This is to certify that the

thesis entitled

MASS TRANSFER OF 3, 5-DI-TERT-BUTYL-4-HYDROXYTOULENE (BHT) FROM HIGH DENSITY POLYETHYLENE FILM AND ITS INFLUENCE ON PRODUCT STABILITY

presented by

Parvin Hoojjat

has been accepted towards fulfillment
of the requirements for

M.S. degree in Packaging

Bruce Harte

Major professor

Date May 12, 1988

Drs. B. Harte and J. Giacin

MASS TRANSFER OF 3,5-DI-TERT-BUTYL-4-HYDROXYTOLUENE (BHT) FROM HIGH DENSITY POLYETHYLENE FILM AND ITS INFLUENCE ON PRODUCT STABILITY

By

Parvin Hoojjat

A THESIS

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

School of Packaging

1988

ABSTRACT

MASS TRANSFER OF 3,5-DI-TERT-BUTYL-4-HYDROXYTOLUENE (BHT) FROM HIGH DENSITY POLYETHYLENE FILM AND ITS INFLUENCE ON PRODUCT STABILITY

By

Parvin Hoojjat

The rate of loss of the antioxidant, 3,5-di-tert-butyl-4-hydroxy-toluene (BHT) from BHT-impregnated high density polyethylene (HDPE) film was determined using high pressure liquid chromatography (HPLC), UV spectrophotometry and by direct measurement of the film weight change with time. There was good agreement between the respective methods.

The loss of BHT from the film followed a first order or pseudo first order rate expression. The rate constants and the activation energy were calculated from the rate loss data. The diffusion coefficient of BHT in HDPE film and the mass transfer coefficient of BHT from HDPE to air were estimated by an analytical model that assumed the rate of evaporation was the loss rate controlling factor.

The potential ability of BHT impregnated film to inhibit the oxidation of an oatmeal cereal was also evaluated. Oxidation was more rapid in the samples which were packaged in pouches with low BHT content. Oatmeal cereal containing antioxidant (tocopherol) was packaged in HDPE pouches (low level of BHT) and oxidation measured as a function of time. The results were comparable to those for the cereal containing no antioxidant which was packaged in the high level BHT impregnated film. Control studies established the sorption of BHT by the product.

To my Mom

ACKNOWLEDGMENTS

A great deal of appreciation is expressed to Dr. Bruce R. Harte and Dr. Jack R. Giacin for their support and guidance throughout my study. Sincere appreciation is also extended to Dr. J. Ian Gray, Department of Food Science and Human Nutrition for serving as a member of the thesis committee.

Appreciation is also extended to Ruben Hernandez for his help and technical support in this research study.

A very special thank you is extended to Kuang-Naw Taw for his excellent help in preparation of this thesis.

A special acknowledgment of appreciation goes to my father and my husband who provided encouragement, motivation and support throughout this research study.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Additives of several types are commonly incorporated into polymers, at concentrations ranging from 0.01 to 1.0 wt%, 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) leading to the formation of complex mixtures of thermal and photochemical reaction products derived from the antioxidant. Other factors may contribute to antioxidant failure, such as loss by evaporation from the polymer surface.

For an antioxidant to be lost from a polymeric film or sheet, it has to diffuse through the bulk of the polymer towards the surface and then evaporate from the surface into surrounding environment. Depending upon the nature and structure of the polymer as well as the properties of the additives, including their diffusivity and volatility, the loss process is controlled either by bulk phase diffusion, or by surface volatilization, or by combination of the two.

Antioxidants are also utilized widely as food additives to retard oxidation of lipid components. The effectiveness of natural, as well as synthetic antioxidants has been extensively documented (Pokorny, 1971; Cort, 1974; Dugan, 1976; Reinton and Rogstad, 1981; Widicus and Kirk,

1981).

Since oxygen first attacks food at the surface, treating packaging material with antioxidant may help to protect the product from oxidation. The proposed mechanism of antioxidant activity involves diffusion through the polymer bulk phase, evaporation of antioxidant from the surface of the packaging material and subsequent sorption onto the surface of the product.

Recently, it has been suggested that cereal and cracker manufacturers might reduce the total amount of antioxidant consumed by putting less into the product and more into the packaging material (Food Engineering, 1979). In general, these fat or oil-rich products have large surface areas which are subject to rapid oxidation. Since these products are inexpensive, the solution to their packaging should also be inexpensive. Packaging in metal or glass, vacuum packaging or inert gas packaging is usually unacceptable from an economic stand point. Using the packaging material as an antioxidant carrier might however be effective in solving this problem.

The specific objectives of this study were to investigate: (1) the rate of loss of BHT from a high density polyethylene (HDPE) film, as a function of time and temperature; and (2) the effectiveness of BHT (3,5-di-tert-butyl-4-hydroxytoluene) impregnated film in preventing lipid oxidation in oatmeal cereal via an evaporation/sorption mechanism.

LITERATURE REVIEW

Lipid Composition of Oats

The lipid content of oats is among the highest of the cereal grains, with the oil level ranging from 2-12% (Frey et al., 1975; and De La Roche et al., 1977). Kalbasi-Ashtari and Hammond (1977) showed that oat oil was comparable to soybean oil in stability. However, degumming and refining losses were higher for oat oil because of the higher percentages of components other than triglycerides in the crude oil, including free fatty acids (FFA).

In a study carried out with 9 strains of oats, De La Roche et al. (1977) showed that high lipid oats contain a greater amount of phospholipids than the low lipid oats. Sahasrabudhe (1979) separated oat lipid extracts from 6 strains into various classes and obtained average values of 71.9% neutral lipid, 8.3% glycolipid and 19.7% phospholipid.

The fatty acid composition of oats (Avena sativa L) and oat groats have been reported by several authors. Lindberg et al. (1964) compared the fatty acid composition of rye, wheat, barley and oats. All contained palmitic, oleic and linoleic acid as the major fatty acids, but oats contained more oleic acid and less linoleic acid than the others. Hutchinson and Martin (1955) showed that the oil content of oats was affected by environmental conditions. Beringer (1967, 1971)

demonstrated that lower temperatures (when grain development took place) increased both the lipid content of oats and the proportion of unsaturated fatty acids in the total lipid profile.

Due to the high concentration of unsaturated fatty acids in cereal grains, a high potential for rancidity development exists. Two types of rancidity in oat cereal can be found, hydrolytic and oxidative. The development of hydrolytic rancidity in oats results from the action of lipases located in the pericarp, on the oil in the kernel (Hutchinson et al., 1951; Martin and Peers 1953). These enzymes act very slowly at low moisture levels (13%) and temperatures (18°C), but unless inactivated or removed it can produce high levels of FFA's when they are released in the milling process (Hutchinson et al., 1951). FFA will then undergo rapid oxidative reactions (Dugan, 1976).

Mechanism of Lipid Oxidation

Lipid oxidation is one of the most important and complex deteriorative reactions occurring in foods. The most undesirable aspects is the development of rancid off odors and off flavors in fatty foods, which make the food unacceptable. Oxidation of various unsaturated fats can also lead to loss of essential fatty acids, destruction of several vitamins and pigments, and can ultimately result in a reduction of the biological value of the proteins (Labuza, 1971).

Susceptability of lipids to oxidative deterioration is not solely dependent on the concentration of lipid present, but also on the fatty acid composition. From the standpoint of food oxidation, the most

important lipids are the unsaturated fatty acid moieties, particularly oleate, linoleate, and linolenate, the principal ones in foods (Labuza, 1971).

The autoxidation of an unsaturated organic substance (RH) involves a free radical chain process which is described in its early stages by the following simplified scheme. This theory has been reviewed by Swern (1962).

Initiation

$$RH \xrightarrow{\text{activation}} \text{free radicals}$$

$$\underset{(ROOH)_2}{ROOH} \longrightarrow \text{free radicals (e.g. } R\bullet,\ RO\bullet,\ RO_2\bullet,\ HO\bullet, \text{ etc.)}$$

Propagation

$$R\bullet + O_2 \longrightarrow ROO\bullet$$

$$RO_2\bullet + RH \longrightarrow R\bullet + ROOH$$

Termination

$$R\bullet + R\bullet \longrightarrow RR$$

$$R\bullet + RO_2\bullet \longrightarrow ROOR \text{ stable (nonradical) end product}$$

$$RO_2\bullet + RO_2\bullet \longrightarrow ROOR + O_2$$

A hydrogen atom is lost from the alpha methylenic carbon atom, leaving an unstable free radical. Oxygen readily adds to this active site, forming an unstable peroxy free radical ($RO_2\bullet$). This peroxy free radical abstracts a hydrogen atom producing a hydroperoxide which is fairly stable at low temperature.

The rate of oxidation is dictated by the substrate (Nawar, 1985).

Methyl linolenate is oxidized more quickly than methyl linoleate, which in turn is oxidized more quickly than methyl oleate. The greater the degree of unsaturation, the shorter the induction period.

The hydroperoxides formed during oxidation are not responsible for the rancid odor of fatty foods, as they are odorless (Lundberg, 1962). The rancid flavors and odors are due to the presence of compounds such as aldehydes, ketones and hydrocarbons which are formed by hydro peroxide decomposition (Pokorny, 1971).

Measurment of Lipid Oxidation

Among the different methods used for the determination of rancidity in food products, the 2-thiobarbituric acid (TBA) procedure is one of the most popular.

Kohn and Liversadge (1944) observed that animal tissues which had been incubated aerobically, gave a red color with TBA. This red color was found to be the result of complexes formed from the oxidation products of unsaturated fatty acid and TBA. The compound responsible has been shown (Sinhuber, et al., 1958) to be the dicarbonyl compound, malonaldehyde. The red pigment was found to result from the condensation of two moles of TBA with one mole of malonaldehyde (Sinhuber and Yu, 1958).

Malonaldehyde is generated by the degradation of polyunsaturated fatty acids, particularly trienoic and tetraenoic fatty acids (Dahle et al., 1962). It may also be derived from oxidation of 2,4-decadienal,

a secondary oxidation product of linoleate (Dugan, 1976).

There is general agreement that absorption occurs in the range of 532-538 nm. However, with certain foods and tissues an orange or yellow shade results instead of the normal red pigment. The red color is associated with oxidized flavor (Dunkley and Jennings, 1951), while the yellow color has been attributed to the presence of sugar in the digestion step of the reaction (Biggs and Bryant, 1953). In order to apply the test to extracts of cereal, a chromatographic procedure for separation of yellow components has been devised, allowing the residual red color to be estimated in an ordinary colorimeter or spectrophotometer (Caldwell and Grogg, 1954).

The rate of lipid oxidation is affected by factors such as lipid composition, temperature, presence or absence of light, metal catalysts, inhibitory compounds and oxygen (Lea, 1962; Labuza, 1971). The shelf life of a product can be influenced by controlling these factors.

