Therefore, because of the volatile nature of antioxidants, caution must be exercised during

extraction and quantification, to provide a material balance for the added antioxidant (Hudson, 1990).

The issue of food additive safety involves the toxicology of antioxidants. For example, 2-tertiary-butyl-4-methoxy phenol (BHA) and BHT have recently been shown in long term studies, to be potential tumor causing agents in animals (Hudson, 1990). Because antioxidants may exhibit toxic properties at high doses, it is essential to compare the quantity of antioxidant deemed safe when evaluating toxicity to the daily human intake (Hudson, 1990). From animal data, BHT was found to be more toxic at lower dose levels than other commercial food antioxidants. It is unlikely, however, that the daily quantity of BHT intake has any adverse effects in humans (Hudson, 1990).

Polyethylene can undergo both thermal and oxidative degradation. High temperature processing, as well as exposure to ultraviolet (UV) light in the presence of oxygen, can initiate free radical chain reactions, leading to the deterioration of the polymers physical and mechanical properties. Sterically hindered phenols like BHT are commonly added to stabilize the polymer (Lichtenthaler and Ranfelt, 1978).

Mechanism of Antioxidant Activity

Swern (1961) showed that autoxidation, a free radical chain process involving unsaturated organic substances, is described as follows:

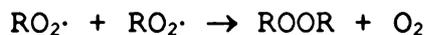
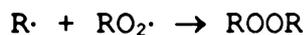
Initiation



Propagation

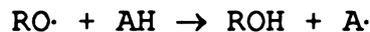
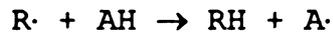


Termination



The methylenic carbon atom loses a hydrogen atom resulting in formation of a free radical. A hydroperoxy free radical ($RO_2\cdot$) is formed when oxygen adds to the site. The hydroperoxy radical can react by abstraction of a hydrogen atom to form a stable hydroperoxide and a new free radical species. This is referred to as the chain propagation step.

The most effective and efficient way to reduce rancidity in fat containing foods is with the use of antioxidants. Antioxidants (AH) inhibit free radical chain propagation in the following manner.



The basic mechanism is competition between the inhibitory reaction and the chain propagation reaction (Nawar, 1985).

Typically, antioxidants deactivate or terminate active free radicals by reacting with hydroperoxy radicals or free fatty acid radicals. The antioxidant free radical formed is quite stable and does not react to initiate autoxidation and react with other free radicals, but undergoes further oxidation to yield quinones (Everson et al., 1957).

Role of Antioxidants in Food Preservation

Antioxidants protect foods such as fats and fat-soluble components such as vitamins, oils, carotenoids and other nutritive ingredients by retarding the oxidative rancidity caused by atmospheric oxidation. Discoloration, browning or

'scald' on vegetables and fruits are unpleasant changes caused by oxidation reactions in foods. The addition of antioxidants to food products and food packaging materials can minimize such degradation reactions (Hudson 1990).

The types of food to which antioxidants are added varies from convenience and snack foods, dry products (cereal), nuts, biscuits, fruit drinks, chewing gum and meat products, to fats and oils. There is a limit to the quantity of antioxidants that can be added to food products, which is based on federal regulations. An antioxidant needs to function at low concentrations and not alter food flavor or texture, be substrate compatible, easy to handle and be cost effective (Hudson, 1990).

Antioxidants cannot reverse oxidation and should be added immediately to a fresh product for optimal effectiveness (Sherwin, 1976). Oxidation is a problem for food preservation, notably when an unpleasant taste or odor has developed which is associated with the oxidized products. The flavor threshold of oxidation products is possibly much below 1 ppm (wt/v). Traces of unpleasant substances may therefore be detectable by consumers and result in economic losses (Berger, 1975, and Hall and Andersson, 1983). In addition to the use of antioxidants, manufacturers can also reduce oxidation when packing by: (I)

minimizing light; (II) reducing or avoiding trace metals or peroxides; (III) keeping oxygen uptake as low as possible during storage and processing; and (IV) employing proper containers and packaging materials (Hudson, 1990).

Till et. al. (1982) used a radiolabeling technique to estimate the quantity of migration of dioctyl adipate (DOA), BHT and Irganox 1010 (tetrakis[methylene-3-(3',5'-di-t-butyl 4' hydroxyphenyl) propionate] methane) that occurs with food simulating liquids, such as distilled water, 3% acetic acid, 8% ethanol, 50% ethanol and n-heptane, under abusive storage conditions. The storage conditions were 14 hours for n-heptane and 5 days for other simulants, at 49°C. It was found that migration to the food simulating liquids was not indicative of the migration of the additive into the respective food classes that they represent. Although the food stimulants are effective in overestimating migration into food systems, the degree of exaggerated migration is variable. This results in a high level of uncertainty when predicting an untested system (Till, 1982).

Antioxidants Role in Polymeric Films

A variety of polymers are susceptible to oxidation from processing to end use. Polypropylene, for example, is unable to endure high temperature extrusion or exposure to ultraviolet light without the incorporation of additives.

Antioxidants such as BHT and BHA, when incorporated into polyolefins, provide processing stability and photo oxidative/thermal endurance (Chan et al., 1989).

The presence of oxygen and its diffusion within the polymer bulk phase plays a significant role in the thermal aging of low density polyethylene (LDPE). Increased film thickness functions as a stabilizing reservoir for replacing exhausted oxygen zones on the surface. Antioxidants alone provide inadequate protection against photo-oxidation of the polymer without the incorporation of a UV absorber (Ram and Meir, 1980).

The additive loss mechanism is determined by the rate of diffusion through the polymer phase. The uniform incorporation of antioxidant into the polymers below saturation results in loss, by surface evaporation, into the air. The rate loss mechanism involves the following two (2) processes: (1) the additive first is removed from the surface; (2) the additive then diffuses from the polymer bulk phase to the surface to replenish the lost material. Migration follows Ficks Law and is controlled by the additive diffusion coefficient. The loss time is related to the geometry of the sample. Migrant solubility, the diffusion coefficient for the additive through the polymer, and the rate of evaporation of the additive are the

parameters describing the mass transport process (Billingham and Calvert, 1982).

As low molecular weight additives migrate from the polymer and are depleted, the properties of the polymer are modified. There is a correlation between the solubility of the antioxidant in the polymer and the volatility of the additive. Studies described by Mar'in et al. (1991) attempted to predict the quantity of additive remaining in the polymer as a function of time and contact phase. BHT was incorporated into low density polyethylene (LDPE) and exposed to air, water and soil. The results showed the rate of loss followed a first order rate equation. BHT was lost most rapidly to the air, with the rate limiting step being evaporation from the polymer surface (Mar'in et al., 1991).

Alpha-tocopherol has recently been incorporated into polymers as a stabilizer for film and bottle products. Tests showed that the migration of alpha-tocopherol is within the guidelines for safe indirect food contact (Laermer et al., 1992). The authors conducted tests with HDPE film used as a dry cereal liner, to which alpha-tocopherol had been added. Data showed that α -tocopherol retarded the loss of acceptable product flavor over a simulated 1 year test period. These investigators further

indicated that alpha-tocopherol is cost effective, and answers to the new demands of the food and drug industry.

Figge et al. (1978) described the results of migration studies designed to establish test conditions that would accurately simulate actual end use storage conditions of the product/package system. The investigators found that [^{14}C]BHT migrated from HDPE to cheese, mayonnaise, whole milk powder and dehydrated soup at a faster rate than its migration from rigid polyvinyl chloride (PVC) containers. BHT is a small molecule, which appears to diffuse readily in polyolefins (Figge et al., 1978). Han et al. (1987) studied the loss of BHA from a HDPE film and reported the rate loss process follows a first-order or pseudo first order rate expression, with an activation energy of 15.2 kcal/mol calculated for the diffusion of BHA in HDPE. No data for the diffusion of BHA in HDPE at ambient temperature levels were found in the literature, although Comyn et al. (1986) reported a value of $12 * 10^{-8} \text{ cm}^2/\text{sec}$ for the diffusion coefficient of BHT in HDPE at 100°C. While BHA is a different additive than BHT, the structures of the two additives are similar in that both are hindered phenols. Using the value of 15.2 kcal/mol for the activation energy for diffusion of BHA in HDPE, Han et al. (1987) calculated a value of $8.9 * 10^{-8} \text{ cm}^2/\text{sec}$ for the diffusion coefficient

at 100°C. The value is of the same order of magnitude as reported by Comyn et al. (1986) for BHT. Hoojjat et al. (1988) used an activation energy of 22 kcal/mol for the diffusion of BHT in HDPE to calculate a diffusion coefficient of 23.67×10^{-7} cm²/sec for BHT at 100°C. This value is 20 times greater than that found by Comyn et al.. The discrepancy between the values may be attributed to differences in the polymer morphology or chemistry.

Haesen et al. (1984) determined the relative percent loss or migration of a series of antioxidants from HDPE, until the system reached equilibrium. In these studies, the polymer was placed in contact with high fat foods, resulting in the migration of antioxidant from the polymer to the contact food phase. The authors found that the molecular volume of the additives (i.e., antioxidant) was directly related to the extent of additive migration. BHT is a small hindered phenol as compared to Irganox 1010 and DMD (5,5-dimethyl-2-(3,4-di-tert-butyl-4-hydroxyphenyl)-1,3-dioxane), and was found to have a higher percent migrating as compared to the other antioxidants evaluated.

The initial concentrations of additives in polymeric packaging materials have been shown to have a direct relationship to the extent of migration into a packed

product. The food/package contact time and the temperature of the system also relate to the extent of migration of the additive. This is valid without restriction. Component migration depends on the type of polymer used, as well as the chemical and physical characteristics of the additive. Studies reported by Figge and Hilpert (1990) showed the proportionality between the quantity of additive which migrates into a food product and the initial concentration of the additive in the contact polymer phase. The following equation was derived by the authors to describe this relationship:

$$M_A^F(t,T) (C_A^P) = K_{(t,T)} \cdot C_A^P \quad (1)$$

Where K is the proportionality constant which is dependent on time and temperature, M_A^F is the fraction of additive which migrates into the food product, and C_A^P is the initial concentration of the additive. The equation demonstrates the direct linear relationship between the additive fraction M_A^F and the initial concentration C_A^P .

Under the Food, Drug and Cosmetic Act as amended in 1958, the FDA defines food additives as, "substances, the intended use of which results or may be reasonably expected to result directly or indirectly, either in their becoming a

component of food or otherwise affecting the characteristics of food." In this regard, migration data have been determined as a function of time by radioactive tracer techniques, gas chromatography, high pressure liquid chromatography and thin-layer chromatography techniques, as well as by atomic absorption spectrometry. These techniques were employed to study and define the chemical purity of migrating species. The migration of BHT from a film to a series of food simulant systems at 40°C was studied by Till et al. (1987) utilizing a radio labeling procedure. BHT was extracted into the contact phase in order of increasing aggressiveness, as follows: 3% acetic acid, 8% ethanol with water, 50% ethanol, propylene glycol, diethylene glycol, HB-307 fat simulant, lauryl alcohol, n-octanol, and n-heptane. Increasing the temperature resulted in an increase in the rate and the quantity of BHT migrated. The quantity of BHT migrated was generally higher in polymers with low crystallinity. For example, LDPE lost BHT more rapidly than HDPE under similar conditions. The external phase penetrates the polymer and changes the molecular environment, to allow an increased migration rate of BHT.

FDA testing designed to evaluate the extent of global or specific migration from a polymeric packaging material to food contact phase typically involves the use of food simulating solvents in contact with a film or sheet of the

polymer to be tested. Antioxidant migration from HDPE injection molded cups, deep-drawn tubs and blown bottles into the test fat HB 307, showed a decrease, as compared to the migration levels observed from films. Polymer molecules at the surface, as compared to polymer molecules in the bulk phase, have a higher degree of orientation in the formed packages, as compared to polymer films. Therefore, the higher-oriented surface polymer molecules provide a barrier layer which inhibits or restricts penetration of fat into the containers, resulting in a decrease in migration of antioxidant from the containers. HDPE with differing melt flow indexes were shown to have no bearing on migration. Variation in the densities of the HDPE resulted in a decrease in antioxidant migration, for the higher density samples (Figge and Freytag, 1984).

The current industry practice for determining compliance with FDA guidelines for the migration of indirect additives involves elevated temperatures, which allows for the determination of the extent of migration from a packaging material exposed to food simulants within a shorter time frame. HDPE is used extensively for food packaging. Various food simulants and actual food products contain ingredients that are anticipated to penetrate HDPE, resulting in modification of the structure and the mobility of BHT. Till et. al. (1982) found that penetration of HDPE

by components of food or food simulants occurs in a Fickian wave, with a velocity proportional to $t^{1/2}$. The diffusivity of the migrant is therefore independent of position, time and concentration of the migrant or penetrant. This may differ from the diffusivity characteristic of the migrant through the polymer, free of penetrant phase.

