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AROMA ANALYSIS OF A FRUIT FLAVORED CEREAL PRODUCT:
INFLUENCE OF PACKAGE LINER SYSTEMS ON HEADSPACE D-LIMONENE
CONCENTRATION AS MEASURED BY GAS CHROMATOGRAPHY
AND CORRESPONDING SENSORY EVALUATION

presented by

Sherry Hsien-Wen Hsia

has been accepted towards fulfillment
of the requirements for

M.S. degree in Packaging

Jack R. Giacin

Major professor
Jack R. Giacin

Date May 27, 1988

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BY

Sherry Hsien-Wen Hsia

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

School of Packaging

1989

ABSTRACT

AROMA ANALYSIS OF A FRUIT FLAVORED CEREAL PRODUCT: INFLUENCE OF PACKAGE LINER SYSTEMS ON HEADSPACE D-LIMONENE CONCENTRATION AS MEASURED BY GAS CHROMATOGRAPHY AND CORRESPONDING SENSORY EVALUATION

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Two analytical procedures, namely package headspace analysis for quantification of flavor volatiles and the analysis for sorbed flavor constituents by the cereal liner structures, as well as two sensory evaluation methods (i.e. triangle test and consumer preference test) were applied to assess the relative performance of two commercial package liner structures on the flavor quality change of a fruit flavored cereal product, where quality is dependent upon the retention of aroma constituents. Storage stability studies were carried out over a period of twelve months. For these studies, d-limonene was selected as the probe compound due to its dominant role in the cereal product's aroma profile and its characteristic flavor.

The results of the objective and subjective tests performed were evaluated to establish a relationship between consumer preference to the product during storage and the d-limonene headspace concentration for the respective package liner structures.

Dedicated to my parents,
for their love, support, and strength
with sincere gratitude.

ACKNOWLEDGEMENTS

I would like to thank my major advisor, Dr. Jack Giacin, for his guidance, encouragement, and support through my academic endeavors.

Special thanks is extended to Dr. Mary Ann Filadelfi-Keszi for her guidance in the sensory analysis and time spent in evaluating my progress.

Appreciation is also expressed to Dr. Bruce Harte and Dr. Dana Ott for their serving on the guidance committee.

I would like to acknowledge the efforts of Dr. Heidi Hoojjat, members in the lab, and panels participated in the sensory evaluation, for their patience, support and technological advice through this research study.

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INTRODUCTION

For many years researchers have been studying consumer behavior to foods. This information is not only of value theoretically, but it gives a better understanding of those factors which influence the acceptance of new food products or product/package interrelationships. In the past, consumer reactions were observed by the fluctuation of monthly sales figures or by the sudden appearance of numerous letters from consumers critical of the product (Horton, 1987). Researchers agree that a much more productive method would be to predict consumer preferences. Product development scientists believe that by precise and diverse instrumental measurements, consumer attitudes of food quality can be accurately predicted, and consistent control of food properties maintained (Rutenbeck, 1985). Unfortunately, the buying public is not at all reticent about making its sentiments known regarding its likes and dislikes. While instrumental analyses are effective in assessing many food properties, they cannot mimic human perception of food quality precisely. Thus, sensory evaluation techniques have gained more and more attention through the years. A new approach for better understanding of consumer attitudes towards foods is the correlation of human sensory responses with the traditional chemical and physical measurements.

Although information on the importance of various quality attributes for food purchase and consumption is still fragmentary, the relative importance of sensory attributes such as texture, flavor, and appearance have been accentuated (Peryam, 1963; Szczesniak and Kleyn, 1963; Schutz and Wahl, 1981). Moskowitz and Chandler (1978) investigated consumer "trade off" propensities for flavor, nutritional quality, and cost, and found that flavor usually prevailed over the other sensory attributes. Schutz et al. (1986) studied the relative importance of nutrition, brand, cost, and sensory attributes to food purchase and consumption. It was found that flavor was consistently the most important attribute in consumer response.

Loss of flavor from foodstuffs during storage has become a major stumbling block to higher consumer acceptance. Flavor scalping, a phenomenon resulting in the loss of flavor compounds from products due to their absorption or adsorption by the packaging material, is a potential concern in those foods whose quality is associated with the retention of volatile aroma constituents. It can shorten product shelf life dramatically. Mohney (1986) indicated that consumer preference was based, in part, on the intensity of the aroma moieties (i.e. d-limonene) found within the headspace of a fruit-flavored cereal package liner. The use of appropriate packaging can maintain a desirable intensity level of volatile aroma constituents in foodstuffs. The retention of a foodstuff's aroma will, in

part, depend upon: (i) the vapor pressure of the individual components of the total aroma; (ii) the interaction of these volatile organic moieties with other food components; and (iii) the mass transfer characteristics of the package. (Mohney, 1986).