Type and Mechanism of Antioxidant Activity

Among different methods employed to combat rancidity in fat containing foods, the use of antioxidants has been found to be the most effective and efficient (Food Engineering, 1979).

The concentration of an antioxidant in a food fat is important for reasons of cost, safety, sensory properties and functionality. The Code of Federal Regulations specifies the levels to which additives can be

added to a food product. As given in the Code of Federal Regulation title 21 part 172 section 115, the maximum allowable amount of BHT and BHA in dry breakfast cereal is 50 parts per million (ppm).

In food systems, the most effective antioxidants function by interrupting the free radical chain mechanism, while antioxidants used in gasoline, lubricants, rubber and other applications may function as peroxide decomposers. Antioxidants such as ascorbic acid function by being preferentially oxidized and they afford relatively poor protection (Dugan, 1976).

Antioxidants (AH) react with radicals produced during autoxidation according to the following scheme:

$$R\bullet + AH \longrightarrow RH + A\bullet$$

$$RO\bullet + AH \longrightarrow ROH + A\bullet$$

$$ROO\bullet + AH \longrightarrow ROOH + A\bullet$$

$$R\bullet + A\bullet \longrightarrow RA$$

$$RO\bullet + A\bullet \longrightarrow ROA$$

Antioxidants react either with free fatty acid radicals or with free hydroperoxide radicals, and in both cases the active free radicals are deactivated. Antioxidant free radicals are produced, which are not able to initiate another autoxidation chain. These react with other free radicals or can be further oxidized to quinones (Everson, et al., 1957).

Phenolic antioxidants, often in combinations of two or more are used in products containing fat and oils that are susceptive to rancidity. Some major antioxidants are 3(2)-tert-butyl-4-hydroxy-anisole (BHA), 3,5-di-tert-butyl-4-hydroxytoluene (BHT), Tert-butyl-hydroquinone (TBHQ), and n-propyl gallate (PG).

Many naturally occuring substances function as antioxidants, most notably are the tocopherols (α, β, γ, δ). The tocopherols have vitamin E activity that decreases from α to δ, and antioxidant activity that increases from α to δ.

The widespread use of phenolic antioxidants in food products has stimulated the development of numerous techniques for their determination. Over the past twenty years, the identification and quantitative determination of antioxidants in fats and oils have been largely carried out by a variety of chromatographic techniques. Generally, these techniques have relied on the isolation of the antioxidants from the food matrix by solvent extraction and or distillation, followed by analysis of the isolated material by either spectrophotometry or gas chromatography.

The use of high pressure liquid chromatography (HPLC) to separate antioxidant mixtures, has been demonstrated by several researchers (Endean, 1976; Majors, 1970). Recently Hammond (1978) described the use of reverse phase gradient elution HPLC to quantitate propyl gallate, octyl gallate, dodecyl gallate, BHA, and BHT in fat and oil. BHT and TBHQ have also been directly determined in oils, using gel permeation

chromatography (Doeden et al., 1979).

To date, incorporation of antioxidants into food products has been the most successful and least expensive method of protecting fatty foods from oxidative rancidity. This may be still the best method available (Food Engineering, 1979).

Antioxidants are also incorporated into plastic films in order to protect them from degradation (Ram et al., 1980). These antioxidants, however, diffuse through the film and evaporate at its surface into the environment (Calvert and Bilingham, 1979; Han et al., 1987).

Since permeating oxygen attacks food at the surface, treating a packaging material with antioxidant should protect the product from oxidation. This technique has been used for up to 20 years in the breakfast cereal industry. (Food Engineering, 1979). The mechanism of antioxidant activity involves the migration of a particular antioxidant from the packaging material to the product surface. The Code of Federal Regulations specifies how much of an additive can migrate to a food from packaging material. These limits are written under regulations 181.22 through 181.30 (Food Engineering, 1979).

Woggon et al. (1968) and Franzke et al. (1970) carried out a series of experiments in which BHT was allowed to migrate from both high density polyethylene (HDPE) and low polyethylene (LDPE) into sunflower oil. These investigators attempted to determine if the migrating BHT from plastic films could effectively improve the shelf

life of sunflower oil. While much of the study dealt with variations in the sunflower oil properties during storage, some data were presented in terms of migration of BHT (mg migrated/kg of oil) for both HDPE and LDPE films containing 1000-4000 ppm (wt/wt) BHT initially. The polyethylene was formed into 250 cm^3 bottles to hold the oil.

Environmental factors such as temperature and relative humidity can contribute to the oxidation of antioxidants during storage (Daun et al., 1974), and can also result in migration of the antioxidant out of the packaging material. Therefore, the packaging material which has been impregnated with antioxidant must be kept tightly wrapped and stored under controlled conditions prior to use.

Loss of Additives from Packaging Material

One objective of packaging is to select those systems which provide the necessary protection to the product at minimal cost. Presently plastic packaging materials are widely used because of their cost and outstanding service properties.

HDPE has high usage for food packaging. The largest single use is for milk bottles and closures. Other uses include packages for edible oil and salad dressing, margarine, frozen deserts and topping and institutional packages for pickles and margarine. (Arthur D. Little, Inc., 1981).

Polyolefins such as polyethylene can undergo thermal and oxidative degradation. During the processing of polymers at high temperatures

(i.e., 200-300°C) and their subsequent exposure to the environment in the presence of oxygen, free radical chain reactions can take place, leading to deterioration of the physical properties of the polymer (Lichtenthaler and Ranfelt, 1978).

To protect against degradation, a mixture of additives consisting of one or more antioxidants are used. HDPE is usually compounded with an antioxidant such as BHT which has about a 50% share of the market (Authur D. Little, Inc., 1981). BHT is used at concentrations up to 400 ppm (wt/wt). However, because of its relatively high vapor pressure, substantial losses are experienced during compounding and fabrication of packaging material (Authur D. Little, Inc., 1981).

The effectiveness of stabilizers to inhibit oxidation depends primarily on their ability to interfere with the chemistry of the oxidation process. They must also remain in the polymer long enough to be effective as potential stabilizing agents.

Migration through or loss of additives from polymers, together with an understanding of the factors affecting these processes is of practical value.

There are four factors which control migration of additives (Downes and Gilbert, 1975); (1) solubility of the migrating species in the food system; (2) diffusion of the migrating species into the food system; (3) solubility of the migrating species in the polymer system; and (4) diffusion of the migrating species into the polymer system. The

addition of these processes results in a time, and temperature-dependent property which can be called mobility.

As part of a study on additive migration, Vom Bruck et al. (1981) investigated the interaction of fat-containing food with plastic packaging.. These investigators were able to show the migration of BHT from rigid polyvinyl chloride (PVC) and from HDPE into fat.

Figge et al. (1978) summarized their results for BHT migration into simulants, foods, cosmetics and medical compounds. HDPE was used with an initial concentration of BHT of 2000 ppm. In all cases aqueous solvents showed significantly lower migration rates than fats and oils. The same results were obtained by Till et al. (1982).

Although additive loss has been seen as important for many years, there has been little effort to develop a general quantitative model of the loss process in terms of measurable parameters of the additive and the polymer. Angert et al. (1961) was the first to point out the rate of evaporative loss of an additive from a polymer depends upon two parameters. Initially, the loss rate is determined by the rate of volatilization of additive from the polymer surface, which will cause a concentration gradient near the surface. Subsequent replacement of this loss by diffusion from the bulk occurs, such that the overall loss process depends on the rate of mass transfer across the sample surface and the bulk diffusion rate within the polymer.

Angert et al. (1961) concluded that the loss of phenyl-β-naphthylamine from thick samples of rubber was determined by the rate of removal from the surface. Unfortunately, more recent investigators have largely considered additive loss in terms of either diffusion or volatility but the possibility that both may be important has been neglected.

Till et al. (1982), measured the migration of the antioxidant BHT from HDPE into a variety of foods and food simulants. In almost all cases, the BHT loss appeared to be rate limited by diffusion within the polymer.

Smith et al. (1974) described the loss of phenyl-β-naphthylamine from thin films of neoprene as a diffusion limited process. In contrast, Durmis et al. (1975) and Plant and Scott (1971) have correlated loss from polyolefins with the volatility of the pure additive measured separately, without considering the role of diffusion.

Calvert and Billingham (1979) pointed out that the loss of a simple low molecular weight additive such as BHT from thick films and bulk solids is determined by diffusion, while loss from thin film is controlled by the evaporation rate of the additive.

According to Billingham and Calvert (1980), a correct model for additive loss must take into account both the rate of mass transfer

across the surface and the corresponding rate in the bulk polymer.

MATHEMATICAL EXPRESSION FOR ADDITIVE (BHT) LOSS

Crank (1975) has described a mathematical expression for a film from which the additive is lost by surface evaporation with finite boundary conditions. According to this model, the total amount of additive leaving the polymer in time (t) is expressible as a fraction of the corresponding amount leaving at infinite time by equation (1).

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

where M_t = amount of additive leaving the polymer in time = t

M_∞ = amount of additive leaving the polymer at infinite time

$T = Dt/l^2$

$L = l\alpha/D$

l = half of film thickness, cm

t = time, sec

D = diffusion coefficient of additive in polymer, cm^2/sec

α = mass transfer constant of additive from polymer, cm/sec

β_n values are the positive roots of $\beta_n \tan \beta_n = L$ which are given by Carslaw and Jaeger (1959).

Determination of Antioxidant in Polymer

The analytical procedures used in the determination of polymers additives and problems associated with these analyses have been reviewed by Wheeler (1968). Difficulties arise from three factors; (1) the high reactivity and low stability of antioxidants; (2) the low

concentration (0.1% to 1%) at which they are present; and (3) the relatively insoluble polymer matrix.

Wyatt and Sherwin (1979) used direct sampling gas chromatography to measure the loss of BHT from polyethylene. Howard (1971) has shown how useful liquid exclusion chromatography (LEC) can be for the analysis of the polymer additive system. Wims and Swarin (1975) used LEC and liquid absorption chromatography (LAC) to determine antioxidant levels in commercial polypropylenes. They concluded that both LEC and LAC are very good routine monitoring techniques providing qualitative and quantitative analysis for quality control. LAC can be used when faster analysis of antioxidants is required, but both LEC and LAC analysis times are controlled by the time necessary to extract the additives.

EXPERIMENTAL

Packaging Materials

Two high density polyethylene films (density, 0.959g/ml; thickness 2.6mil) were provided by Crown Zellerbach's Film Production Division (Greensburg, Indiana). The films contained differing levels of antioxidant (BHT), 0.022% (w/w); and 0.32% (w/w) respectively. These films were used to prepare 18 by 19 cm pouches in which storage stability studies of the oatmeal cereal were carried out.