Till et al. (1982) presented the results of studies designed to evaluate the diffusivity of BHT in HDPE as a function of time and food simulant used. High pressure liquid chromatography (HPLC) and UV spectrophotometric methods were utilized to monitor the loss of BHT from HDPE. BHT was found to be unstable in water. This unexpected phenomenon was not fully understood and is the object of further investigation by the authors. The diffusion of penetrants into the packaging material from fatty foods resulted in an enhanced rate of the relative percent BHT migrated, as compared to the migration of BHT into aqueous foods. For fatty foods the FDA recommends using n-heptane as a food simulant, which is very aggressive, resulting in swelling of the polymer. This can lead to problems of distortion, dissolution, or cracking of the polymer. BHT migration was found to be rate-limited by diffusion within the HDPE polymer. The diffusion coefficient varied with the food or simulant system used and temperature. In a few instances, with an aqueous simulant such as 3% acetic acid,

dilute orange juice or 50% ethanol, there was evidence of BHT partitioning between the polymer and the aqueous contact phase. Migration levels approached a constant value, thus inferring an equilibrium partition distribution of BHT between the polymer and contact phases. The partitioning was not noted for water. BHT being a reactive migrant may have reacted with the external phase, resulting in degradation (Till et. al. 1982).

Gandek et al. (1989) described studies using ^{14}C labeling to monitor the migration of BHT from HDPE to water over a temperature range of 5-60°C. Migration levels were found to increase with temperature. The rate of increase of migration with time, however, was very small at lower temperatures. A first-order reaction was inferred, with the rate constants being a function of temperature, but independent of polymer thickness, water volume, and additive concentration. The solubility of BHT in both water and HDPE increased with temperature. Partition equilibrium between the two phases was reached. The partition coefficient for BHT between HDPE and water was found to increase with temperature. The increase in the solubility of BHT in HDPE with temperature does not appear to be to the same extent as that of BHT in water. The findings of this study agree with the results reported by Arthur D. Little, Inc. (1983), that the BHT levels extracted from the film are greater than the

levels expected, based on the partition equilibrium alone. Thus BHT is assumed to react chemically in the aqueous phase. Gandek et al. (1989) concluded that the rate-limiting step for the migration of BHT from HDPE to a fluid contact phase is either mass transfer through the convective boundary layer or diffusion in the polymer (or a combination of both processes).

Difficulties in determining antioxidant levels in a polymer occur as a result of low initial concentrations of antioxidant added to the polymer, the high reactivity and low stability of antioxidants, as well as the insolubility of antioxidants in the polymer matrix. Lichtenthaler and Ranfelt (1978) identified a series of BHT transformation products in polyethylene by mass spectrometry and comparison to synthetic standards. In these studies, the authors exposed antioxidant (BHT)-containing polyethylene film to thermal degradation, and thermal degradation with exposure to sunlight. In both cases BHT was completely lost from the polymer sample. The sunlight exposed samples showed a slight yellowing and a drastic increase in transformation products. Over 20 thermal and photochemical transformation products were found with two transformation products identified as 2,6-di-tert.-butyl-p-quinomethane and 2,6-di-tert.-butyl-4-methyl-4-hydroperoxy-2,5-cyclohexadiene-1-one.

Three analytical problems arise from determining antioxidant levels in polymers. The first is that the antioxidant is incorporated into a generally insoluble polymer matrix. Because the antioxidant is not separated from the polymer, the analytical techniques are limited. Solvent extraction may result in the extractant phase being contaminated by a soluble, low molecular weight polymer "wax", which is hard to remove from the extractant phase. The second problem is the low stability and high reactivity of antioxidants, while the third is the low concentrations of antioxidants present. The second and third issues make precise quantification of extracts difficult. Data are further complicated by the complex decomposition products formed from the unstable antioxidant. There are a number of commercially used antioxidants, and their identification and quantitation is made more difficult by the possible presence of other types of additives such as slip-agents, plasticizers, and UV-stabilizers (Wheeler, 1968).

Antioxidants are mainly hindered phenols and aromatic amines. The end products formed by the free radical A· may not be identified. Therefore, the sample may be contaminated with unknown quantities of unknown decomposition products (Wheeler, 1968).

To avoid the difficulties of extraction, alternative methods of UV spectroscopy and Infrared (IR) spectroscopy have been used. The UV method requires the polymer to be non-absorbant in the range of the wavelength used for quantification of antioxidant levels, while the IR technique is limited by the low concentrations of antioxidant, which do not allow sufficient absorbance levels (Wheeler, 1968).

Modeling of BHT Loss

The additive loss from the surface of a polymer is determined by three factors- the solubility of the additive within the polymer, the rate the additive volatilizes from the surface and the migrants diffusion coefficient within the polymer. Volatilization of the additive from the surface of the polymer creates a concentration gradient on the surface. The evaporated additive is replaced by diffusion from the bulk. The rate of mass transfer across the surface and the rate of diffusion within the film determine the overall loss mechanism (Angerts et al., 1961).

Crank (1975) derived a mathematical expression describing additive loss from a film by surface evaporation with finite boundary conditions. The quantity of additive leaving the polymer in time (t), is expressed as a fraction of the corresponding amount lost after infinite time by the Equation:

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

where:

M_t = quantity of additive leaving the film in time (t)

M_{∞} = quantity of additive leaving at infinite time

$$T = Dt/l^2 \quad (3)$$

$$L = l\alpha/D \quad (4)$$

l = half of film thickness

t = time

D = diffusion coefficient of the additive in the polymer.

α = mass transfer coefficient of additive from film surface.

and β_n values are the positive roots of the equation

$$\beta_n \tan \beta_n = L \quad (5)$$

Calvert and Billingham (1979) analyzed the rate of loss of BHT and other simple low-molecular weight compounds from thick and thin films and fibers. In a film where loss of the additive is through surface evaporation, the rate of loss is determined by: (I) a combination of the additive lost being replaced by diffusion from the bulk with a diffusion coefficient, D and (II) by the concentration of additive at the surface. Additive concentration is not dependent on D . The authors made the assumption that when

the average concentration of additive falls to 10 percent, mainly, when $Mt/M\alpha = 0.9$, polymer degradation will proceed quickly to sample failure. Neglecting terms other than $n=1$ in equation 2, the following failure criterion was suggested by the authors:

$$\frac{2L^2 \exp(-\beta^2 T)}{\beta^2 (\beta^2 + L^2 + L)} = 0.1 \quad (6)$$

From a plot of L as a function of $T(Dt/L^2)$, it was concluded that for high values of L (thick film, rapid evaporation and low diffusion rate), the failure time is given by the expression:

$$t = 0.87 L^2/D \quad L > 10 \quad (7)$$

and is dominated by diffusion and independent of α (or the evaporation rate). For low values of L (thin film, slow evaporation and fast diffusion rate), the plot of L vs. T was described by the expression:

$$\text{Log } L + \text{Log } T = 0.383 \quad (8)$$

which leads to the failure time given by

$$t = 2.42 L/\alpha \quad L < 0.6 \quad (9)$$

Equation 9 indicates that for values of L lower than 0.6, the diffusion rate is not important and the failure time is dominated by surface evaporation. From these relationships, the authors concluded that loss of low-molecular-weight compounds from thick polymeric slabs is

determined by bulk diffusion, while loss from thin films is dominated by surface evaporation.

The permeability of a polymer film or sheet is a measure of the steady state transfer rate of the permeant which is dependent upon polymer thickness, surface area and partial pressure. It is a combination of the solubility coefficient and diffusivity coefficient. The concentration across the bulk phase remains constant.

Diffusion is the rate of molecule advancement and the time necessary to reach steady state. Diffusion is effected by the size and shape of the permeant, number of sites available for movement, chain forces and T_g . A concentration gradient is established and the permeant moves from high concentration to low. Solubility is the quantity of molecules absorbed by the polymer structure.

General Natural Antioxidant Use

Natural antioxidants occur in and are extracted from plant or animal sources and are capable of being incorporated into food systems. Although these natural substances have been used for a number of years and are generally regarded as safe, they have never undergone the same examination required of a synthetic additive. The

molecular composition and quantity of active ingredients is not well known. Tocopherol activity is concentration dependent (Dugan, 1980). Kovats and Berndorfer-Kraszner (1968) and Dewdney et al. (1977) reported the most effective concentrations of tocopherol to be between 0.01% and 0.02% in a food product. Dewdney et al. (1977) found tocopherols less effective in vegetable oils than animal fats. Antioxidant activity decreases from delta to alpha-tocopherol, while the vitamin E activity increases. Alpha-tocopherol has been incorporated into a HDPE film. As a natural antioxidant with GRAS (Generally Recognized as Safe) status, alpha-tocopherol does not have the environmental and health risks associated with synthetic antioxidants in contact with a food surface (Laermer, 1992).

Dewdney et al. (1977) evaluated antioxidant properties of thirty-two substances finding rosemary and sage to be the most effective of the commonly used spices.

Rosemary extract shows the greatest antioxidant activity of all the spices. Ostric-Matajasevic (1963) compared rosemary extract in lard to other frequently used antioxidants. The study found rosemary extract to be more effective than BHT as an antioxidant, but less effective than nordihydroguaiaretic acid (NDGA). Duxbury (1989) found rosemary extract sufficiently inhibited oxidative rancidity

at low concentrations and maintained antioxidant properties while submitted to stress (heat, freeze, thaw).

Natural antioxidants need to undergo the same critical evaluations and criteria to which synthetic antioxidants must comply. Reaction products formed during processing may exhibit antioxidant activity and thus increase the keeping quality (i.e. shelf life) of the product. These newly formed substances however, contribute to a lack of understanding (Dugan, 1980).

Natural antioxidants potentially can be used in food processing if the production cost is not excessive, the flavor and color are favorable, found free of pathogenic or toxic activity, and if the extend of antioxidant activity is great enough (Dugan, 1980).

EXPERIMENTAL METHODS

Packaging Materials

A multi-layer lamination consisting of an outer heat seal layer (10.16 μ Surlyn-EVA), a core layer of HDPE impregnated with BHT (29.97 μ) and an outer HDPE layer (15.75 μ) was prepared by the United Film Corporation (Odon, IN). Figure 1 gives a cross sectional view of the structure.

The outer HDPE layer of the test film was prepared from a resin source containing the lowest possible level of antioxidant (e.g. BHT) available. Analysis of this resin by high pressure liquid chromatography (HPLC) showed BHT levels at 0.005 percent (wt/wt), while HPLC analysis of the heat seal layer resin gave a BHT concentration of 0.03 percent (wt/wt). The total concentration of BHT incorporated into the laminate film structure was 0.157 percent (wt/wt), as determined by HPLC analysis.

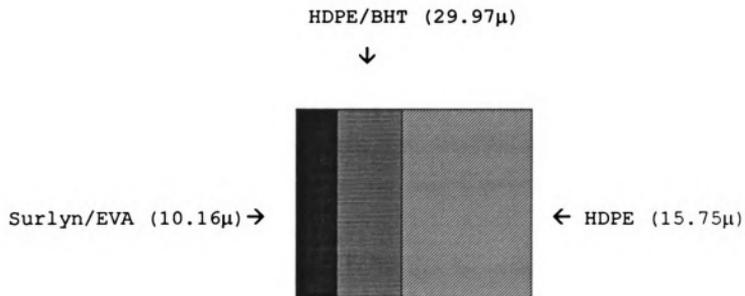


Figure 1. Schematic representation of a cross section of the laminate test material.

Methods

Antioxidant Loss Studies

The rate of loss of BHT from the test film was determined as a function of storage time and temperature. Film samples were taken from the roll, mounted in a sample holder and stored in a constant temperature oven (Blue M, electric Stabil-Therm, Electric Oven), maintained at 23, 30 and $40^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. Before a film sample was taken from the roll for study, several plies were removed to ensure that the loss of BHT from the surface layers was minimized.

The level of retained BHT was determined as a function of time and temperature using two analytical procedures, a UV spectrophotometric technique and a HPLC method.