The latter point, which includes the permeability and solubility properties of the aroma moieties/package system, should be of major concern in the selection and use of plastic packaging materials for foods. The transport and sorption of organic vapors through polymeric packaging materials has been, and continues to be, the subject of numerous investigations (Gilbert et al., 1983; Murray and Dorschner, 1983; Zobel, 1982, 1984, 1985; Hernandez, 1984; Baner et al., 1985; DeLassus, 1985; Murray, 1985; Hernandez et al., 1986; and Mohney, 1986).

This study represents an extension of the studies reported by Mohney (1986) and considers the effect of two cereal package liner structures, namely a high density polyethylene/ethylene vinyl acetate (HDPE/EVA) coextrusion and a high density polyethylene/ethylene vinyl alcohol/ Suryln (HDPE/EVOH/Surlyn) coextrusion, on the quality of a fruit-flavored cereal product, during twelve months of storage. D-limonene was selected as the probe compound due to its dominant role in the cereal product's aroma profile and its characteristic flavor.

The major objectives of this study are summarized below:

(1) Evaluation of the relative performance of two commercial cereal package liner structures with respect to flavor retention (i.e. d-limonene headspace concentration) and flavor sorption (i.e. the amount of d-limonene being absorbed) during twelve months of storage.

(2) Sensory evaluation of cereal product packaged in the two commercial cereal package liners structures, with respect to flavor quality change, during twelve months of storage.

(3) Determination of consumer acceptance/preference for the respective cereal package liner structures with respect to product quality.

(4) Evaluation of quantitative relationships between the respective package liner systems with regard to the headspace concentration of d-limonene and the sensory responses to product quality, as a function of storage time.

LITERATURE REVIEW

BARRIER AND SHELF LIFE

There has been an increase in recent years in the use of plastics as food packaging materials. This has also prompted researchers into investigating the potential interactions that might arise between foods and packages and the effects that these might have on food quality (Karel and Heidelburgh, 1975; Gilbert and Mannheim, 1982).

In most cases, the environmentally omnipresent gaseous reactants, water vapor and oxygen, can seriously effect product stability (i.e. quality) under the usual food storage and distribution conditions. The rate of transport of such reactants across the partial barrier of the package wall (intact or through breaks) can become the limiting factor in shelf life. The corresponding transport rate of low molecular weight compounds affecting flavor and aroma may also be involved in quality changes during storage (Gilbert, 1985).

Factors invloved in food/package compatibility which influence the acceptability of foods include migration from the packaging material to the product, absorption and adsorption of flavor compounds inherent to product by the packaging material (commonly referred to as scalping), and

wicking (Harte and Gray, 1987). Scalping of flavor compounds is a concern for many products currently being packaged. For example, citrus flavored products contain volatile, highly aromatic compounds. When these compounds are selectively sorbed by the packaging material, they no longer function as flavor compounds and thus, the perceived quality of the product is diminished.

These problems can be eliminated or reduced by employing the appropriate barrier materials. Thus, selection of the appropriate barrier to maintain the expected shelf-life of foods is critical for successful marketing. Shelf-life of foods is usually defined as the length of time that a container or the material in a container will remain in a saleable or acceptable condition, under specified conditions of storage.

Product shelf-life is controlled by four factors: (1) product characteristics; (2) the environment to which the product is exposed during distribution; (3) the properties of the package; and (4) the interaction of product and package (Harte and Gray, 1987).

FLAVOR CHARACTERISTICS

Flavor represents a vast array of chemical classes. Often, a flavor is composed of a number of related compounds in precise proportions. Flavor of foods is the subtle

balance of various volatile and nonvolatile flavor compounds (Gianturco and Biggers, 1974). It is not uncommon to encounter flavors of 200 constituents or more (Heath and Reineccios, 1986). Maarse (1984) reported that by the mid-1980's, 4,300 different flavor compounds had been identified in foods. Rijkens and Boelens (1975) have estimated that probably 5,000-10,000 flavor compounds actually exist.