Oatmeal Cereal

Fresh oat flake cereal was obtained from the Gerber Product Company (Fremont, MI). Samples of cereal product containing no antioxidant as well as product containing antioxidant (mixed tocopherols) were provided.

Methods

Antioxidant Loss Studies

Studies of antioxidant depletion from the test films were carried out on the high level BHT-impregnated film sample. Film samples were cut (1 × 1 cm), mounted on a frame and unless otherwise stated stored in open air at several temperatures (10, 21.5, 30 and 40°C). The level of retained antioxidant was then determined as a function of storage time.

BHT Determination in HDPE:

BHT in the film samples was determined in one of three ways: (1) by using a high pressure liquid chromatography (HPLC) procedure, (2) by using a U.V. Spectrophotometric procedure, (3) by monitoring the change in the film weight with time using a Cahn electrobalance.

High Pressure Liquid Chromatography (HPLC) Method:

Extraction Procedure: For antioxidant extraction, 5 g of the film sample were cut into small pieces and extracted with 150 ml of acetonitrile in a Soxhlet extraction apparatus for 12 hours. The extracts were brought up to volume (200 ml) using acetonitrile. These samples were then filtered and analyzed using HPLC.

Chromatographic Apparatus: Analysis of extracted BHT was carried out using a HPLC system consisting of a Perkin Elmer Series 3B Solvent Delivery System and a LC-1000 Column oven with a Perkin Elmer LC-85 spectrophotometric detector. The detector was interfaced to a Spectra Physics/SP 4200 Computing Integrator for quantitation. The chromatographic conditions were as follows:

1) Column: a 0.24 × 25 cm ODS-HC Sil-x-1 Stainless steel
2) Solvent: 60% Acetonitrile/40% distilled water (v/v)
3) Flow rate: 1 ml per min
4) Detection wavelength: 280 nm
5) Amount injected: 10 μl
6) Elution time: 6 min.

Peak areas and retention times were determined using the computing integrator. The concentration of BHT in the film samples were determined using a standard curve constructed by analyzing pure BHT samples in acetonitrile.

To prepare standard curve, 0.01 g pure BHT obtained from Eastman Company (Eastman Chemical Product, Inc., Kingsport, Tennessee) was weighed and transferred into a 100 ml volumetric flask. The flask was brought up to the volume with acetonitrile. Standards of different concentrations were prepared from the stock solution by a serial dilution technique. The concentration of the solutions was expressed as wt/wt. Sample of 10 μl were withdrawn from the standard solution and injected directly into the HPLC.

UV Spectrophotometric Method:

A Perkin Elmer Lambda 3B UV/Visible Double beam, spectrophotometer with an intergrating sphere was used to measure the BHT content of the films at different time intervals. Film samples were mounted directly in the sample holder of the Intergrating Sphere and the absorbance (O.D. units) at 280 nm was recorded.

The relative concentration of BHT in the film was obtained by the expression

$$\text{relative \% BHT} = \frac{\text{O.D. (t)}}{\text{O.D. (o)}} \times 100 \qquad (2)$$

where the parameter in parenthesis is a time factor.

Gravimetric Method:

The loss of BHT was also measured directly using a Cahn-RG Electrobalance (Cahn Instruments Inc., Cerritos, CA) by continuously flowing nitrogen gas through the sampling hang down tube at room temperature (Hernandez et al., 1986). The electrobalance and sample tube were maintained at room temperature (21.5°C). For a sample mass of 26 mg the sensitivity of the system was 5 μg. The system allows for continuous measurment of weight loss over time.

Product Storage Studies

For storage studies, pouches (18 × 19 cm) were fabricated from HDPE film containing high and low levels of incorporated antioxidant. 120 g of cereal (without antioxidant) were filled into the pouches and the pouches were sealed. The sealed pouches were stored at 39±1°C and 45±2% RH. Two pouches for each BHT concentration were removed weekly from storage and the cereal product was analyzed for extent of lipid oxidation. The pouches were also analyzed for retained antioxidant (BHT).

For cereal product containing antioxidant (mixed tocopherols) similar studies were carried out. The product was analyzed for extent of lipid oxidation as well as the amount of sorbed BHT. The BHT content of the films used to make the pouches was also determined.

Thiobarbituric Acid Analysis:

The extent of lipid oxidation of the oatmeal cereal, as a function of storage time was determined using a modification of the method of

Caldwell and Grogg (1955). A 20 g sample of cereal was extracted overnight at room temperature with 100 ml of hexane. The extracted lipid fraction was filtered and the filtrate concentrated in a rotary evaporator maintained at 48°C. The extracted sample was weighed, 10 ml of benzene and 10 ml of TBA reagent (prepared from 0.67 g of TBA in 100 ml of distilled water and 100 ml of glacial acetic acid) were then added. The sample was vigorously shaken and then centrifuged for 15 min. The top layer (benzene) was discarded and the aqueous layer transferred to a screw cap glass test tube which was placed in a boiling water for 30 min. The sample (7 ml) was then cooled and passed through a cellulose powder column. Sample aliquots were eluted from the column under positive pressure (10 psi) to yield a yellow and a red fraction. Extraction and transfer steps involving benzene were carried out under the hood with proper safety measures being exercised.

The yellow pigmented fraction was eluted with distilled water (5 ml), while the red pigmented fraction, which is associated with the lipid oxidation products, was eluted with 10 ml of aqueous pyridine (20% v/v) and collected in a 10 ml volumetric flask. The absorbance was then recorded at 532nm and expressed in the basis of absorbance units per g sample basis.

BHT Content of Cereal

Lipid Extraction: The oatmeal cereal was extracted for total lipid using the method of Bligh and Dyer (1959). An 80 g sample of cereal was extracted using a mixture of chloroform, methanol, and water in the proportion of 2:2:1, respectively.

After removing the residue by vacuum filtration, the phases were separated by centrifugation for 10 min at 1500 rpm. The chloroform layer was collected and evaporated using a Buchi rotary evaporator (Buch, Inc., Switzerland). This layer was then transferred to a screw capped test tube and redissolved in chloroform and stored under nitrogen in a $-20\pm2^{\circ}C$ freezer for later analysis.

BHT Content of Extracted Fat: BHT content of cereal was determined using the modified method of Wyatt (1981). To a 1 ml volumetric flask containing 0.5 g of extracted oil, 0.5 ml of acetonitrile was added. The mixture was then shaken gently by hand for 10 to 15 seconds and allowed to stand. Following separation of the two phases, the top layer was removed and transferred into a small (17 × 60 mm, 2 dram) vial. This extraction procedure was repeated 5 more times using 0.5 ml acetonitrile each time. The acetonitrile (3 ml) which was collected was then filtered and analyzed by HPLC for its BHT content.

Equilibrium Vapor Pressure

To measure equilibrium vapor pressure of BHT, approximately 1 g of pure BHT was weighed and transferred into a series of 35 ml septa seal vials and the vials capped. The sealed vials were then stored at a series of temperatures (-5, 5, 28 and $35^{\circ}C$). Every 3 days, aliquots of 500 μl were withdrawn from the headspace above the sample and injected directly into a Hewlett Packard Model 5830A Gas Chromatograph for quantitation of BHT concentration in the vapor phase. This procedure was repeated until the respective system obtained equilibrium.

The concentration of BHT was determined from standard curves constructed by analyzing pure BHT samples in petroleum ether.

The GC conditions were as follows:

1) Column: 5% SP 2100 on 100/120 Supelcoport, 1.83 m × 0.32 cm stainless steel
2) Column Temperature: 150°C
3) Injection Port Temperature: 175°C
4) Carrier gas: helium
5) Flow rate: 32 ml per minute
6) Detector: Flame Ionization Detector
7) Detector temperature: 350°C
8) Elution time: 5 minutes

RESULTS AND DISCUSSION

Equilibrium Vapor Pressure of BHT

The results of the equilibrium vapor saturation studies for BHT, expressed as saturation vapor concentration (ng/ml) at equilibrium, are summarized in Table 1.

The equilibrium vapor concentration values obtained were converted to partial pressures and the following expression derived to describe the relationship between temperature and BHT saturation vapor pressure in air.

$$\text{Log } p = 27.9 \text{ Log } (T/449.1) \qquad (2)$$

where p is the vapor pressure of BHT in atmospheres and T is temperature in degrees Kelvin.

As shown in Table 1, equilibrium vapor saturation levels for BHT in air are very low. For example, for a package (18 x 19 cm) fabricated from the high level BHT impregnated HDPE film (0.32% BHT) with a headspace volume of 3 liters, only 2% of the initial BHT content of the HDPE film (8g total film weight) would be sufficient to saturate the package void volume. Thus, surface evaporation will play an important role in the mass transfer process.

Loss of BHT from HDPE Film

The loss of BHT from the high level BHT test film (0.32% wt/wt) was determined over the range of 10 to 40°C. The results obtained by

Table 1: Equilibrium Vapor Saturation of BHT

Temperature	BHT Equilibrium Saturation Concentration in Air	BHT Equilibrium Partial Pressure in Air
($^{\circ}$C)	(g/ml x 10^{-9})	(atm x 10^{-6})
-9.4	3.5	0.34
5.0	17.4	1.80
28.0	141.0	15.8
35.0	226.0	26.0

HPLC analysis summarized in Tables 2 through 5 respectively.

From the first term of the power series equation describing the solution for additive loss from a polymer film or slab (Crank, 1975), an exponential expression is obtained which relates the loss of the additive and its diffusion coefficient (D) in the polymer bulk phase (Han et al., 1987):

$$\ln (C_t/C_o) = -kt \qquad (3)$$

where C_o is the initial concentration of BHT in the film and C_t is the concentration (wt/wt %) at any time (t) ; k is a constant which is related to the diffusion coefficient of BHT in the polymer film; and t is the time interval.

A linear relationship was found for a semi-logarithmic plot of C_t/C_o versus time (Fig. 1). Nearly all of the BHT (greater than 95%) was lost within one day at 40°C and within three days at 30°C (Fig. 1, Tables 2-5). At 21.5°C, the HDPE film sample showed a loss of approximately 80% after one week, while samples stored at 10°C showed 50% loss at the same amount of time. As shown (Fig.1), the loss of BHT appears to follow a first order or pseudo first order rate expression. Han et al. (1987) measured the loss of BHA from HDPE film and obtained similar results.

The values of k determined for the loss of BHT from the HDPE film (high antioxidant level) and the activation energy for this process, determined from an Arrhenius plot of the rate data (Fig.2) are summarized in Table 6.