Ultraviolet (UV) Spectrophotometric Method

For the UV spectrophotometric procedure, film samples were cut (4 cm x 4 cm) and mounted in a masking device (Modern Controls, Inc. Minneapolis, MN). The masking device consisted of 2 mil aluminum foil affixed to a paperboard back with a die cut hole in the center. The film sample was mounted between the aluminum foil layer and the paperboard back. Once mounted, the film sample had contact with the aluminum barrier and had a 5 cm^2 diameter die cut hole which allowed precise definition of sample area. To determine bulk loss, the die cut hole from the paperboard back was

removed, allowing exposure of both film surfaces to the environment. Mounting in the masking device allowed exposure of the individual surface layers of the multi-layer coextrusion to the environment. By preventing evaporation of BHT from the film surface exposed to the foil, the rate of loss of BHT from the exposed surface was determined. By removing the die cut hole, both sides of the film were simultaneously exposed, thus allowing for loss of BHT from both surface layers. Rate loss studies were carried out at 23, 30 and 40°C ± 0.5°C, respectively. The mounted film samples were taken from the constant temperature chamber at predetermined time intervals, removed from the mounting device and relative concentration of BHT in the film samples determined by a UV spectrophotometric procedure.

Following the method outlined by Hoojjat et al. (1988), a Perkin Elmer Lambda 3B UV/Visible double beam spectrophotometer equipped with an integrating sphere attachment was used to measure the absorbance (as optical density units) of BHT, as a function of storage time. Film samples were placed directly in the sample holder of the integrating sphere and the absorbance was recorded at 280 nm. The relative concentration of the antioxidant in the film was calculated by substitution into the equation:

$$\text{Relative \% BHT} = \text{Abs}_{(t)} / \text{Abs}_{(0)} * 100 \quad (10)$$

where $Abs_{(t)}$ and $Abs_{(0)}$ represent the absorbance at storage time (t) and at time = 0, respectively.

High Pressure Liquid Chromatography (HPLC) Method

For quantification of BHT levels in laminate film samples by HPLC analysis, the following procedure was employed. Film samples weighing approximately 2 grams were cut into pieces approximately 1 cm x 1 cm and extracted with 110 ml of acetonitrile (Aldrich Chemical Company, 99.9% purity) in a Soxhlet extraction apparatus for 16 hours. Second and third extractions were performed to insure complete extraction of BHT. The extractants were brought up to volume (100 ml) using acetonitrile and then filtered prior to analysis by HPLC. The individual resins used to fabricate the lamination were also subjected to Soxhlet extraction and the extractant phase analyzed by HPLC to determine BHT levels in the respective resin samples. For the outer layer HDPE resin, the heat seal resin, as well as the second and third extracts from the laminated film, no detectable levels of BHT were indicated by HPLC analysis. To increase analytical sensitivity, the extracts were concentrated to 5-8 ml and brought up to a final volume of 10 ml with pure solvent. Samples were concentrated using a Buchi Rotavapor Model RE III series with a 40°C water bath and water aspirator pressure. Following concentration, the

extractant phases were again analyzed by HPLC. In all cases, an injection volume of 50 μ l was used.

The concentration of BHT in the respective extractant phases was determined by a Waters high pressure liquid chromatograph, interfaced to a Waters Model 440 absorbance detector and a Hewlett Packard Model 3396 integrator. The HPLC conditions were as follows: column, Waters Nova-Pak[®] C18, 3.9 x 150 mm; mobile phase, acetonitrile/water (70/30, v/v%); flow rate, 1 ml/min, detector wavelength, 280 nm, to give a retention time of 9.0 min for BHT. In all cases, a standard curve of response vs. quantity injected was constructed from standard solutions of known concentration. Calibration solutions were prepared by dissolution of known quantities of BHT in acetonitrile.

Standard curve preparation involved placing approximately 0.1 g of pure antioxidant (Aldrich Chemical Company) into a 100 ml volumetric flask and bringing it up to volume with acetonitrile. A serial dilution technique was employed to prepare standard solutions of known concentrations from the stock solution. The calibration data are shown in Appendix A.

The BHT concentrations in the respective resin and film samples were calculated by substitution into the following equation:

$$\text{Polymer BHT Conc. (wt/wt)} = \text{AU} \times \text{CF} \times (1/V_{\text{inj}}) \times V_t \times (1/\text{Wt}) \times 100 \quad (11)$$

AU = Average area units from HPLC

CF = Calibration factor (g/AU)

V_{inj} = Sample volume injected (50 μ l)

V_t = Total extractant phase volume

Wt = Weight of polymer sample (g)

UV Spectrophotometric Procedure to Determine BHT in

Extracts:

A Perkin-Elmer Lambda 4B Double Beam UV visible spectrophotometer was used to measure the absorbance of BHT at 280 nm with a 1-cm path length quartz cuvette. Three ml of extract were transferred to the quartz cuvette, and the absorbance recorded.

The concentration of BHT in the film and resin samples was determined by comparison with standard solutions of known concentration. Calibration solutions were prepared by adding approximately 0.1 g of BHT to a 100 ml volumetric flask and bringing it up to volume with acetonitrile. Serial dilutions were made from the 100 ppm (wt/v) stock solutions to give standard solutions of 4, 10, 20, 30 and 50 ppm (wt/v). Standard solutions of known concentration were

used to construct a standard curve of absorbance (O.D. units) vs. BHT concentration. The calibration data are summarized in Appendix B.

Fourier Transform Infrared Spectroscopy Analysis

In an attempt to determine the distribution profile of BHT across the bulk phase of the lamination, a Fourier Transform Infrared (FT-IR) - microscopy technique was employed.

In this procedure the width of the lamination is based on scanning recording infrared spectra at 10μ intervals and examining the spectra for the OH stretching band at $2850-2900\text{ cm}^{-1}$. This is characteristic of the OH functional group of BHT.

Analyses were performed using the Perkin-Elmer Series 1800 Fourier Transform Infrared Spectrophotometer equipped with a SpectraTech IRPLAN Microscope attachment with Redundant Aperturing. The unit is located in the Composite Materials and Structures Center laboratory (MSU). The system consists of an optical bench, a computer and a plotter/printer. The optical bench is a software controllable Fourier transform infrared spectrometer providing a double beam, single beam, and a single ratio recording of spectral data.

In operation, Infrared radiation enters the microscope attachment, which focuses the infrared radiation to a width of 10 μ . The mercury cadmium telluride (MCT) detector operates at a range of 4000-700 cm^{-1} and at liquid nitrogen temperature, -195.8°C .

A sample holder was designed and constructed to help position the polymer film in the microscope attachment. The film sample was mounted in the sample holder, allowing for scanning over a cross section of the laminate. After film mounting, the sample holder was positioned inside the microscope attachment. A glove bag enclosed the microscope and was purged with nitrogen to remove any residual carbon dioxide or water vapor. When adequate time had passed and the assembly was considered free of water vapor, the infrared beam was focused on one edge of the sample and scanned across the film width.

Analysis of Laminate Cross Section by Optical Microscopy

The polymer film was mounted in an acrylic matrix and polished with sand paper using consecutively finer sand paper grades from 400-2000 grit. When a mirror finish was achieved, the samples were mounted in the Olympus Model BH2-UMA Optical Microscope located in the Composite Materials

and Structures Center laboratory (MSU), and examined at 60x magnification. Precise measurement of each layer in the polymer required a calibration photo be made to use as a grid. Each division of the grid was equal to 10 μ .

RESULTS AND DISCUSSION

Resin and Film Characterization

Thickness of Laminate Structure

The thickness of the respective layers of the coextruded laminate film was determined by an optical microscopy procedure. However, the optical microscope could not differentiate the BHT-impregnated HDPE layer from the outer HDPE layer. The average results are summarized in Table 1. All thickness measurements recorded are tabulated in Appendix C. As shown in Table 1, the thickness of the Surlyn/EVA layer was determined to be 11.08 μ , while the total HDPE layer which included the center and outer layers was determined to be 66.28 μ .

TABLE 1: Average lamination ply thickness determined by an optical microscopy procedure. (a)

Surlyn/EVA Layer	HDPE and HDPE with BHT Layers	Total Laminate Thickness
11.08 μ	66.28 μ	77.36 μ

(a) Average of 10 thickness readings.

United Film Corporation reported the film thickness to be 55.88 μ . The outer heat seal layer was reported at 10.16 μ , the core layer 29.97 μ and the outer HDPE layer 15.75 μ . For a comparison to the values reported by United Film Corporation and those by the optical microscopy procedure, the total thickness of the film sample was determined using a micrometer (Model 549M, Micrometer, Testing Machines, Inc., Amityville, L.I. N.Y.). The film measured 62 μ . Measurement varied by approximately 20% of that determined by the optical microscope. The thickness values indicated by United Film Corporation are nominal values based on processing extrusion rates and can account for the variation observed between the reported thickness and experimental values.

BHT Levels in Resin and Laminate Structure

Quantification of BHT levels was based on HPLC analysis. The level of BHT in the resin used to form the core layer was found to be 0.173 percent (wt/wt), while the level in the fabricated film was 0.157 percent (wt/wt). The difference is assumed to be the result of loss due to processing.

BHT levels in the resin and film were also quantified using a UV spectrophotometric procedure. The antioxidant

levels determined by this procedure were approximately 30% higher than the values determined by high pressure liquid chromatography (HPLC) analysis. Since the spectrophotometric procedure is based on total absorption at 280 nm, the presence of additional extractant compounds absorbing at the same frequency could account in part for the differences in BHT levels obtained by the two procedures. Compounds such as oxidation products of BHT absorb at 280 nm and may contribute to the overall absorbance. To establish the presence and levels of BHT in both the Surllyn/EVA heat seal layer and the outer HDPE layer, samples of the respective resins were extracted by Soxhlet extraction and the extractant solvent assayed for BHT levels. HPLC and UV spectrophotometric analyses yielded similar results, in that the respective resins of the outer layers were found to contain less than 20% of the loading level of BHT present in the core resin sample. HPLC analysis determined the outer heat seal layer resin to contain 0.03% BHT, while the UV method showed 0.05%. The HDPE outer layer resin was found to contain 0.04% BHT (wt/wt) by both methods. The level of BHT determined for the laminate is therefore derived primarily from the core HDPE layer. The bulk phase distribution of BHT within the lamination following fabrication and storage of the film is not known.

Fourier Transform Infrared Spectroscopy

An attempt was made to determine the BHT distribution profile across the laminate structure by a FTIR - microscope system. Infrared spectroscopy has a wide range of applications for qualitative and quantitative analysis. The spectrum of organic compounds gives a unique fingerprint that is distinguished from the absorption patterns of other compounds.

The simplest modes of vibrational motion in an infrared active molecule are stretching and bending modes. Scissoring, rocking, twisting and wagging are terms commonly used to describe the infrared band origin. When three or more atoms are present, two of which are identical, there will be two types of bending and/or stretching: the asymmetric mode and the symmetric mode. These fundamental absorptions originate from excitation from the ground state to the lowest energy excited state. The abscissa scale of an infrared spectra is linear in units of reciprocal centimeters, known as wavenumbers and the ordinate is linear in transmittance. The frequency of absorbed radiation is the molecular vibrational frequency responsible for the absorption process.

The attempt to differentiate the distribution profile of BHT within the laminate bulk phase was unsuccessful as

the focusing capabilities of the microscope were not powerful enough. While the experiment is theoretically valid, the instrumental shortcomings made it too difficult to achieve the desired results.

Effect of Time and Temperature on the Relative Rate of Loss of BHT From the Lamination

Bulk Loss of Antioxidant

The relative loss of BHT from the test laminate, as a function of time and temperature, was determined by the integrating sphere-UV spectrophotometric procedure previously described. The results are summarized in Tables 2-4, respectively. A graphical representation of the data is presented in Figure 2, where the relative percent BHT remaining in the film is plotted as a function of time.

Graphical analysis indicated that a first order expression, provided a good description of the rate of loss of BHT from the laminate, through more than 90% loss. From a least squares fit, the following expressions were derived:

$$23^{\circ}\text{C } (C/C_0) = 100.428 * \exp(-0.00430x) \quad (14)$$

$$30^{\circ}\text{C } (C/C_0) = 90.318 * \exp(-0.02933x) \quad (15)$$

$$40^{\circ}\text{C } (C/C_0) = 75.4190 * \exp(-0.0651x) \quad (16)$$

The R^2 values were 0.99, 0.97, and 0.79, for the 23, 30 and 40° C experiments, respectively. Tables 2-4 indicate that

Table 2: Loss of BHT from laminate film at 23°C determined by UV spectrophotometry.

Time (hours)	BHT Concentration* (Optical Density Units)	Relative % BHT (C/Co*100)
0	.081	100
30	.058	70.9
66	.039	48.0
96	.032	38.9
140	.022	26.6
216	.011	13.5
293	.005	6.1
379	.002	2.0
551	N/D	N/D

* Adjusted for instrument background absorption.
Results are the average of three film samples with triplicate analyses per sample.