Table 2: Loss of BHT from HDPE (high level BHT) at 10°C (a)

Time (day)	BHT Concentration (% BHT, wt/wt)	Relative % of BHT (C_t/C_o x 100)
0	0.35	100
1	0.29	85
3	0.21	62
5	0.17	50
7	0.15	45

(a) determined by HPLC

Table 3: Loss of BHT from HDPE (high level BHT) at 21.5°C (a)

Time (day)	BHT Concentration (% BHT, wt/wt)	Relative % of BHT (C_t/C_o x 100)
0	0.36	100
1	0.24	65.5
4	0.13	34.7
6	0.10	27
7	0.07	20

(a) determined by HPLC

Table 4: Loss of BHT from HDPE (high level BHT) at 30°C (a)

Time (day)	BHT Concentration (% BHT, wt/wt)	Relative % of BHT (C_t/C_o x 100)
0	0.35	100
0.5	0.16	46
1	0.10	30
1.5	0.06	18
3	0.02	5.4

(a) determined by HPLC

Table 5: Loss of BHT from HDPE (high level BHT) at 40°C (a)

Time (day)	BHT Concentration (% BHT, wt/wt)	Relative % of BHT (C_t/C_o x 100)
0	0.36	100
0.5	0.06	17.5
1	0.01	2.0
1.5	N.D	-----

(a) determined by HPLC

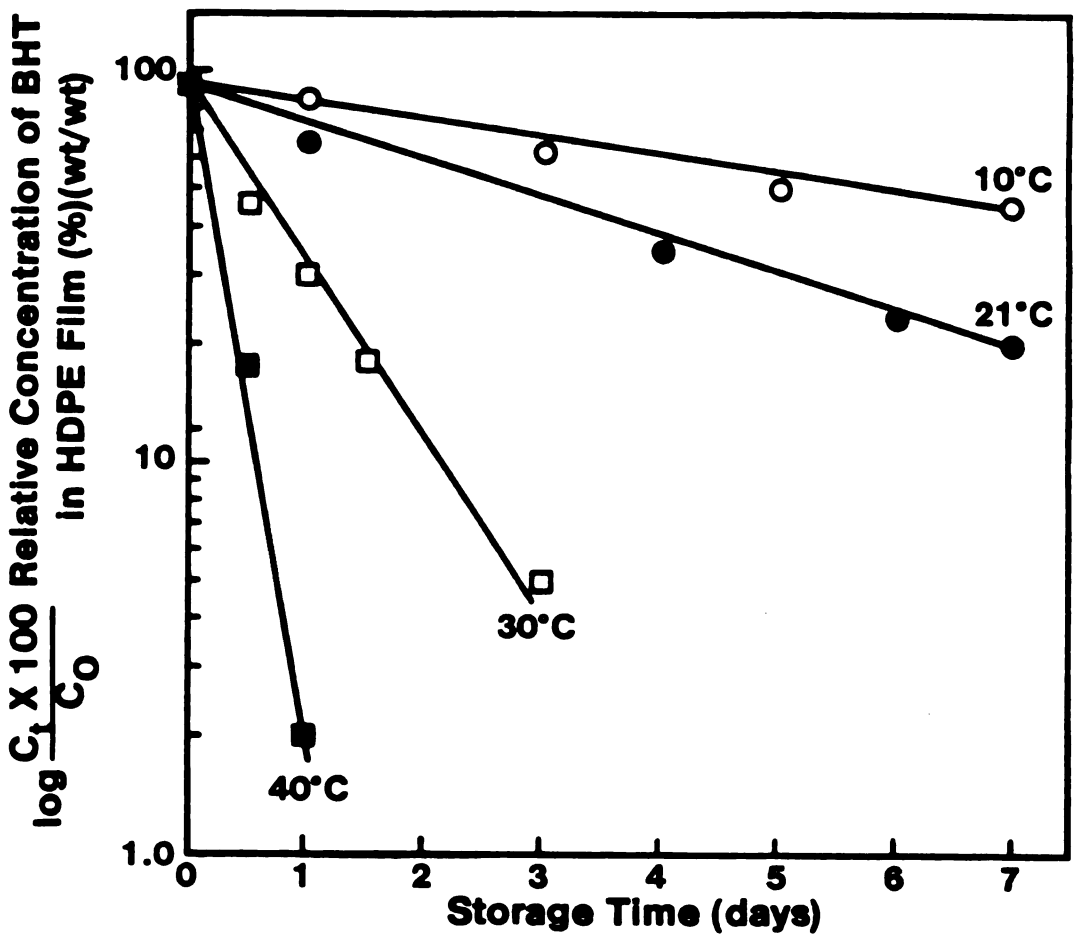

Figure 1 LOSS OF BHT FROM HDPE FILM DURING STORAGE

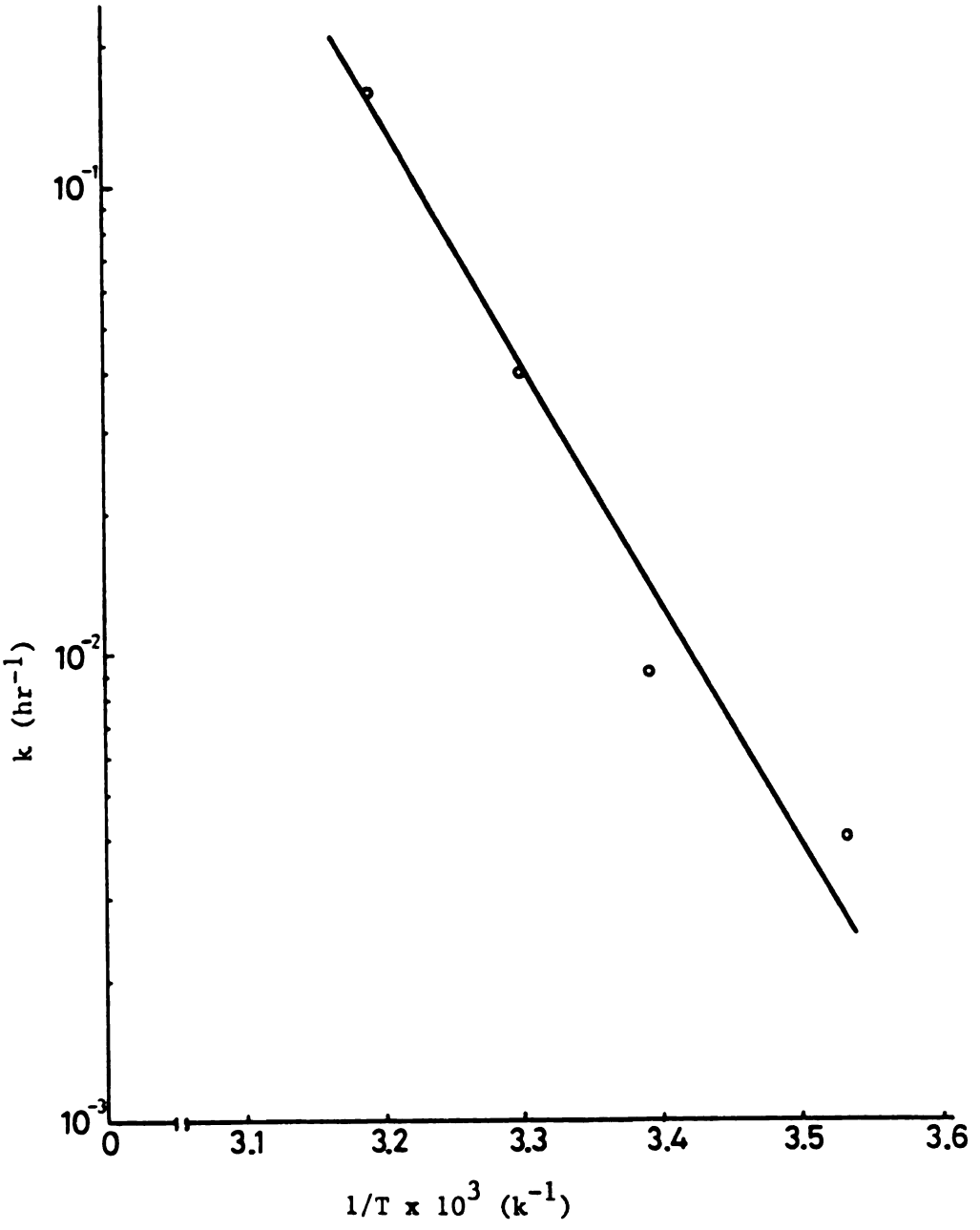

Figure 2 ARRHENIUS PLOT OF LOSS RATE CONSTANT (k) VS TEMPERATURE

Table 6: Rate constants for loss of BHT from the HDPE film (0.32% BHT wt/wt) and The activation energy

Temperature (°C)	Loss rate constant $k \times 10^{-3}$ (1/hr)	Activation energy for k (kcal/mole)
10	4.2	
21.5	9.1	22.4
30	39.0	
40	163.0	

As decribed earlier, the relative concentration of BHT in the HDPE film was determined by three different procedures. In Table 7 to 10 are shown the results of BHT loss as a function of time obtained by UV spectrophotometry at 10°C, 21.5°C, 30°C, and 40°C, respectively. The concentration data obtained by the chromatographic and spectrophotometric methods were compared to determine the agreement between assay methods. As shown in Fig. 3, a linear relationship was obtained between the two methods with a correlation coefficient of 0.997 showing good agreement between these two procedures. In Fig. 4, the relative loss of BHT as a function of time, as determined by HPLC and UV spectrophotometric techniques, is shown at two different representative temperatures. Results were comparable between the methods. The loss of BHT from the film, determined by directly monitoring weight loss on the Cahn electrobalance is shown in Fig. 5 for a third temperature (21.5°C). Comparable results were obtained by the UV spectrophotometric technique. All three methods gave similar results and could be used for determination of BHT in film samples.

Modelling of The BHT Loss Process

The physical loss of a soluble polymer additive involves two distinct processes: (1) the removal of additive from the surface by evaporation or dissolution; and (2) the replacement of additive in the surface layer by diffusion from the bulk polymer.

A mathematical model describing the loss of additive from the polymer therefore requires two parameters: a mass transfer constant (α) characterizing transfer across the polymer surface-air interface, and a

Table 7: Loss of BHT from HDPE (high BHT level) at 10°C (a)

Time (day)	Absorbance (O.D. units)	Relative % of BHT (C_t/C_o x 100)
0	0.183	100
1	0.155	84.2
3	0.114	62.4
5	0.092	50
7	0.083	45
10	0.080	43.7

(a) determined spectrophotometrically at 280 nm

Table 8: Loss of BHT from HDPE (high BHT level) at 21.5°C (a)

Time (day)	Absorbance (O.D. units)	Relative % of BHT (C_t/C_o x 100)
0	0.214	100
1	0.118	55
4	0.074	34
6	0.055	26
7	0.038	18
10	0.020	9.4

(a) determined spectrophotometrically at 280 nm

Table 9: Loss of BHT from HDPE (high BHT level) at 30°C (a)

Time (day)	Absorbance (O.D. units)	Relative % of BHT (C_t/C_o x 100)
0	0.168	100
0.5	0.092	55
1	0.059	35
1.5	0.037	22
3	0.012	7

(a) determined spectrophotometrically at 280 nm

Table 10: Loss of BHT from HDPE (high BHT level) at 40°C (a)

Time (day)	Absorbance (O.D. units)	Relative % of BHT (C_t/C_o x 100)
0	0.178	100
0.5	0.034	19
1	0.006	4
1.5	0.001	0.5

(a) determined spectrophotometrically at 280 nm

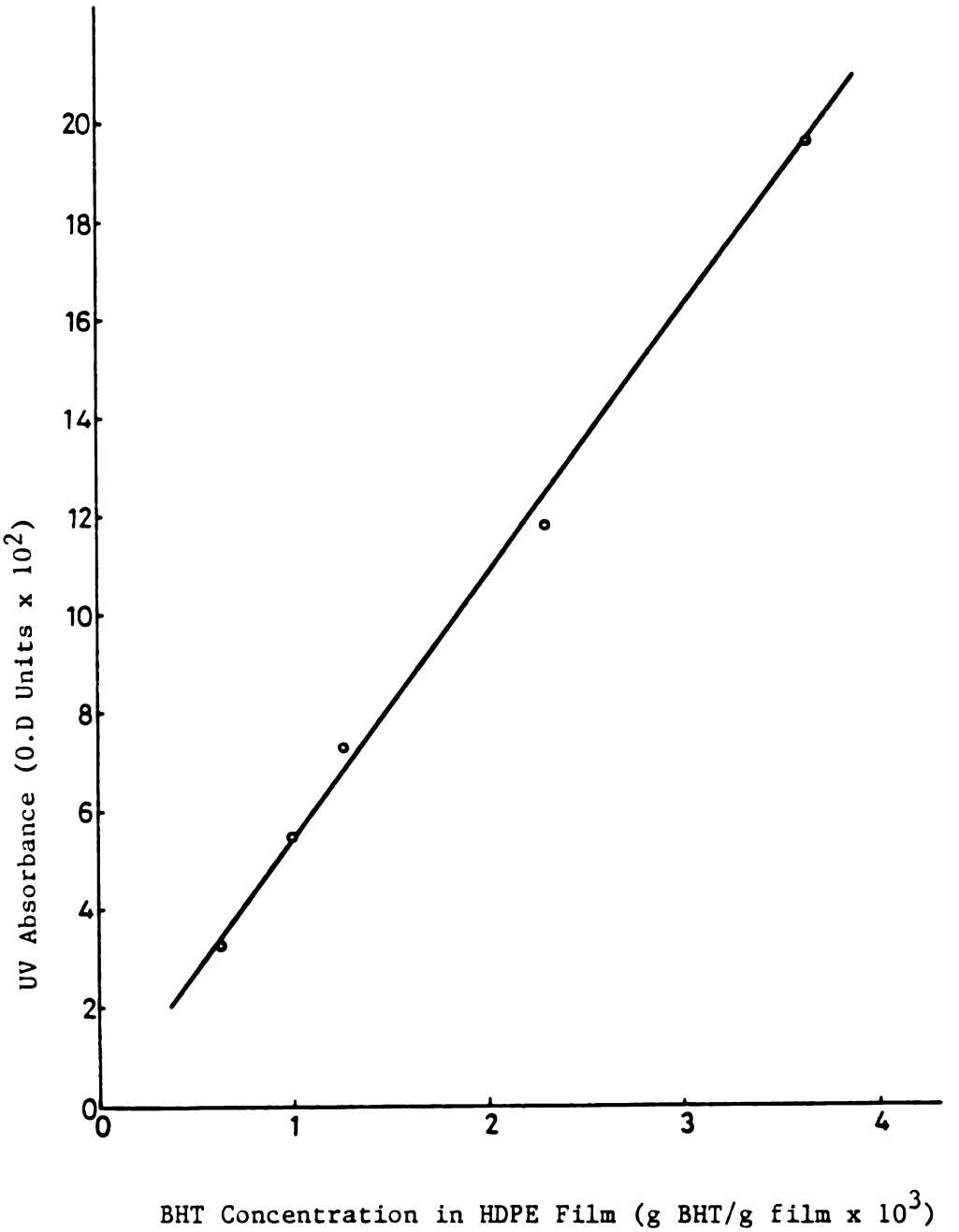

Figure 3 BHT CONCENTRATION ANALYZED BY HPLC VS ABSORBANCY MEASURED SPECTROPHOTOMETERICALLY AT 21.5°C

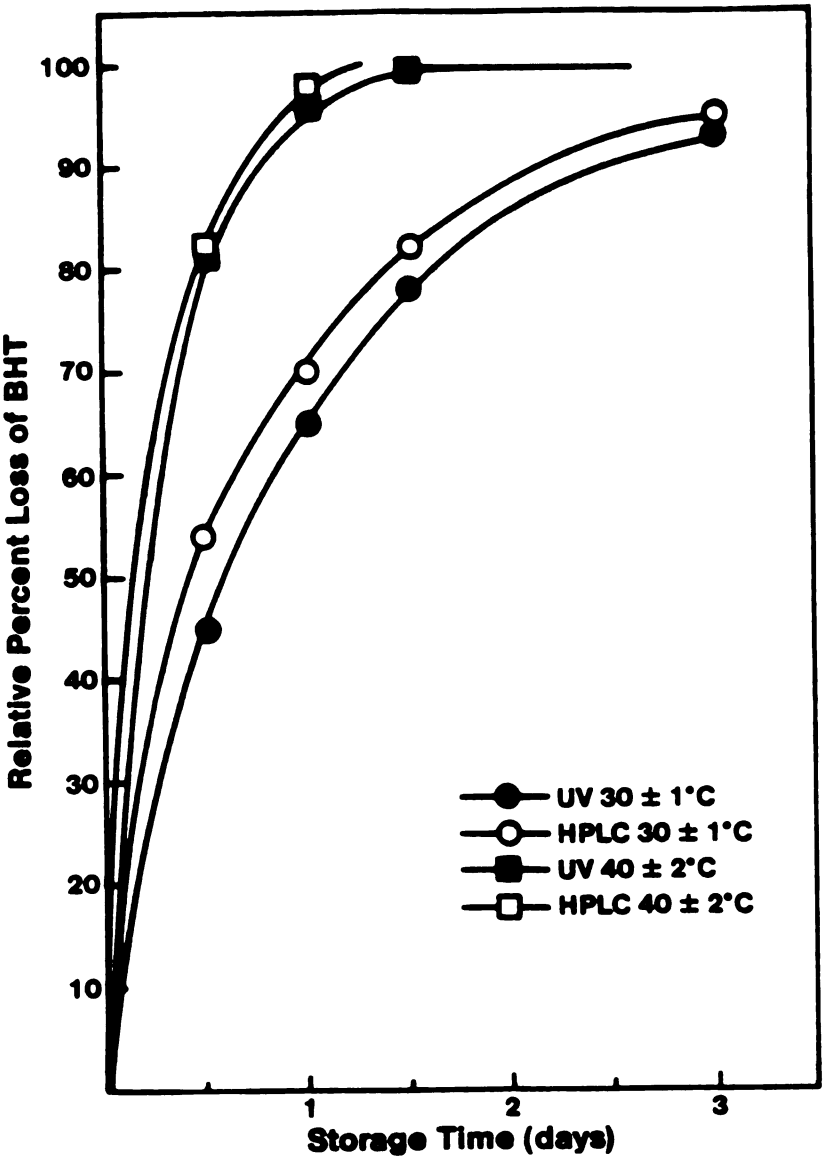

Figure 4 RELATIVE PERCENT LOSS OF BHT AT 30 AND 40°C AS A FUNCTION OF TIME

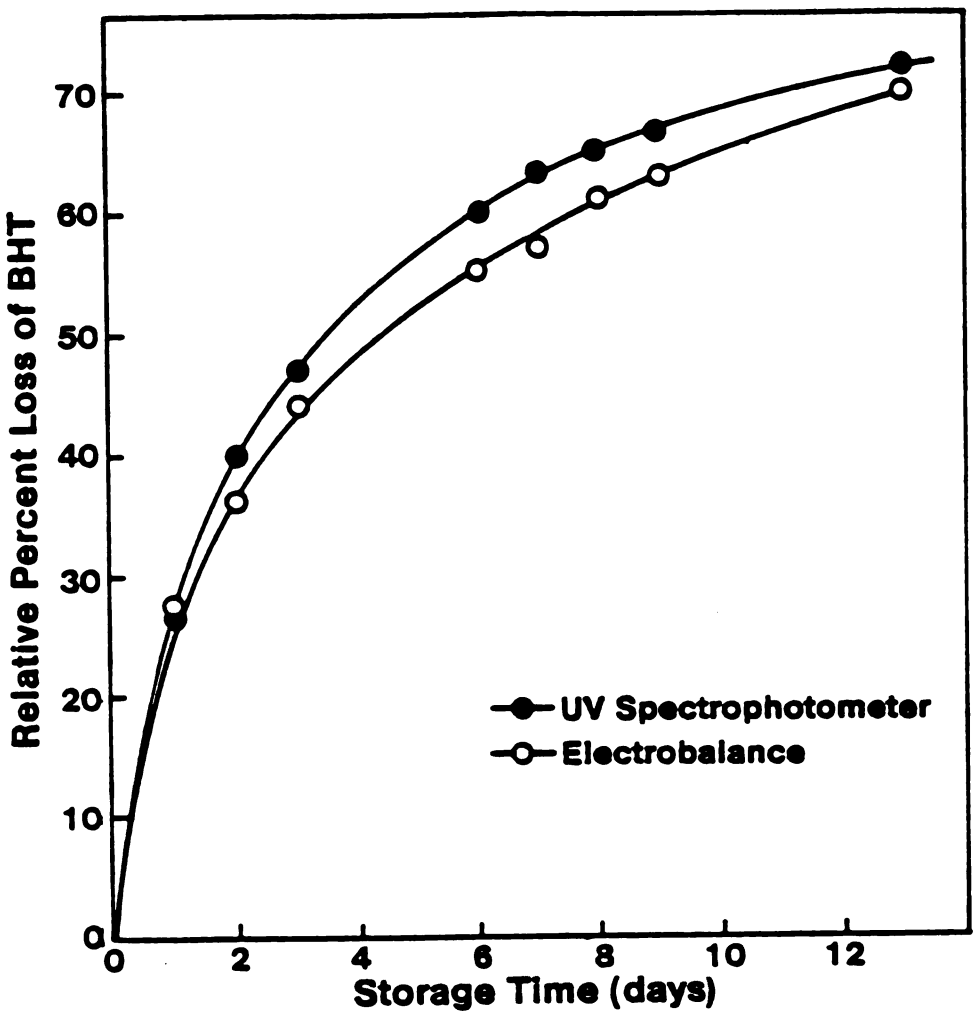

Figure 5 COMPARISON OF UV SPECTROPHOTOMETER AND ELECTROBALANCE IN MEASURING PERCENT LOSS OF BHT AT ROOM TEMPERATURE (21.5°C)

diffusion coefficient (D) characterizing mass transfer within the polymer bulk phase.