Table 3: Loss of BHT from laminate film at 30°C determined by UV spectrophotometry.

Time (hours)	BHT Concentration* (Optical Density Units)	Relative % BHT (C/Co*100)
0	.088	100
8	.039	44.7
16	.027	31.1
24	.016	18.6
48	.006	6.4
60	.008	8.7
120	.001	1.1
200	N/D	N/D

* Adjusted for instrument background absorption.
Results are the average of three film samples with
triplicate analyses per sample.

Table 4: Loss of BHT from laminate film at 40°C determined by UV spectrophotometry.

Time (hours)	BHT Concentration* (Optical Density Units)	Relative % BHT (C/Co*100)
0	.089	100
3	.028	31.8
6	.027	30.5
9	.020	22.6
24	.004	5.1
36	.001	1.1

* Adjusted for instrument background absorption.
Results are the average of three film samples with
triplicate analyses per sample.

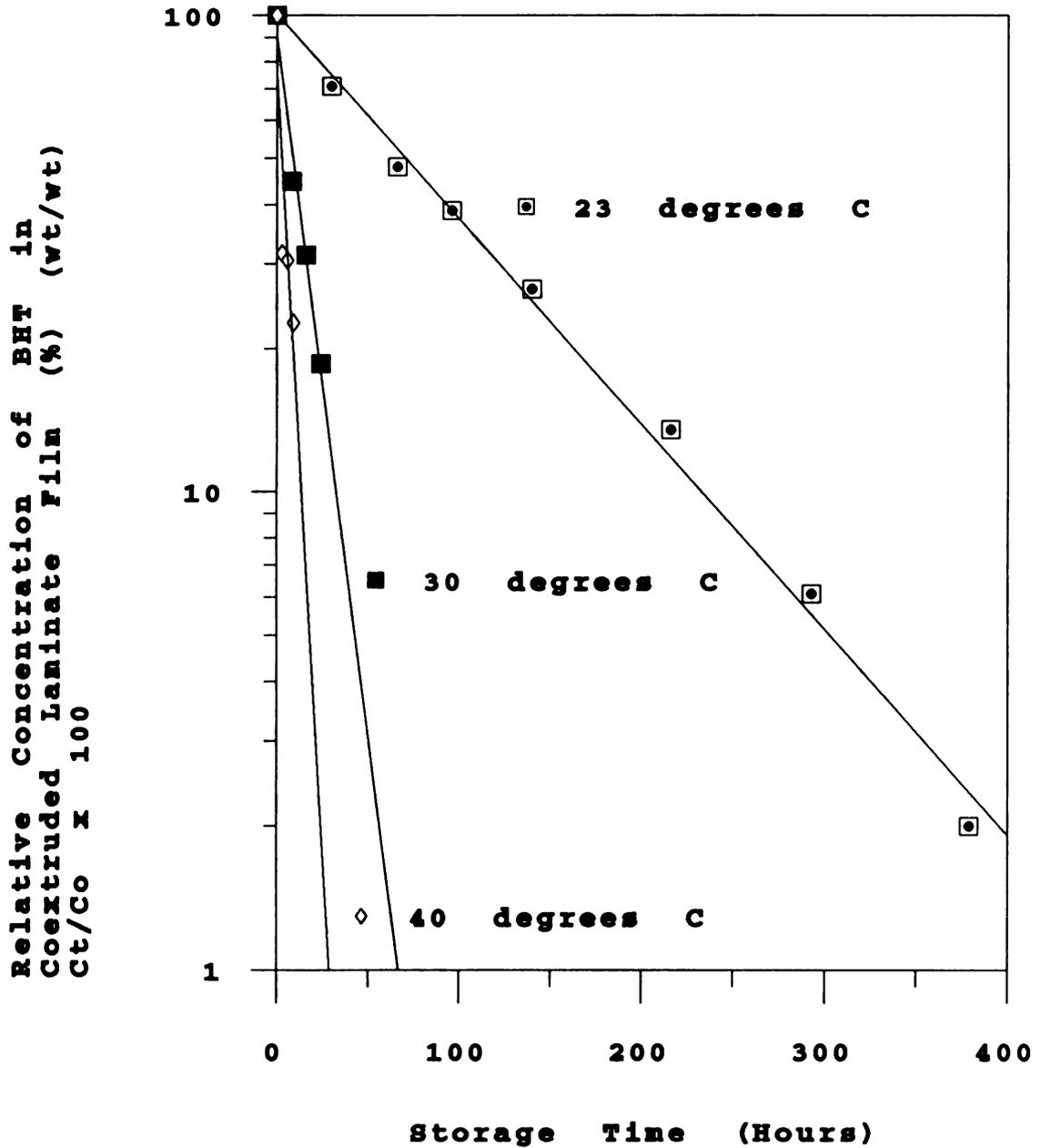


Figure 2. Relative loss of BHT from coextruded laminate film as a function of time/temperature.

greater than 95% of BHT was lost from the laminate within 36 hours at 40°C, within 5 days at 30°C and within 15.8 days at 23°C.

The rate constants for the rate of loss of BHT were determined from Equation 17:

$$\log C/Co = -kt/2.3 \quad (17)$$

Where Co and C are the initial and time (t) concentrations of BHT in the film sample (weight percent), respectively; k is the rate constant; and t is the time interval.

The rate constant values determined are summarized in Table 5. The relationship between the rate loss constant and temperature is illustrated in Figure 3, where k is plotted as a function of temperature ($1/T$ (°K)). As can be seen, the temperature dependency of the transport process, over the temperature range studied, follows an Arrhenius relationship. From the slope of the Arrhenius plot, the activation energy for the loss of BHT from the laminate was determined to be 26 kcal/mol.

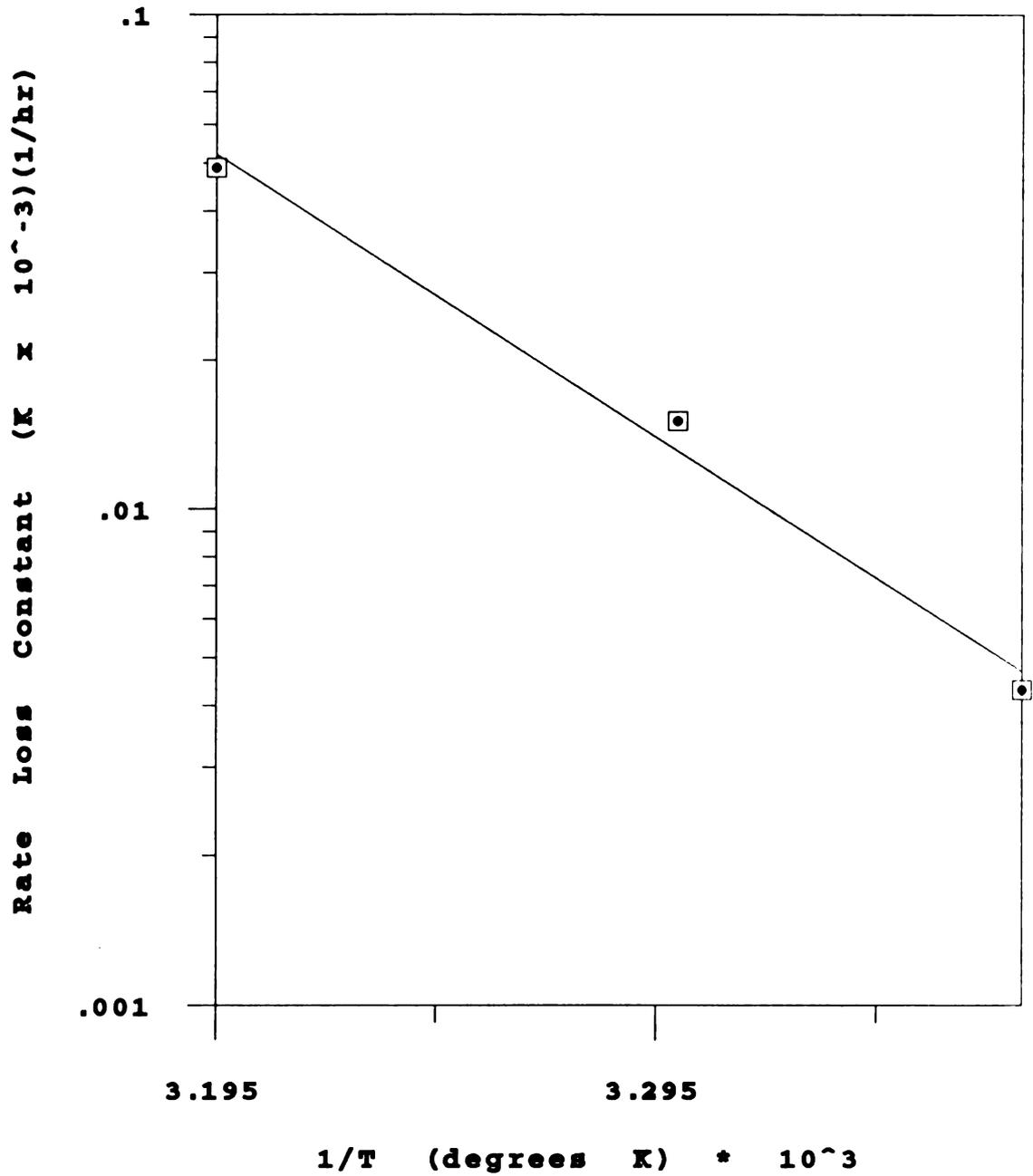


Figure 3. Arrhenius plot of BHT loss from Coextruded lamination.

TABLE 5: Rate constants for the loss of BHT from the laminate film Structure.

Temperature (° C)	Loss Rate Constant $k \cdot 10^{-3}$ (1/hr)
23	4.30
30	29.3
40	65.1

Calvert and Billingham (1979) showed that the loss of BHT and other simple low molecular weight additives from thin films is controlled by evaporation. Diffusion controls the loss of additive from thick films and bulk solids. The multi-layer lamination used in this study has a thickness of 62 μ (2.2 mil). It was therefore assumed that the rate of additive loss is controlled by surface evaporation.

Antioxidant Loss From Respective Surface Layers

The rate loss of BHT from the individual surface layers of the lamination were determined by UV absorption of the film at 280 nm, as a function of temperature. The results are summarized in Tables 6-11, and presented graphically in Figures 4, 5 and 6, respectively, where the relative loss of BHT is plotted as a function of time. Superimposed in Figures 4, 5 and 6 is the relative loss of BHT from the bulk

Table 6: Loss of BHT from heat seal layer at 23°C determined by UV spectrophotometry.

Time (hours)	BHT Concentration* (Optical Density Units)	Relative % BHT (C/Co*100)
0	.081	100
30	.071	87.3
66	.058	70.7
96	.051	62.7
140	.045	54.7
216	.021	25.8
293	.016	19.7
379	.015	17.8
551	.004	4.3

* Adjusted for instrument background absorption.
Results are the average of three film samples with
triplicate analyses per sample.

Table 7: Loss of BHT from heat seal layer at 30°C determined by UV spectrophotometry.

Time (hours)	BHT Concentration* (Optical Density Units)	Relative % BHT (C/Co*100)
0	.088	100
8	.048	54.5
16	.057	64.7
24	.038	43.2
48	.026	29.5
60	.016	17.6
120	.011	12.5
200	.010	10.6

* Adjusted for instrument background absorption.
Results are the average of three film samples with triplicate analyses per sample.

Table 8: Loss of BHT from heat seal layer at 40°C determined by UV spectrophotometry.

Time (hours)	BHT Concentration* (Optical Density Units)	Relative % BHT (C/Co*100)
0	.089	100
3	.043	48.6
6	.047	53.7
9	.031	35.0
24	.010	11.3
36	.008	9.6

* Adjusted for instrument background absorption.
Results are the average of three film samples with
triplicate analyses per sample.

Table 9: Loss of BHT from high density polyethylene layer at 23°C determined by UV spectrophotometry.

Time (hours)	BHT Concentration* (Optical Density Units)	Relative % BHT (C/Co*100)
0	.081	100
30	.081	100
66	.078	95.9
96	.077	94.7
140	.075	91.6
216	.074	91.0
293	.054	66.4
379	.045	54.7
551	.044	54.1

* Adjusted for instrument background absorption.
Results are the average of three film samples with triplicate analyses per sample.

Table 10: Loss of BHT from high density polyethylene layer at 30°C determined by UV spectrophotometry.