Crank (1975) described a mathematical expression for a film from which an additive is lost by surface evaporation with finite boundary conditions. According to this model, the total amount of additive leaving the polymer in time (t) is expressible as a fraction of the coressponding amount lost after infinite time (equation 1).

In application of this equation to the BHT/HDPE system, it was assumed that: (1) the addditive was homogeneously dissolved in the film; (2) the additive is lost by dissolution to the air in contact with the film surface (excluding chemical reactions such as oxidation); and (3) if the additive is lost by surface evaporation at a rate determined by the surface concentration and the parameter α, the lost additive will be replaced at the surface by diffusion from the bulk phase at a diffusion coefficient of D.

If the term for n=1 only is taken in equation 1, this equation assumes, after rearrangement, the following form:

$$1 - \frac{M_t}{M_\infty} = \frac{2L^2 \exp(-\beta^2 T)}{\beta^2(\beta^2 + L^2 + L)} \qquad (4)$$

$$\text{or} \quad (1 - \frac{M_t}{M_\infty})(\frac{\beta^2(\beta^2 + L^2 + L)}{2L^2}) = \exp(-\beta^2 T) \qquad (5)$$

$$\text{or} \quad \ln[(1 - \frac{M_t}{M_\infty})(\frac{\beta^2(\beta^2 + L^2 + L)}{2L^2})] = -\beta^2 \frac{Dt}{l^2} \qquad (6)$$

Equation 6 is of the same form as a first order rate expression

($\ln C_t/C_o = -kt$) that was showm to describe this study's experimental results. Since $(1 - \frac{M_t}{M_\infty}) = \frac{C_t}{C_o}$ and the two equations describe the same phenomenon, the following expression should hold:

$$\frac{\beta^2 D}{l^2} = k \tag{7}$$

and

$$\frac{\beta^2(\beta^2 + L^2 + L)}{2L^2} = 1 \tag{8}$$

β_n values are the positive roots of the equation

$$\beta_n \tan \beta_n = L \tag{9}$$

Equation 8 and 9 are then solved simultaneously for β and L (n = 1). The β value is then used to calculate the value of D from equation 7 and the values of L and D are used to calculate α from equation 10.

$$L = \frac{l\,\alpha}{D} \tag{10}$$

The respective α and D values are summarized in Table 11.

The validity of the mathematical model (equation 1) (describing the loss of BHT from the HDPE film sample) was established by appropriate substitution into equation 1 and comparison of the calculated and experimentally determined percent additive loss values. The results are presented in Fig. 6. As shown, the experimental results agreed well with those calculated by the additive loss expression. Han et al. (1987) also showed good agreement between their experimental and calculated values for loss of BHA from thin HDPE film.

Table 11: Mass Transfer and Diffusion Coefficients of BHT in HDPE Film

Temperature (^{o}C)	Mass Transfer Coefficient $\alpha \times 10^{-9}$(cm/sec)	Diffusion coefficient $D \times 10^{-10}$(cm^2/sec)
10	3.9	2.2
21.5	8.6	4.8
30	36.4	20.0
40	152.6	80.0

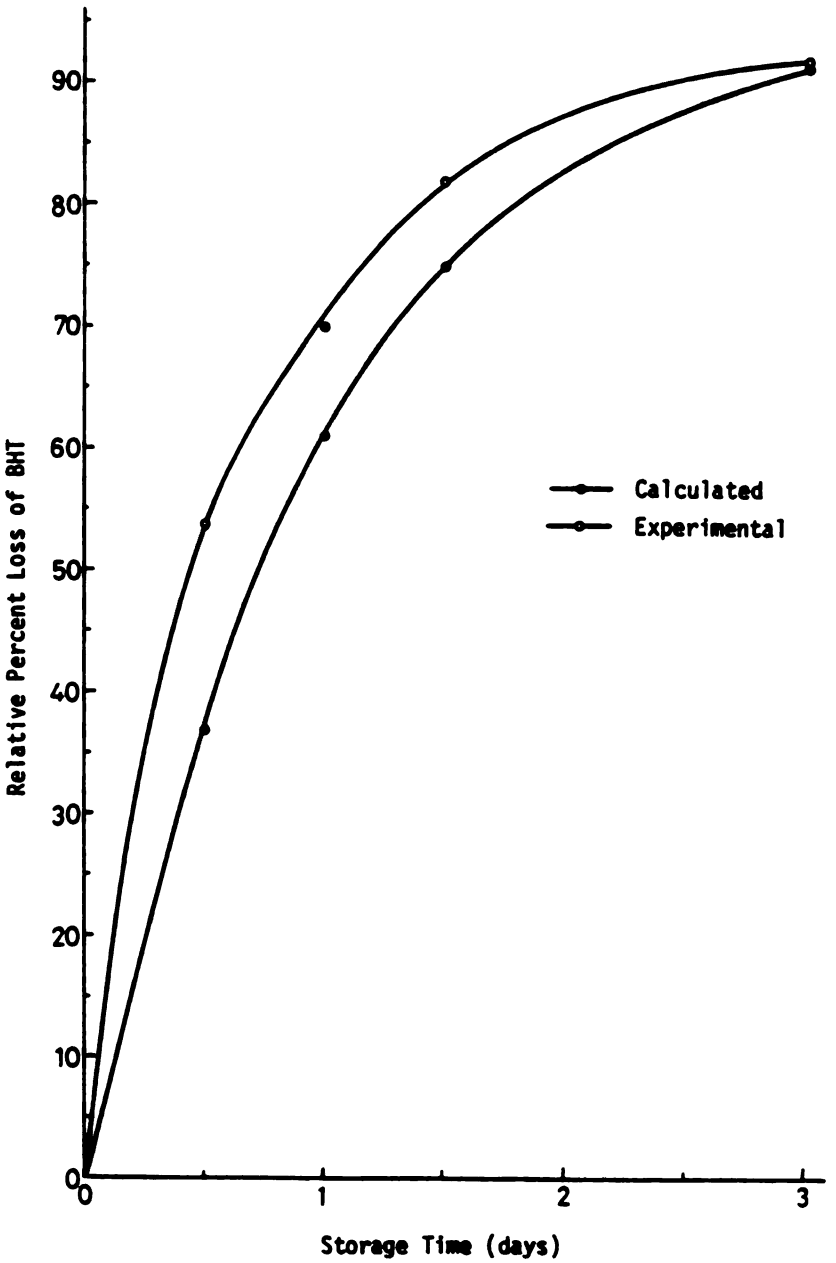

Figure 6 COMPARISON OF EXPERIMENTAL AND CALCULATED LOSS OF BHT DURING STORAGE AT 30°C

No data for diffusion of BHT in HDPE around ambient temperature were found in the literature. Recently Comyn et al. (1986) reported a value of 12 x 10^{-8} cm^2/sec for the diffusion coefficient of 2,6-di-t-butyl-4-methyl phenol (BHT) in HDPE at 100°C. Using an activation energy for BHT diffusion in HDPE of 22 kcal/mole (determined from this study), a value of 236.7 x 10^{-8} cm^2/sec was calculated for diffusion coefficient at 100°C, which is 20 times more than what was obtained by Comyn et al. (1986). This may reflect differences in the polymer chemistry or morphalogy, such as degree of crystallinity of the polymer film tested.

Other investigators (Rudolph, 1979; Arthur D little's, 1981) also measured the diffusion of BHT in HDPE at different temperatures. However, most of their work was related to migration of BHT from HDPE to food and food simulants. Thus the results would be different because the boundary conditions are different. Vom Bruck et al. 1981 measured the interaction of fat containing food with plastic packaging and concluded that there is an interaction between fatty food and packaging material, which may result in a higher migration rate of additive into contacted food.

Product Storage Studies

Because of the unacceptable nature of oxidized fats, it is both necessary and important to protect products against rancidity development during storage. Modern methods of food processing and handling often require the addition of certain chemicals to the product

in order to improve their shelf stability.

Antioxidants can be added to foods such as cereal, bakery products, snack foods, animal feeds, intermediate moisture and dehydrated foods, as well as the packaging material (Labuza, 1971). The function of phenolic antioxidants such as BHA and BHT in HDPE is to degrade sacrificially upon exposure to oxygen, in order to protect the polymer from oxidation via a free radical process. Furthermore, some antioxidant may migrate into the contained products, and protect it from oxidation.

In the present study the effectiveness of BHT impregnated HDPE film in retarding the oxidation of a packaged oatmeal cereal (no antioxidant added) was evaluated by determining the extent of lipid oxidation of the cereal product and by monitoring the level of BHT remaining in the packaging material as a function of storage time.

The extent of oxidation of the cereal product, as determined by TBA analysis, is presented in Fig. 7 for the oat cereal product packaged in the high level BHT-impregnated HDPE film (0.32%, wt/wt) and the low BHT level HDPE film (0.022% wt/wt). As shown, over an 8 week storage period (39°C and 45% RH), the cereal packaged in the high level BHT-impregnated film exhibited a lower level of lipid oxidation, as compared to the product packaged in the low level BHT impregnated film.