Time (hours)	BHT Concentration* (Optical Density Units)	Relative % BHT (C/Co*100)
0	.088	100
8	.085	96.0
16	.085	96.0
24	.083	94.3
48	.062	69.9
60	.049	55.7
120	.029	33.0
200	.024	26.7

* Adjusted for instrument background absorption.
Results are the average of three film samples with
triplicate analyses per sample.

Table 11: Loss of BHT from high density polyethylene layer at 40°C determined by UV spectrophotometry.

Time (hours)	BHT Concentration* (Optical Density Units)	Relative % BHT (C/Co*100)
0	.089	100
3	.089	100
6	.070	78.5
9	.078	88.7
24	.055	61.6
36	.053	59.3

* Adjusted for instrument background absorption.
Results are the average of three film samples with
triplicate analyses per sample.

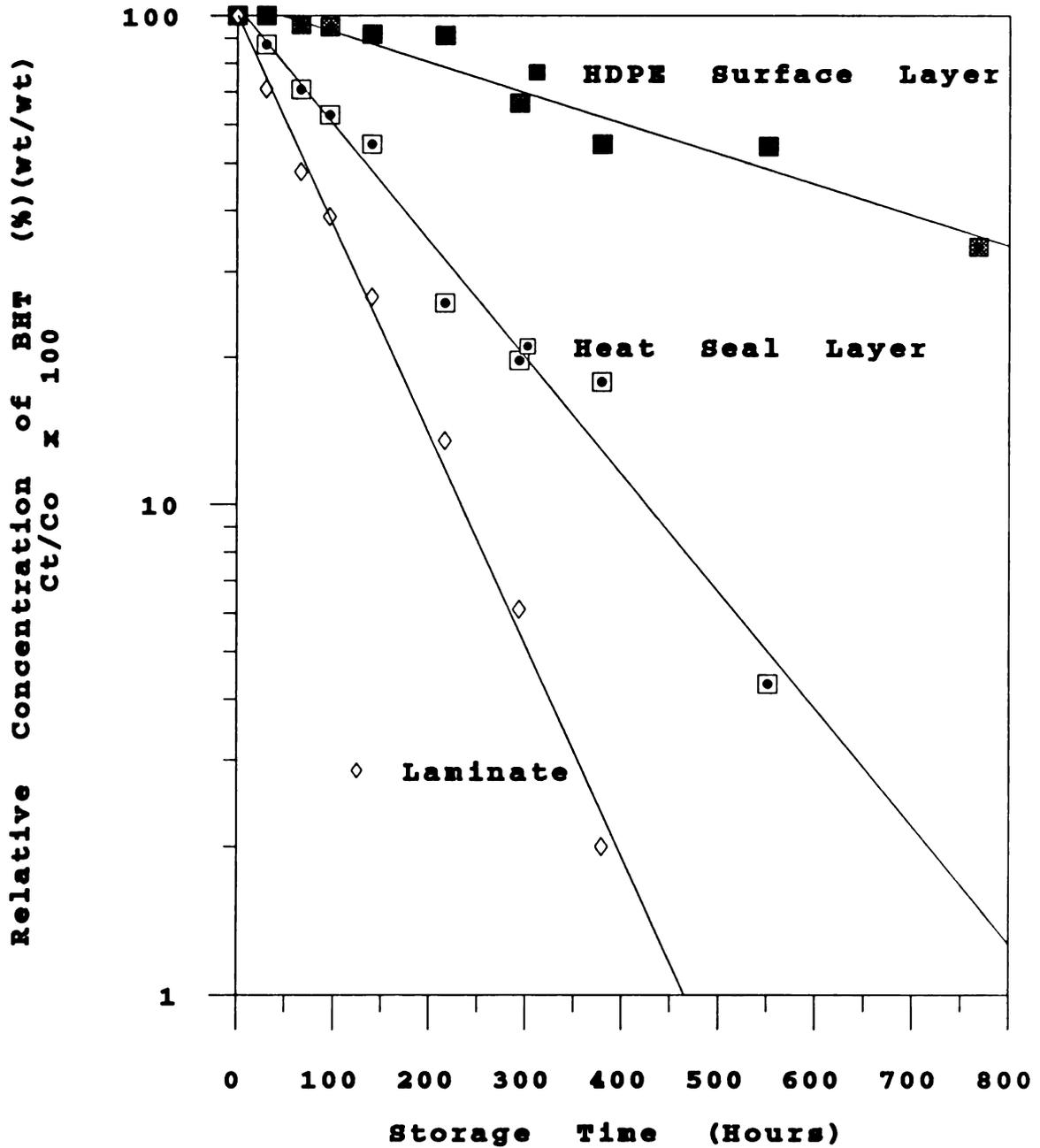


Figure 4. Relative loss of BHT from the laminate surface layers as a function of time (23 degrees C).

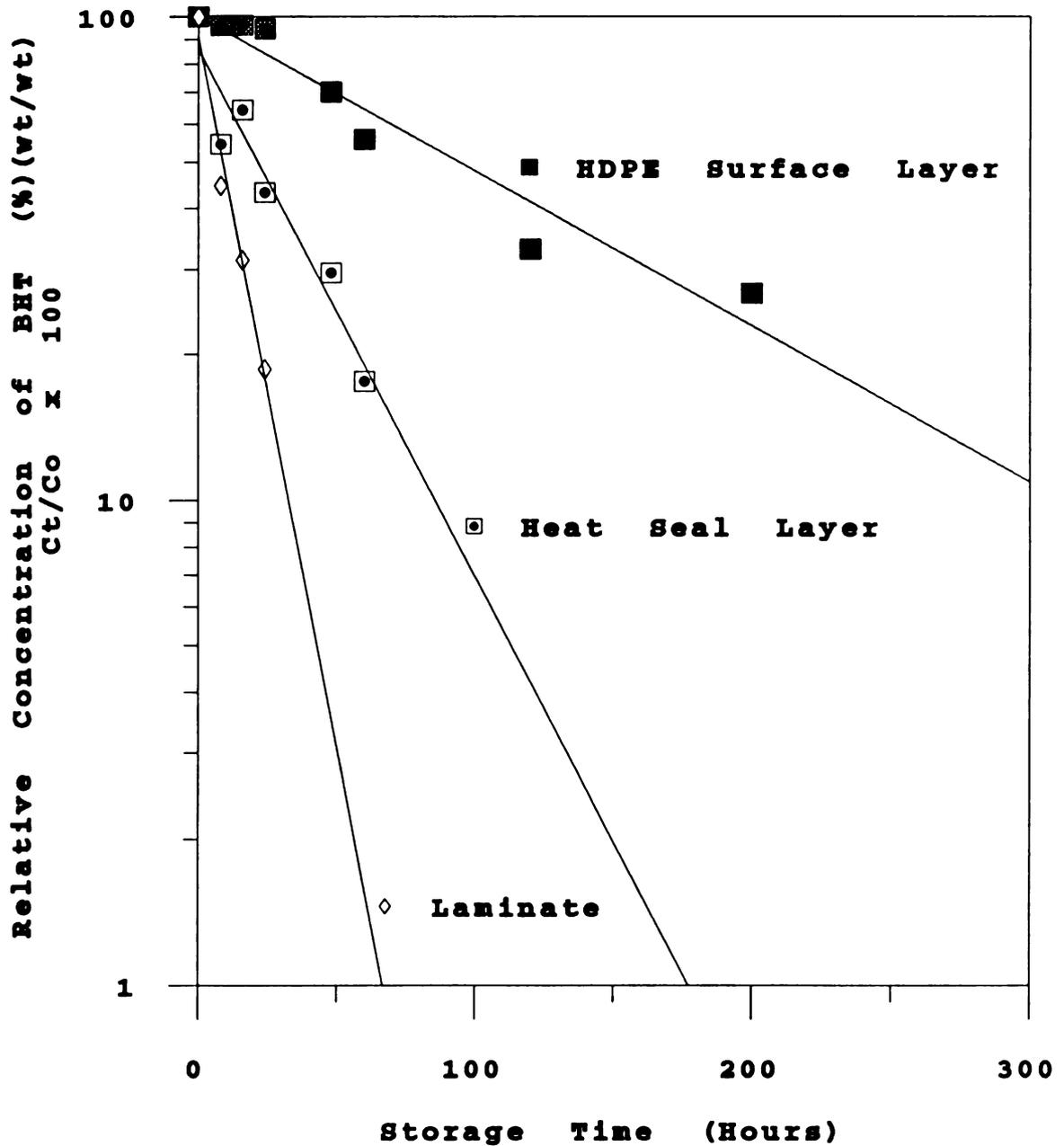


Figure 5. Relative loss of BHT from the laminate surface layers as a function of time (30 degrees C).

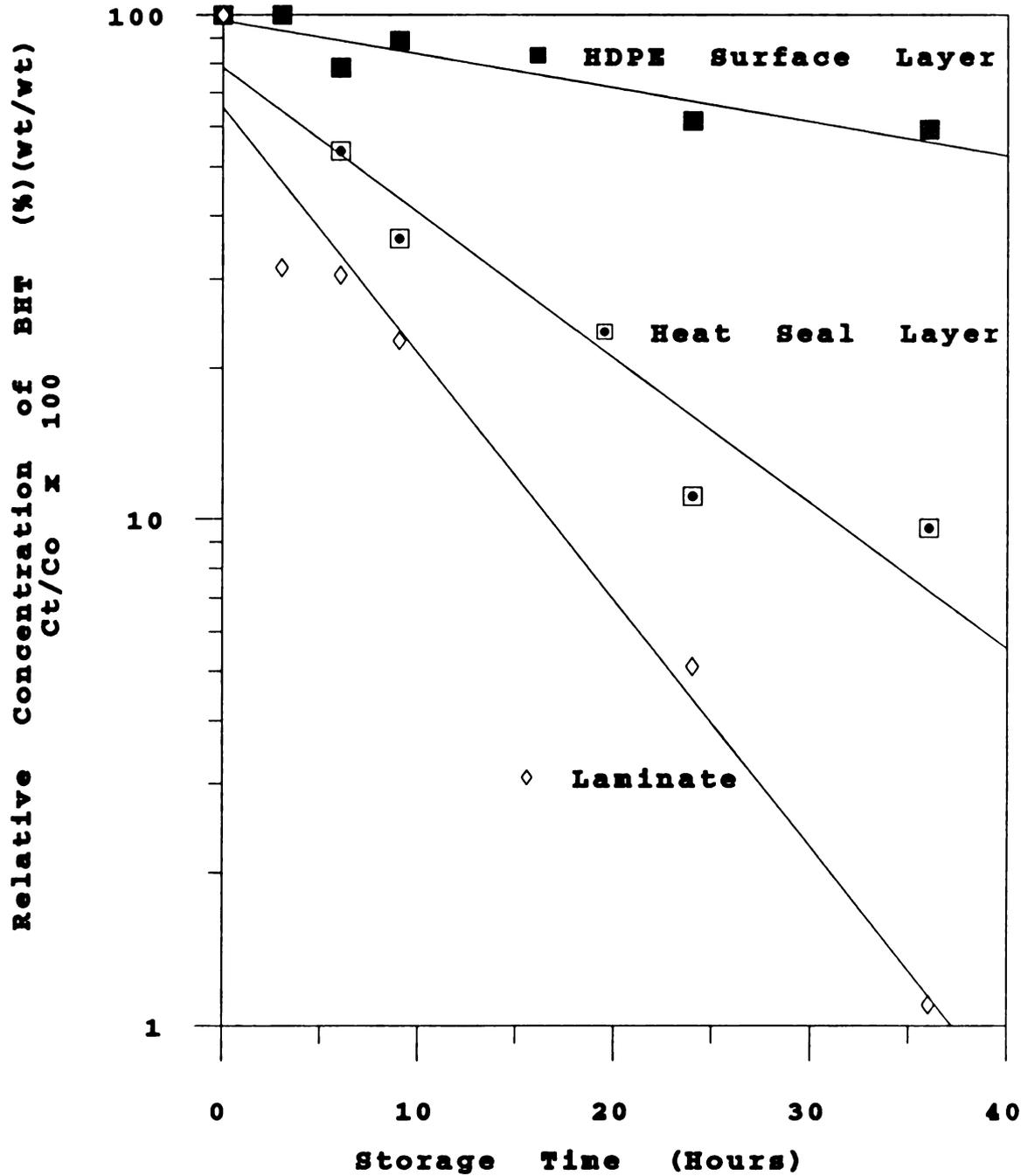


Figure 6. Relative loss of BHT from the laminate surface layers as a function of time (40 degrees C).

structure at the test temperature, to provide a comparison with losses from the respective surface layers.

The effect of temperature on the rate of loss of BHT from the HDPE surface layer and from the heat seal layer is illustrated in Figures 7 and 8, where the relative concentration of BHT remaining in the film is plotted as a function of time for the respective run temperatures.

From Figures 7 and 8, graphical analysis indicated that a first order expression would provide a good description of the rate of loss of BHT for the respective surface layers. From a least squares fit, the following expressions were derived, to describe the rate of loss of BHT from the respective surface layers.

Rate Loss Expressions for HDPE Surface Layer.

$$23^{\circ}\text{C } (C/Co) = 106.723 * \exp(-0.000623x) \quad (15)$$

$$30^{\circ}\text{C } (C/Co) = 100.033 * \exp(-0.003208x) \quad (16)$$

$$40^{\circ}\text{C } (C/Co) = 97.268 * \exp(-0.006697x) \quad (17)$$

The R^2 values were 0.95, 0.94, and 0.87 for the 23, 30 and 40°C experiments respectively.

Rate Loss Expressions for the Heat Seal Layer.

$$23^{\circ}\text{C } (C/Co) = 104.024 * \exp(-0.002393x) \quad (18)$$

$$30^{\circ}\text{C } (C/Co) = 75.074 * \exp(-0.0074548x) \quad (19)$$

$$40^{\circ}\text{C } (C/Co) = 81.660 * \exp(-0.036709x) \quad (20)$$

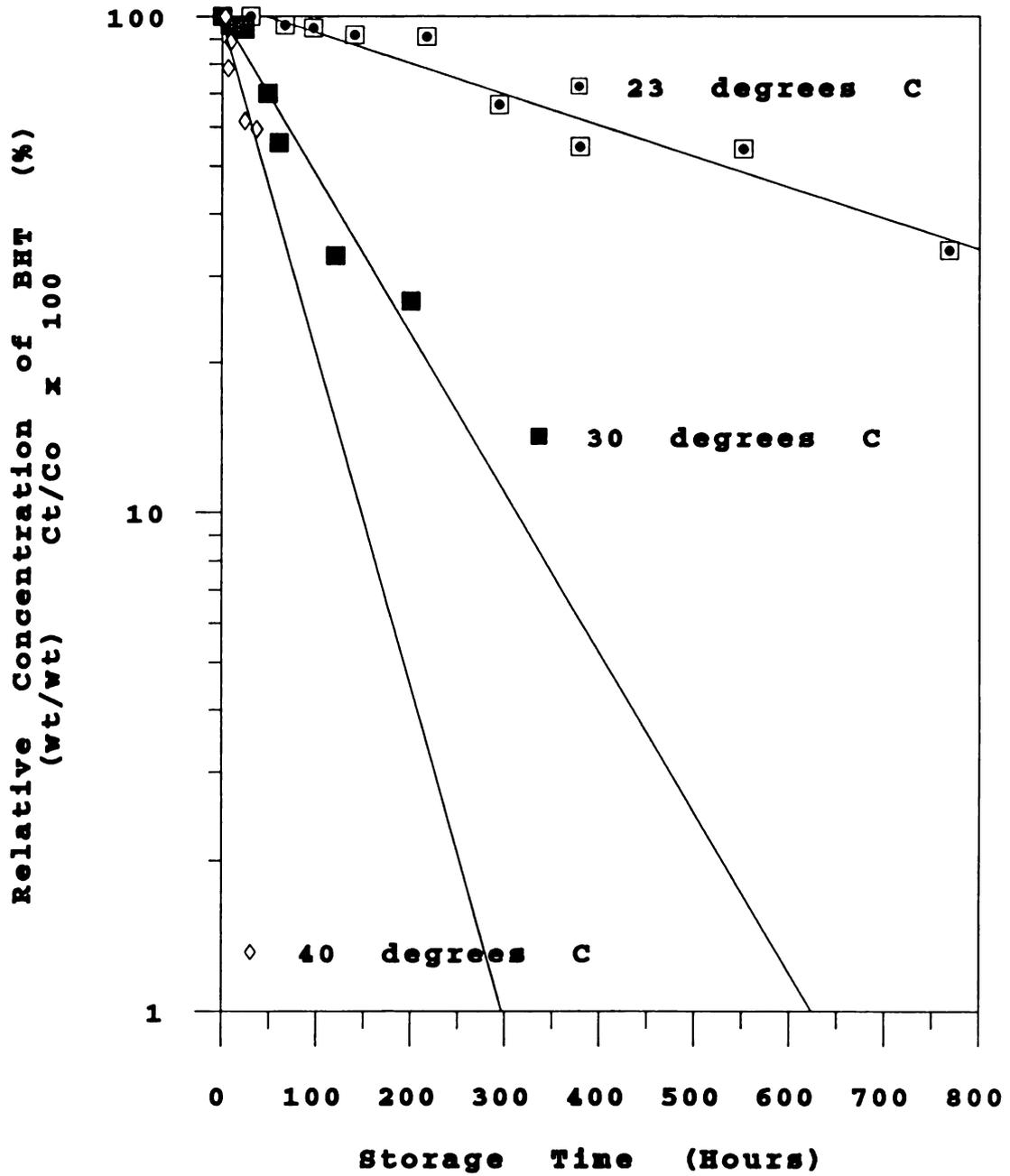


Figure 7. Relative loss of BHT from the HDPE surface layer as a function of temperature.

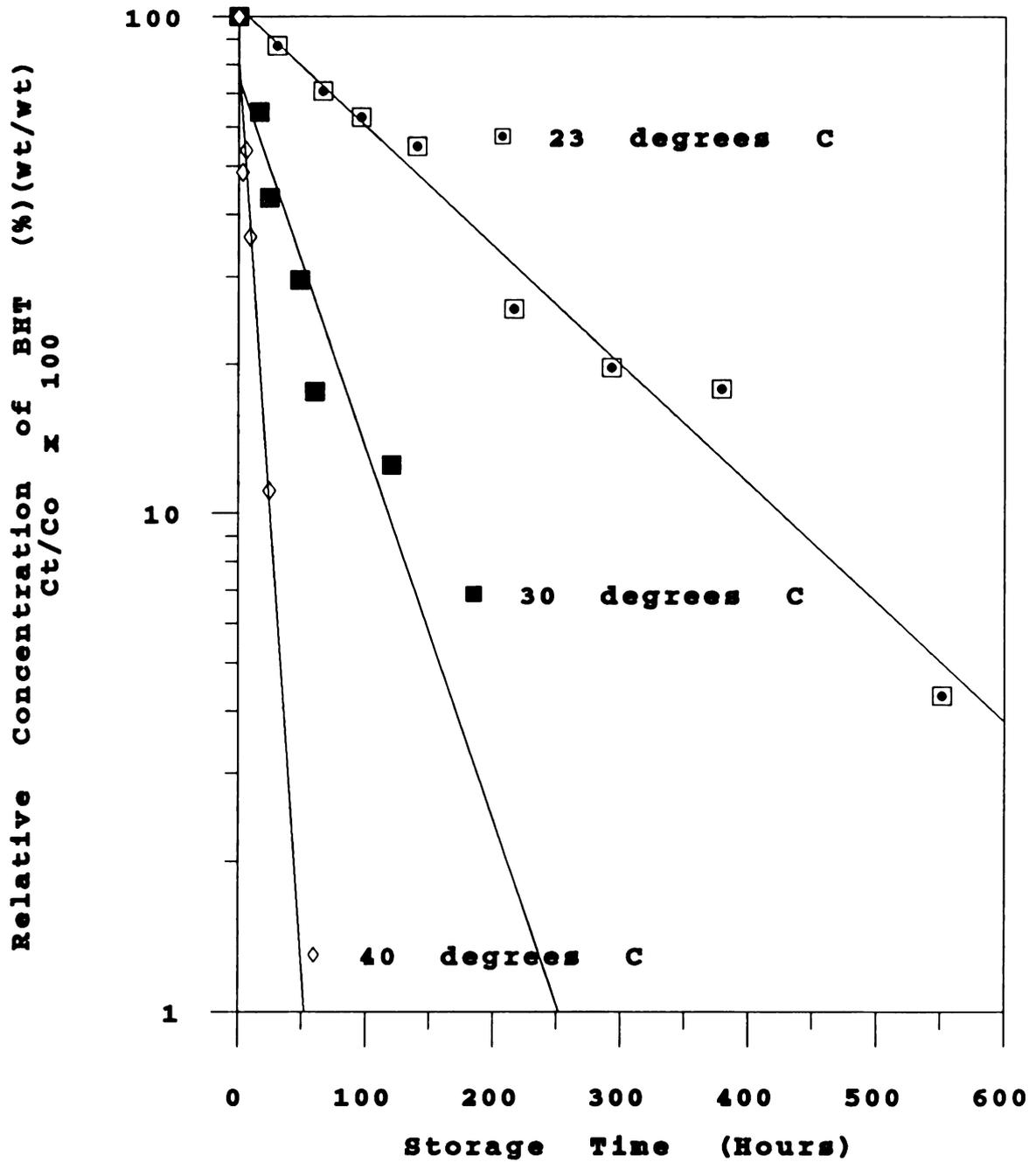


Figure 8. Relative loss of BHT from the heat seal surface layer as a function of temperature.

The R^2 values were 0.98, 0.88, and 0.95 for the 23, 30 and 40°C experiments, respectively for the loss of BHT from the heat seal layer.

The rate constants determined for the loss of BHT from the respective surface layers are summarized in Tables 12 and 13, respectively.

TABLE 12: Rate constants for the loss of BHT from the high density polyethylene layer.

Temperature (° C)	Loss Rate Constant $k \cdot 10^{-3}$ (1/hr)
23	0.623
30	3.21
40	6.70

TABLE 13: Rate constants for the loss of BHT from the heat seal layer.

Temperature (° C)	Loss Rate Constant $k \cdot 10^{-3}$ (1/hr)
23	2.39
30	7.45
40	36.7

The relationship between the rate loss constants and temperature is presented graphically in Figures 9 and 10, where k is plotted as a function of temperature ($1/T(^{\circ}K)$). As can be seen from the least squares fit of 0.99 and 0.912 for the heat seal and HDPE layers, the temperature dependency of the transport process, over the temperature range studied, follows well the Arrhenius relationship. The activation energies of 29.5 and 25 kcal/mol for the heat seal and HDPE layers respectively, show the loss from the heat seal layer being very temperature dependent. Hoojjat et al. (1988) reported an activation energy of 22.4 kcal/mol for BHT loss from a mono-layer HDPE film.

As shown in Figures 4-6, the HDPE surface layer exhibits a significantly lower rate of loss of BHT, as compared to the loss rate from the heat seal layer. While the lower rate of loss for BHT from the HDPE surface layer is not fully understood, it may be attributed in part to a higher rate of diffusion of BHT through the heat seal layer. Differences in the rate of evaporation of the BHT from the respective surface layers, as well as the partition distribution of BHT between the respective layers of the lamination may also contribute to the higher rate of loss of BHT from the heat seal layer. The BHT transport process is related to the solubility of the additive within the respective layers of the lamination and the diffusion of the