The BHT content of the pouch material was determined (after removal of product) as a function of storage time. No detectable amount

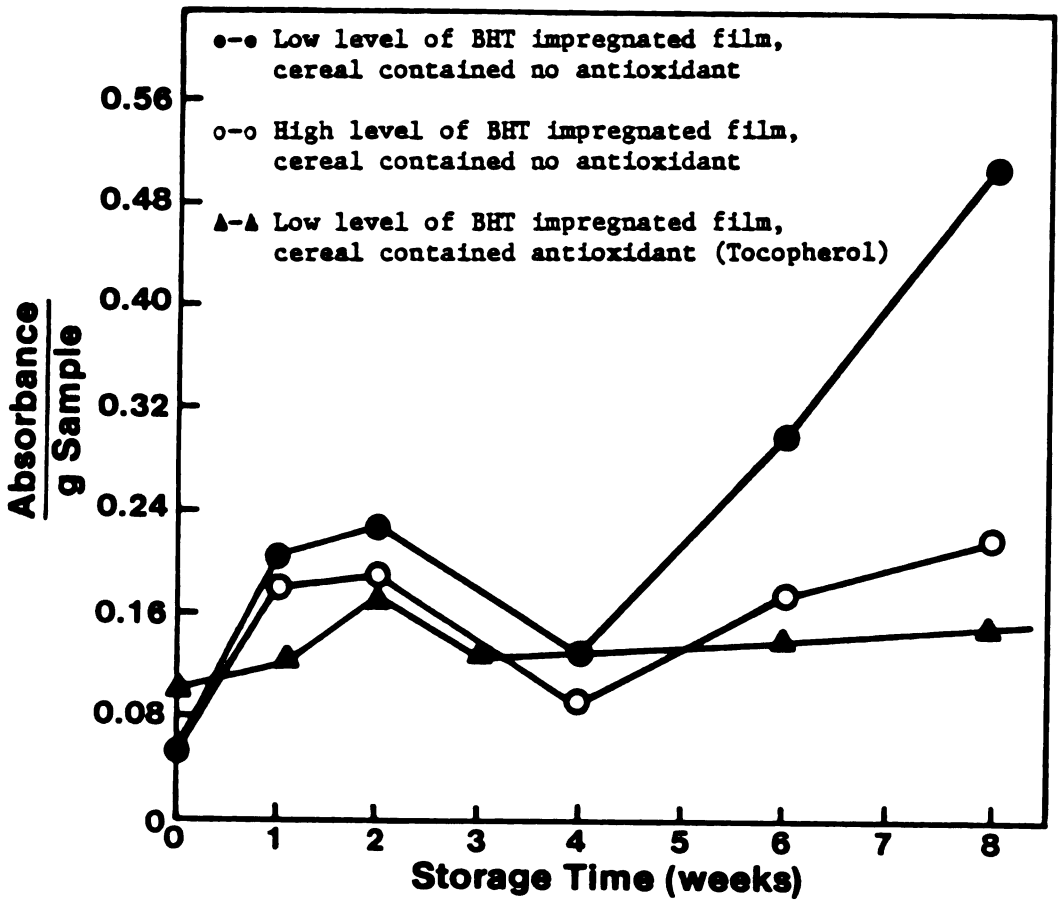

Figure 7 EXTENT OF OXIDATION (TBA VALUES) OF OATMEAL CEREAL PACKAGED IN BHT IMPREGNATED FILM AND STORED AT 39°C

of antioxidant was found after 3 weeks of storage at 39°C and 45% RH.

The extent of lipid oxidation of the oat flaked cereal containing a natural antioxidant (mixed tocopherols) and packaged in the low level BHT, HDPE film was also measured and the results are presented graphically in Fig. 7. As shown, the results obtained for the test cereal product (no antioxidant) packaged in the high level BHT impregnated film compare quite favorably to the control, under similar conditions of storage. No significant differences in TBA absorbancy over time were observed for these treatments during 8 weeks of storage at 39°C. These results provide supportive evidence for the effectiveness of the evaporation/sorption mechanism of antioxidant activity.

Woggon et al. (1968) carried out a series of experiments in which BHT was allowed to migrate from both HDPE and LDPE bottles (0.5% wt/wt) into sunflower oil. After storage for 6 months (20 - 25°C), about 2mg BHT/kg oil migrated from the HDPE container into the oil with no improvement in the shelf life of the product. Seventy mg BHT/kg oil migrated from the LDPE bottle into the oil which did improve the shelf life of the oil. The quantity of BHT migrated was approximately proportional to the initial BHT concentration and to the square root of time.

Many foods and simulants contain ingredients that would be expected to penetrate HDPE and thereby modify the resulting mobility of BHT within the polymer. There is evidence to indicate that penetration

occurs as a Fickian wave with a velocity proportional to $t^{1/2}$ (Figge and Rudolph, 1979).

Till et al. (1982) measured the migration of BHT from HDPE to foods and food simulants. Their results showed, that migration time data were correlated to analytical models that assumed the rate controlling resistance was the diffusion of BHT within the polymer. From their work, the diffusion coefficients increased with temperature and depended on the food/simulant used. They concluded that migration was more rapid in oils and fatty foods than aqueous materials.

Caldwell and Grogg (1955) measured the stability of oatmeal cereal at 38°C using the TBA method. They observed some variability in absorbancy values for different lots of the same cereal. However, they concluded that the modified TBA test would appear to provide a numerical index of oxidative rancidity in oat cereals and other dry baked products, despite the presence of other chromogenic substances.

A schematic of the mechanism by which antioxidant impregnated materials may control lipid oxidation is presented in Fig 8. As shown, the mechanism requires diffusion of antioxidant through the polymer bulk phase, evaporation of the antioxidant from the surface of the packaging material, diffusion of the antioxidant in air and, lastly, sorption of antioxidant onto the product surface. Calculated values of the respective mass transfer parameter are presented in Fig. 8 along with the estimated diffusion coefficient values for oxygen in PE at 21.5°C (Yasuda, 1975) and diffusion coefficient of oxygen in air (Bird

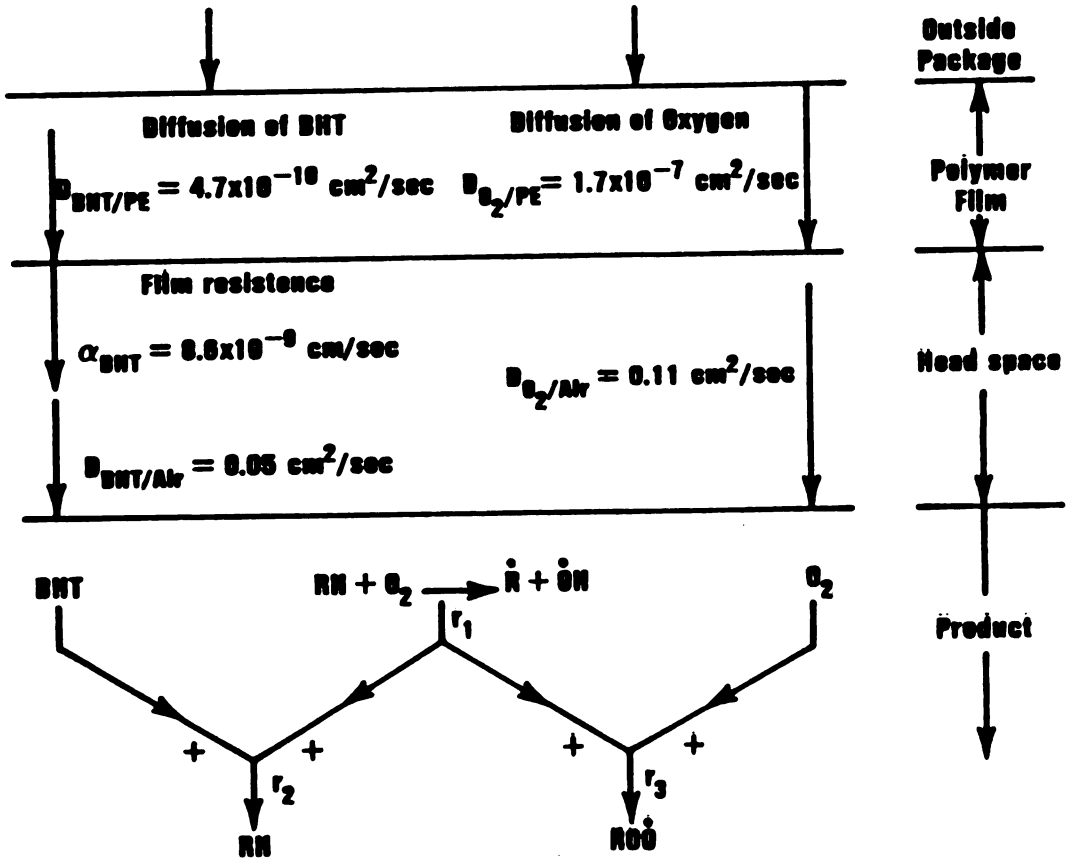

Figure 8 SCHEMATIC OF THE MECHANISM OF ANTIOXIDANT ACTIVITY OF PRESERVATIVE PACKAGING MATERIALS (21.5°C)

et al., 1960). Diffusion coefficient of BHT in air was calculated based on the equation derived by Fuller, Schettler, and Griddings (Reid et al., 1977).

As shown, the diffusion coefficients for oxygen in the polymer and in air are much larger than the diffusion coefficient values for BHT in polymer and air, indicating that the extent of lipid oxidation is controlled by the BHT mass transfer parameter (α) and the diffusion of BHT in the polymer.

To establish the validity of this mechanism of antioxidant activity, storage studies (39°C and 45% RH) were carried out with oat flaked cereal product containing tocopherol and packaged in the high level BHT impregnated HDPE film. The product was analyzed for BHT content (i.e., extent of BHT sorption) and extent of lipid oxidation, as a function of time. The level of BHT remaining in the package material was also monitored. The results are summarized in Table 12.

As shown after one week of storage, 25% of the BHT initially present in the packaging film was transferred or sorbed by the product and the BHT level in the film was reduced by 95%. The BHT concentration in the product remained fairly constant over a 6 week storage period. The product oxidized slightly over this period of time.

Table 12: Sorption of BHT by Cereal Product Packaged in HDPE Pouches

Time (weeks)	g BHT/g cereal × 100	Relative Percent Distribution of BHT		
		in pouches	in cereal	lost to environment
0	0.0000	100	----	----
1	0.0019	5	25	70
3	0.0014	2	18	80
6	0.0015	---	19	81

SUMMARY AND CONCLUSION

The loss of antioxidant (BHT) from HDPE film was measured as a function of time and temperature ($10^{\circ}C$ - $40^{\circ}C$). The loss of BHT from the film appeared to follow a first order or pseudo first order rate expression. The results also showed that the three methods used to determine BHT content in the film were agreeable and could be used to determine BHT content in films.

The mechanism of additive loss from a polymer depends upon the diffusion rate of the additive within the polymer bulk phase and the evaporation rate of the additive from a polymer surface. Both the diffusion coefficient and mass transfer coefficient of BHT from HDPE were determined.

The results of product storage studies demonstrated the effectiveness of BHT impregnated HDPE film to retard lipid oxidation of an oat flaked cereal, as a result of the transfer of antioxidant from package to product via the evaporation/sorption mechanism.

The evaporation of controlled amount of BHT from the film to contained product can provide a mechanism by which BHT can function as an antioxidant without direct incorporation into the food system.

Incorporating antioxidant into packaging material may result in less additive in the food. It is also more economical, because a large amount of antioxidant may not be necessary for some products when combined with other techniques such as inert gas packing.

LIST OF REFERENCES

REFERENCES

Angert, L.G., Zenchenko, A.I. and Kuzminski, A.S. 1961. Volatilization of phenol-2-naphthylamine from rubber. Rubber Chem. Technol 34:807.

Anonymous, 1979. Antioxidants added to packaging materials .... not to food, Food Engineering, April 1979, P.85.

Beringer, H. 1967. The influence of temperature on yield and lipid synthesis in oat grains, Z. Pflanzenernaehr, Bodenkd. 116:45.

Beringer, H. 1971. An approach to the interpretation of the effect of temperature on fatty acid biosynthesis in developing seeds. Z. Pflanzenernaehr. Dueng Bodenkd. 128:115.

Biggs, D.A. and Bryant, I.R. 1953. The TBA test for butterfat oxidation. Can. J. Technol., 31:138.

Billingham N.C. and Calvert, P.D. 1980. The physical chemistry of oxidation and stabilization of polyolefins. Dev. Polymer Stab., 3:139.

Bird, R.B., Stewart, W.E., and Lightfoot, E.N. 1960. Diffusivity and the mechanism of mass transport. In "Transport Phenomena". John Wiley and Sons, Inc. New York.

Bligh, E.G. and Dyer, W.J. 1959. A rapid method of total lipid extraction and purification. Can. J. Biochem. Physiol. 37:911.

Caldwell, E.F. and Grogg, B. 1955. Application of TBA test to cereal and baked products. Food Tech. 4:185.

Calvert, P.D. and Billingham, N.C. 1979. Loss of additives from polymers. A theoretical model. J. Applied Polym. Sci. 24:357.

Carslaw, H.S and Jaeger,J.C. 1959. Conduction of Heat in Solids. Clarendon Press, Oxford Univ. Press, London, England.

Code of Ferderal Regulations 1987. Title 21, part 172 section 115.

Comyn, J. 1986. Plastics and rubber conference on 'Diffusion in polymers',8-9 Jan. London.

Cort, W.M. 1974. Antioxidant activity of tocopherols, ascorbyl

palmitate and ascorbic acid and their mode of action. J. Am. oil Chem. Soc. 51:321.

Crank, J. 1975. The mathematics of diffusion. Second addition, Clarendon Press, Oxford University Press. Ely house, London, England.

Dahle, L.K., Hill, E.G. and Holman, R.T. 1962. The TBA reaction and the autoxidations of polyunsaturated fatty acid methyl esters. Arch. Biochem. and Biophys. 98:253.

Daun, H., Gilbert, S.G. and Giacin, J.R. 1974. Isolation and identification of oxidation product of 2,6-di-(tert-Butyl)4-metoxy Phenol from polyethylene film. J.Am. Oil Chem. Soc. 51:404.

De La Roche, I.A.,Burrows, V.D. and Mckenzie, R.I.H. 1977. Variation in lipid composition among strains of oats. Crop. Sci. 17:145.

Doeden, W.G., Bowers, R.H., and Ingala, A.C. 1979. Determination of BHA, BHT and TBHQ in edible fats and oils J. Am. Oil Chem. Soc. 56:12.

Downes, T.W. and Gilbert, S.G. 1975. The effect of surface treatments on the migration of organotin stabilizer from PVC films to contacting liquid media. Deutsche Lebensmittel-Tundxchal 12:422.

Dugan, L.R. 1976. Lipids Ch.4. In "Principles of Food Science. Part I." Food Chemistry, O.R. Fennema (Ed.), pg. 139. Marcel Dekker, Inc., New York.

Dunkley, W.L. and Jennings, W.G. 1951. A procedure for application of the TBA test to milk. J. Dairy Sci., 34:1064.

Durmis, J., Karvas, M., Daucik, P. and Holcik, J., 1975. Loss of light stabilizers from polypropylene. Eur. Polym. J. 11:219.

Endean, M.E. 1976. The detection and determination of food antioxidants - A literature review, The British Food Manufacturing Industries Research Association, Scientific and Technical Survey No. 91, Leatherhead, Survey, UK.

Everson, C.W., Miller, C.J., and Quackenbush, F.W. 1957. Comparison of antioxidants for fats on an equivalent molar basis. J. Am. Oil Chem. Soc. 34:81.

Figge, K., and Rudolph, 1979. Diffusion in system Kunststoffver packung/Fullgut, Ange. Makromolek. Chem. 78, 157.

Figge, K., Koch, J. and Freytag, W. 1978a. The suitability of simulants for foodstuffs, cosmetics, and pharmaceutical products in

migration studies, Ibid. 16:135

Franzke, C. Uhde W.J., and Woggon, H. 1970. Uber die migration von antioxydanzien und stabili satoren aus plastver packungen in speiseol, plaste U. Kautscuck 17(5):327.

Frey, K.J. and Hammond, e.g. 1975. Genetics, characteristics and utilization of oil in caryopses of oat species. J. Am. Oil Chem. Soc. 52:358.

Hammond, K.J. 1978. Determination of BHA, BHT and individual gallate esters in fats and oils by HPLC. J. Assoc. Public Anal. 16:17

Han, J.K., Miltz, Y., Harte, B.R. and Gray J.I. 1987. Loss of BHA from HDPE film. Polymer Eng. and Sci. 27:934.

Hernandez, R.J., Giacin,J.R., Baner, A.L. 1986. The evaluation of the aroma barrier properties of polymer films. Journal of Plastic Film and Sheeting. 2(3):187

Howard III, I.M., 1971. Gel permeation chromatography and polymer additive systems. J. Chromatogr., 55:15.

Hutchinson, J.B. and Martin, H.F. 1955. The chemical compositon of oats. I. The oil and free fatty acid content of oats and groats. J. Agric. Sci. 45:411.

Hutchinson, J.B., Martin, H.F. and Moran, T. 1951. Location and destruction of lipase in oats. Nature 167:758.

Kalbasi – Ashtari, A., and Hammond, E.G., 1977. Oat oil: Refining and stability. J. Am. Oil Chem. Soc. 54:305.

Kohn, H.J. and Liversedge, M. 1944. On a new aerobic metabolite whose production by brain is inhibited by apomorphine emetine, erogotamine and menadione. J. Pharmocol. 82:292.

Labuza, T.P. 1971. Kinetics of lipid oxidation. CRC Crit. Rev. Food Tech. 2:355.

Lea, C.H. 1962. The oxidation deterioration of food lipids. Symposium on Foods, Lipids and their Oxidation. H.W. Schultz, E.A. Day, R.O. Sinhuber, eds. The Avi Pub. Co., Inc., Westport, Conn., P.3.

Lichtenthaler, R.G. and ranfelt, F. 1978. Determination of antioxidants and their transformation products in polyethylene by high performance liquid chromatography. J. Chromatogr. 149:553.

Lindberg, P.S., Beingfors, N.L. and Tanhaunpa, E. 1964. The fatty acid composition of swedish varieties of wheat, barley, oats and rye.

Act. Agric. Scand. 14:1-11.

Little, A.D. Inc. 1981. Migration of BHT antioxidant from HDPE. Report of Food and Drug Administration, Contract No. 223-77-2360.

Lundberg, W.O., 1962. Autoxidation and antioxidants, Vol. 1, Interscience, N.Y.

Majors, R.E. 1970. High speed liquid chromatography of antioxidants and plasticizers using solid core support. J. Chromatogr. Sci. 8:339

Martin, H.F. and Peers, F.G. 1953. Oat lipase, Biochemistry 55:523.

Nawar, w.w. 1985. Lipids. Ch. 4. In "Food Chemistry", O.R. Fennema (ed.), pg. 139,. Marcel Dekker, Inc., New York.

Plant, M.A. and Scott, G. 1971. Mechanisms of antioxidant action. The evaluation of the effect of stabilizer volatility in polypropylene using Torsional Braid analysis. Eur. Polym. J. 7:1173

Pokorny, J. 1971. Stabilization of fats by phenolic antioxidants. Can. Inst. Food Tech. J. 4:68.

Ram, A., Meir, T. and Miltz, J. 1980. Durability of polyethylene films. Intern.J. Polym. Marter. 8:323.

Reid, R.C., Prausnitz, J.M. and Sherwood, T.K. 1977. Diffusion coefficients Ch. 11. In "The Properties of Gases and Liquids". McGraw-Hill Book Co. New York.

Reinton, R. and Rogstad, A. 1981. Antioxidant acitvity of tocopherols and ascorbic acid. J. Food Sci. 46:970.

Sahasrabudhe, M.R. 1979. Lipid composition of oats (Avena sativa L) J. Am. Oil Chem. Soc. 56:80.

Smith, J.D.B., Jerson, D.D. and Meier, J.F. 1974. Studies on Akroflex CD antioxidant loss from neoprene rubber. I. The determination of antioxidant content and the loss mechanism during aging. J. Appl. Polymer Sci. 18:3543.

Sinhuber, R.O. and Yu, T.C. 1958. 2-thiobarbituric acid in fish II. Quantitative.

Sinhuber, R.O., Yu, T.C. and Yu, Te Chang. 1958. Characterization of the red pigment formed in the 2-TBA determination of oxidative rancidity. Food Res. 23:626.

Swern, D. 1962. Autoxidation of antioxidants Vol. 1. Primary products of olefinic autoxidations. Lundberg, W.O. (ed.), Intersci., New

York: Wiley and Sons, Inc., P.1.

Till, D.E., Ehntnolt, D.J., Reid, R.C., Schwartz, P.S., Sidman, K.R., Schwope, A.D. and Whelan, R.H. 1982. Migration of BHT antioxidant from HDPE to foods and foood simulants. Ind. Eng. Chem. Prod. Res. Dev. 21:106.

Vom Bruck, C.G., Figge, K. and Rudolph, F. 1981. Interaction of fat containing food with plastic packaging. J. Am. Oil Chem. Soc. 58-811.

Widicus, W.A. and Kirk, J.R. 1981. Storage stability of tocopherol in a dehydrated model food system. J. Food Sci. 46:813.

Wims, A.M. and Swarin, S.I. 1975. Determination of antioxidants in polypropylene by liquid chromatography. J.Appl. Polymer. Sci. 19:1243.

Wheeler, D.A. 1968. Summaries for Card Indexes. Talanta 15:1315.

Woggon, H., Uhde, W.J. and Zydek, G. 1968. Paper on the examination of plastic packaging materials; on the migration of BHT into food oil. Lebensm. Unters. Forsch. 138(3):169.

Wyatt, D.M. 1981. Simultaneous analysis of BHA, TBHQ, BHT and Propyl gallate by gas chromatography as extracted from refined vegetable oil. J. Amer. Oil Chem. Soc. 58:917.

Wyatt, D.M. and Sherwin, E.R. 1979. Analysis of BHA in polyethylene by direct sampling gas chromatography. Food Tech. 33(9):46.

Yasuda, H. 1975. Permeability coefficient Ch. III. In "Polymer Handbook". Brandrup, J., Innergut, E.H. editors Wiley and Sons, Inc. New York.