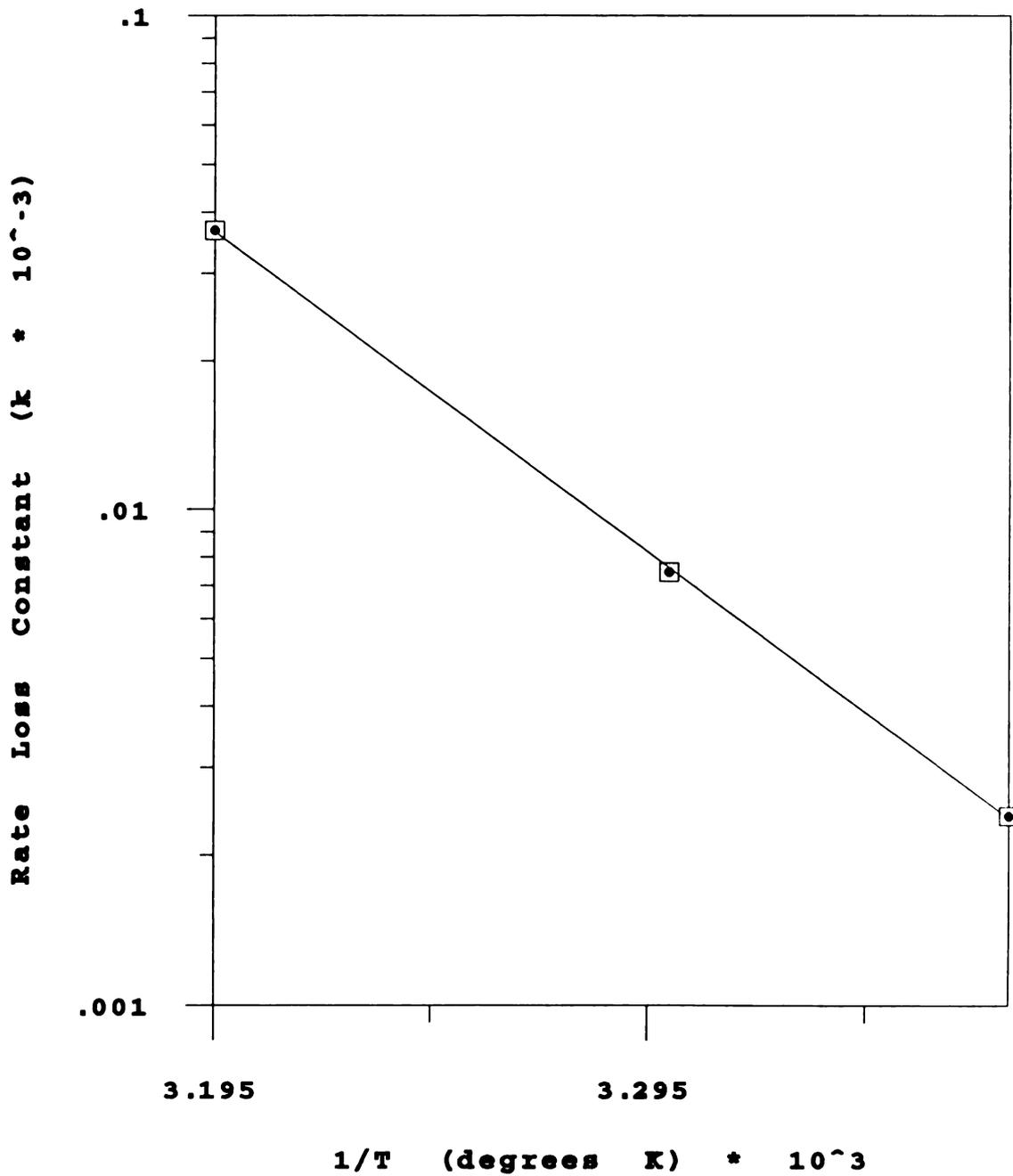


Figure 9. Arrhenius plot of rate loss constant (k) vs. temperature for heat seal layer.

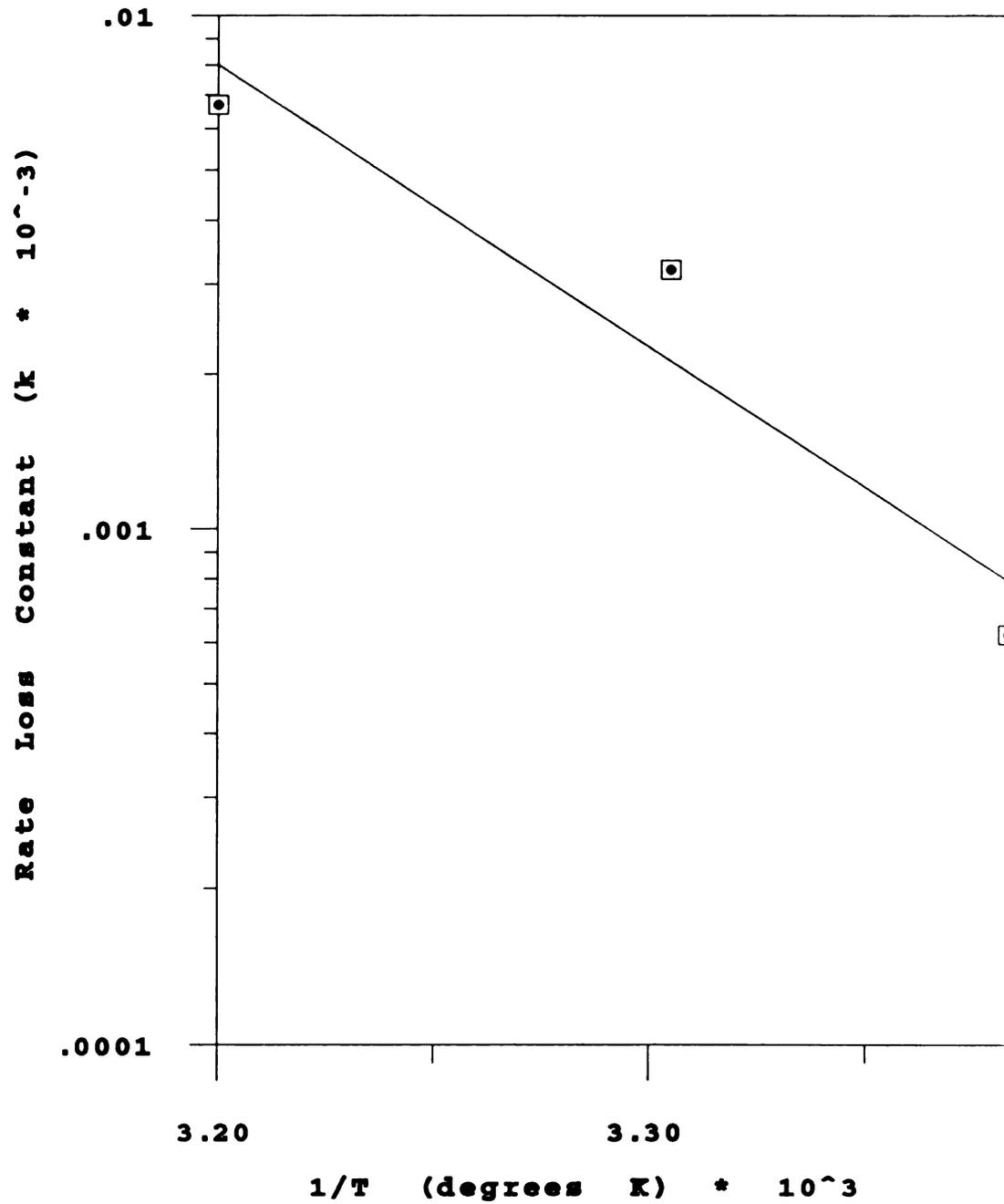


Figure 10. Arrhenius plot of rate loss constant (k) vs. temperature for HDPE layer.

additive through it. Differences in either the solubility or diffusivity can affect the transmission characteristics of BHT. The solubility differences depend primarily on the difference in the physical - chemical nature of the migrating species and the respective laminate layers, and will be reflected in the partition distribution of BHT between the laminate layers. On the other hand, the differences in diffusivity are determined largely by the size and shape of the migrant (i.e. BHT) and by the degree of aggregation among the diffusing species within the polymer layers.

The loss of BHT from the laminate structure, as determined by Soxhlet extraction and HPLC analysis of the extractant phase, gave comparable results to those obtained by the UV spectrophotometric technique. Thus, the quantitative loss determined by the UV method was verified by a direct HPLC procedure.

The morphology of the heat seal layer can be a contributing factor to the observed higher rate of loss of BHT from the heat seal surface as compared to the HDPE surface layer. Polymer morphology refers to the physical state by which amorphous and semi-crystalline regions coexist and relate to each other in the polymer. Ethylene-vinyl acetate (EVA) is a random copolymer. Branching limits

close packing of the polymer chains and thus the ability of the polymer to crystallize. Since the rate of diffusion will be determined by the size of the diffusant molecule and the size and frequency of voids between polymer chains (free volume) factors contributing to an increase in specific volume (free volume) will also contribute to an increase in the rate of diffusion. This leaves free volume for BHT diffusion. The varying level of vinyl acetate (VA) incorporated into the copolymer will also effect the degree of crystallinity. As the polar concentration of vinyl acetate increases, crystallinity, clarity and low temperature flexibility decreases, while density increases. The acetate group is polar, and can contribute to intermolecular and intramolecular forces of attraction between chain segments. EVA was blended with Surlyn®, an ionomer which is an oil resistant thermoplastic with interchain ionic bonding. The intermolecular forces of attraction associated with the Surlyn structure are responsible for it's high bond strength. This EVA/Surlyn blend comprises the heat seal layer.

HDPE is a linear, non polar thermoplastic with a crystallinity of 65-90%, resulting in good moisture-barrier characteristics. The HDPE layer is more crystalline, resulting in a decrease in void volume through which a molecule can diffuse. Thus, permeation rates through HDPE

are inversely proportional to the percent crystallinity, as crystalline domains are considered impermeable to gases and vapors. Polymer morphology can therefore contribute to the observed loss rate of BHT from the respective laminate surface layers. Thus, polymer properties related to structural reordering or redistribution of the free volume elements in the polymer may provide additional sites of appropriate size and frequency of formation, which promotes additive diffusion and account for the observed difference in the rate of loss of BHT from the EVA/Surlyn layer, as compared to the HDPE layer.

The observed enhanced rate of transfer of BHT through the heat seal layer has both theoretical and practical implications. For example, this laminate material is currently being used for a cereal package. The higher rate of loss of BHT from the heat seal layer, implies that the BHT will preferentially transfer to the cereal product, where it can effectively function as an antioxidant, as opposed to its loss through the HDPE layer to the external environment. The practical implication of knowing the rate of diffusion is to enable a structure to be designed for optimal release of additive from a specific surface of the package.

Modeling of BHT Loss

In an attempt to estimate the mass transfer coefficients for BHT from the HDPE and heat seal surface layers of the lamination, the following assumptions were made.

- the rate of loss is controlled by surface evaporation since the sample was in film form.
- the additive had attained an equilibrium partition distribution between the respective layers of the laminate.

A schematic of the system is presented in Figure 11 where $[C_{HDPE}]_s^e$, $[C_{HDPE}]_c^e$, and $[HS]_s^e$ equal the equilibrium concentrations of BHT in the surface HDPE layer, the core HDPE layer and the heat seal layer, respectively and $k_{s/c}$ and $k_{c/hs}$ are equal to the equilibrium partition coefficient of BHT between the HDPE surface layer and HDPE core layer and the equilibrium partition coefficient of BHT between the HDPE core layer and the heat seal layer, respectively.

As indicated above, in estimating the mass transfer coefficient of BHT from the respective surface layers, the first assumption was that the rate of additive loss is controlled by surface evaporation, since the sample was in the form of a thin film. This follows the approach of

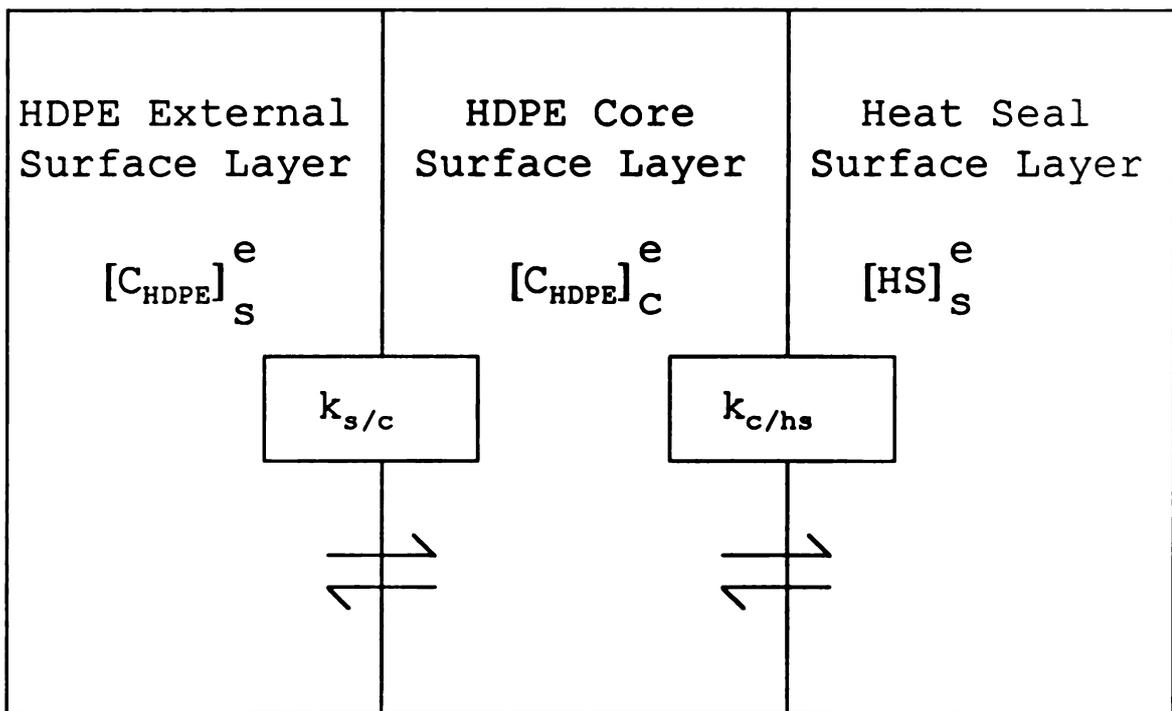


Figure 11. Equilibrium distribution of BHT within the laminate structure.

Calvert and Billingham (1979). Assuming Equation 9 is applicable at L values lower than 0.6, the α value can be calculated from this expression and the time interval required for 90% of the additive (BHT) to be lost from the polymer. The values of α calculated by this method for the HDPE surface layer and the heat seal layer are summarized in Tables 14 and 15 respectively, for the different temperatures.

TABLE 14: Mass transfer coefficient in cm/sec for the high density polyethylene layer.

Temperature (°C)	Mass Transfer Coefficient $\alpha \times 10^{-9}$ (cm/s)	Diffusion Coefficient D x 10 ⁻¹² (cm ² /s)	
		L=0.5	L=0.1
23	.3192	.5027	2.513
30	1.699	2.676	13.38
40	3.590	5.654	28.27

TABLE 15: Mass transfer coefficient in cm/sec for the heat seal layer.

Temperature (°C)	Mass Transfer Coefficient $\alpha \times 10^{-9}$ (cm/s)	Diffusion Coefficient $D \times 10^{-12}$ (cm ² /s)	
		L=0.5	L=0.1
23	.8024	.8152	4.076
30	2.011	2.043	1.022
40	10.96	11.14	55.68

The estimated range for the diffusion coefficients of BHT through the respective surface layers of the lamination are calculated by assuming different values of L and substituting into equation 4. Estimated diffusion values are presented in Tables 14 and 15 respectfully.

The estimated diffusion coefficients were compared to the value reported by Hoojjat et al. (1988), in describing the loss of BHT from HDPE. The results of that study found the mass transfer coefficient to be 9.008×10^{-9} cm/sec at 23°C. The results from the study on the laminate structure yielded a mass transfer coefficient value of 0.3192×10^{-9} cm/sec for the HDPE surface layer at ambient temperature (23°C), which is the same order of magnitude as the Hoojjat study.

SUMMARY AND CONCLUSION

BHT loss from the multi-layer laminate structure was well described by a first-order rate expression. Volatilization from the respective surface layers was assumed to be the rate limiting parameter for mass transfer. The UV spectrophotometric procedure developed allowed for estimation of the rate of loss of BHT from both the outer HDPE layer and the heat seal layer, as well as from the laminate structure. Based on the assumptions that the rate of loss of BHT from the respective surface layers is controlled by surface evaporation, the mass transfer coefficients (α) and the diffusion coefficients were estimated for BHT in the respective surface layers. The calculated diffusion coefficients were compared with those reported for BHT in HDPE and were found to be of the same order of magnitude.

The rate of loss of BHT from the heat seal layer was found to be significantly greater than that from the HDPE surface layer. Such a differential in the rates of additive loss could have significant practical applications in the

packaging field, where the transfer of additives from the package to the product plays a critical role in maintenance of product quality.

Future Studies

Future studies include monitoring the rate of loss of BHT from a mono-layer EVA/Surlyn film. Other heat seal materials could also be explored. The effect of a Saran® coating which is a better barrier and more polar, on the rate of loss of BHT from a laminate structure could also be of interest. Potentially a correlation could be developed to define parameters for transfer, including additive structure, solubility, diffusivity, and polarity. There is also a potential implication to engineer a structure for optimum transfer of a component to the outer surface or food contact surface in a desired time frame.

APPENDIX A

APPENDIX A

Table 16: HPLC calibration curve data.

Quantity (gm)	Area Response (Area Units)
4×10^{-7}	184659
5×10^{-6}	266676
1×10^{-6}	526857
1.5×10^{-6}	832038
2.5×10^{-6}	1271408

Results are the average of three film samples with triplicate analyses per sample.

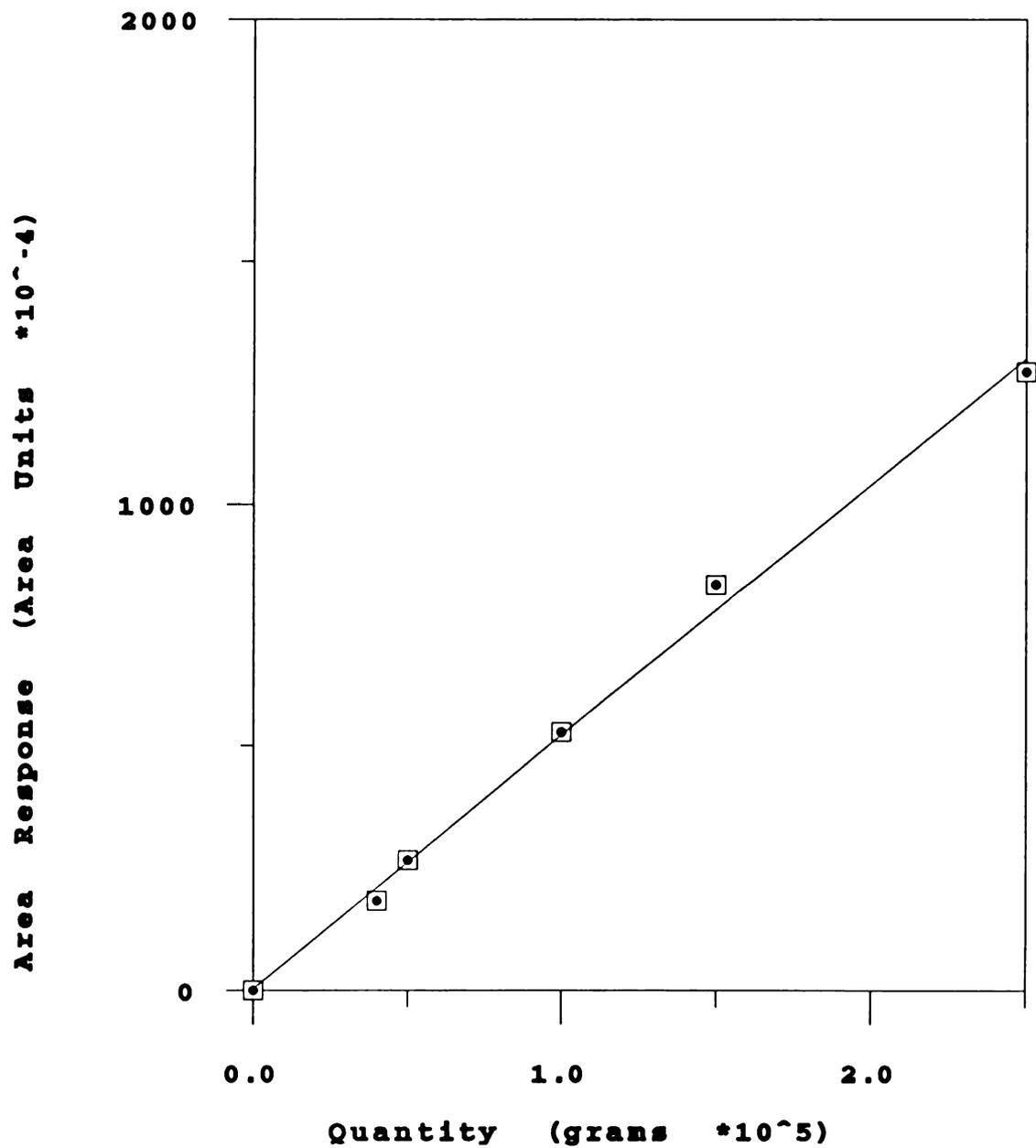


Figure 12. Standard calibration curve for BHT created using a HPLC system.

APPENDIX B

APPENDIX B

Table 17: UV Spectrophotometer Calibration Curve Data

BHT Concentration	Absorbance (Optical Density Units)
4 *10 ⁻⁶	0.035
1 *10 ⁻⁵	0.085
2 *10 ⁻⁵	0.157
3 *10 ⁻⁵	0.246
5 *10 ⁻⁵	0.385

Results are the average of three film samples with triplicate analyses per sample.

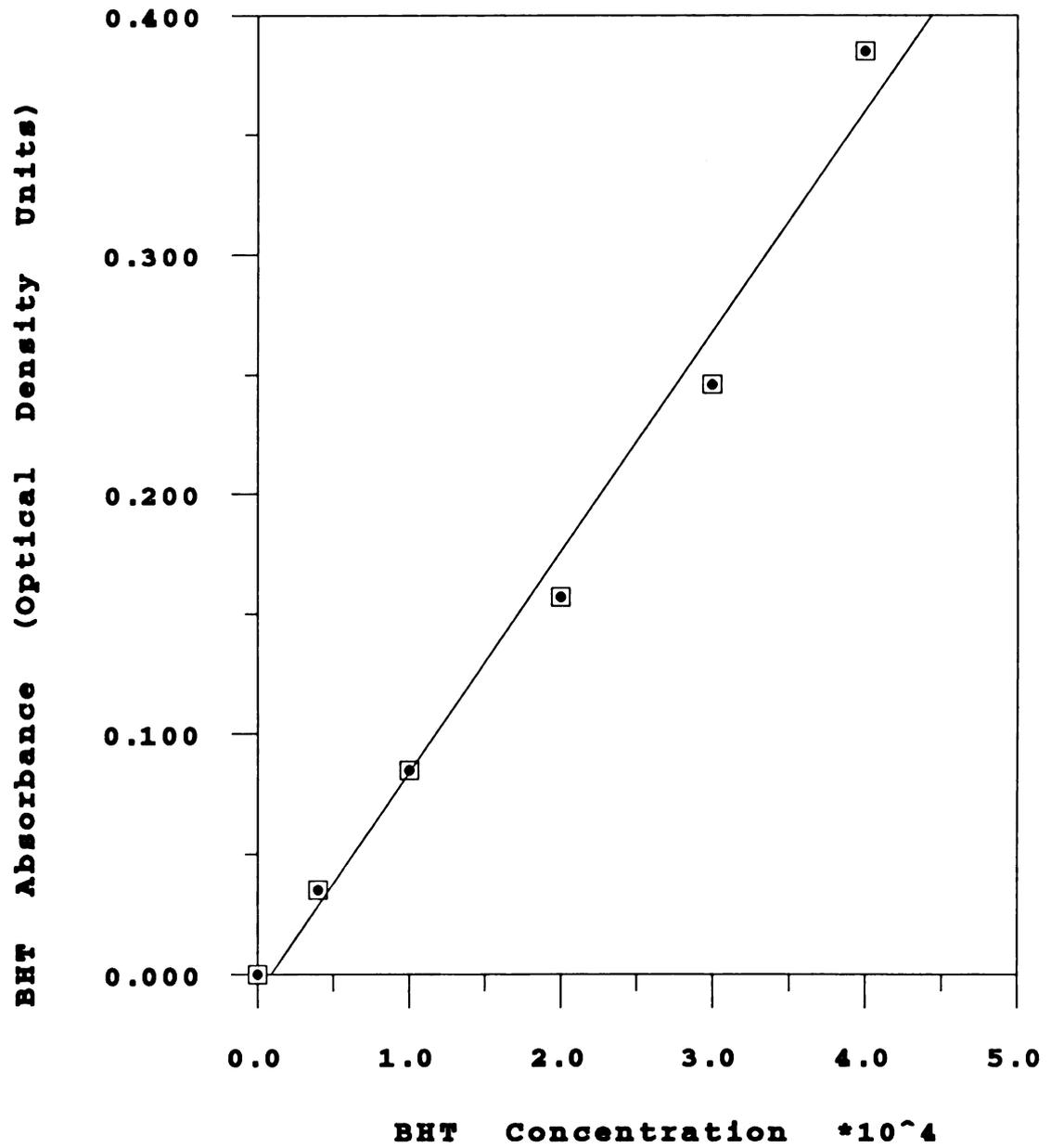


Figure 13. Standard calibration curve for BHT created using a UV Spectrophotometer.

APPENDIX C

APPENDIX C

Table 18: Thickness Measurements Performed Using Optical Microscopy

Sample	EVA Layer Thickness	Total Film Thickness
1	10.48	64.13
2	14.75	69.94
3	9.02	64.21
4	9.39	68.40
5	11.74	64.70
6	10.63	62.84
7	14.85	70.34
8	9.01	64.75
9	9.61	67.61
10	11.30	65.88
Average Thickness	11.08	66.28
Standard Deviation	2.06	2.48

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