While flavors are most often considered as the summation of a large number of compounds, there are studies which show that the quantitative relationship of the individual flavor components present is critical to full fruit flavor (Ahmed et al., 1978b; Shaw, 1979; Schreier, 1981; Moshonas and Shaw, 1986). Hence, 2-isobutylthiazole is critical to tomato flavor; methyl- and ethyl- cinnamates to strawberry flavor; methyl anthranilate to grape flavor; and benzaldehyde to cherry flavor (Whitaker and Evans, 1987).

Cold-pressed peel oil, essence oil, aqueous phase essence (industrially termed "natural citrus aroma"), and folded cold-pressed oil are usually added to foodstuffs to enhance citrus flavor. Over 90% of the essential oil of orange is composed of the monoterpene hydrocarbon, d-limonene (Figure 1). The chemical characteristics of d-limonene are listed in Table 1.

D-limonene is an unsaturated hydrocarbon. This makes it highly susceptible to oxidative and photooxidative degradation. The hydroperoxides from oxidation of d-limonene can decompose very rapidly to yield stable products

Table 1. Chemical Characteristics of D-Limonene.[a]

Molecular Structure	$C_{10}H_{16}$
Molecular Weight	136.24
Density	0.842 gm/mL
Boiling Point	178°C
Melting Point	-74°C
Molar Density	6.17×10^{-3} gmole/mL at 25°C
Soluble in	Ethyl Alcohol, Diethyl Ether
Vapor Mole Fraction in Equilibrium with Pure Liquid	1.9×10^{-3} at 25°C

(a) Weast et al., (1985).

including, limonene-1,2-epoxide and carvone (Farmer and Alvapillai, 1942; Anandaraman, 1986). Such deteriorative reactions are responsible for the off-flavors in orange juice, which are often described as "turpentine-like" or "painty" (Anandaraman, 1986).

Other terpenes in citrus oils include δ,β pinene and β-myrcene. Although these compounds have little flavor impact, they can provide a solvent for the more potent flavorings (Marshall, 1985). The contribution of volatiles to orange juice flavor is shown in Table 2 (Durr, 1981).

FLAVOR ANALYSIS

Advances in chromatographic separation and instrumental identification techniques (Shaw, 1977a, 1977b, 1979) have helped to expand our knowledge of citrus flavors during the past 25 years. Much information has been obtained on specific flavor-contributing components of the major citrus cultivars - orange, grapefruit, tangerine, lemon, and lime. Extensive research conducted by Kirchner and Miller, 1953; Wolford et al., 1961, 1964; Kesterson et al., 1971; and Shaw, 1977a, 1977b has tried to identify, quantitate, and organoleptically evaluate these fruit volatiles. In addition, studies have also attempted to assess the synergistic properties of various flavor blends (Ahmed et al., 1978a; Shaw and Wilson, 1980).

Table 2. Contribution of volatiles to orange juice flavor. [a]

Contribution to Typical Flavor		Contribution to Off-Flavor	
Important	Desirable	Precursors	Detrimental
ethylbutyrate	linalool	linalool	ϭ-terpineol
neral	limonene	limonene	carvone
geranial	ϭ-pinene	valencene	t-carveol
	valencene		nootkatone
	acetaldehyde		hexanal
	octanal		t-2-hexenal
	nonanal		hexanol
	ϭ-sinensal		4-vinyl-guaiacol
	β-sinensal		2,5-dimethyl-4-hydroxy-3-(2H)
			furanone

[a] Durr, 1981.

Moshonas and Shaw (1984) reported that the use of fused silica capillary column gas chromatography (GC) permitted accurate quantification of volatile components in flavor fractions, such as aqueous essence prepared from fresh orange juice. This method led to studies of various indices, component mixtures, and formulations in model systems, as aides for determining profiles of flavor quality in specific types of citrus flavored products (Johnson and Vora, 1983).

Nagy and Klim (1986) suggested that the use of infrared spectroscopy, gas chromatography, and mass spectrometry could greatly reduce the amount of time necessary to identify and to quantify a flavor compound. They added that the mose versatile instrument in flavor analysis is the gas chromatography-mass spectrometer (GC-MS). Resolution of a complex flavor mixture (i.e. fruit-flavored cereal) can be attained by gas chromatography, utilizing highly efficient capillary columns. After separation by GC, the eluted components are identified by the mass spectrometer, through their fragmentation patterns.

Although identification techniques have improved and, many components, both volatile and nonvolatile, have been identified, their subtle influence on quality and flavor characteristics, and their relationships among various citrus components are not fully known. The contribution of essential oils to specific types of citrus flavor, their stability and utilization are also not fully known. Thus, more research on the relationship between flavor chemistry

and sensory evaluation of the individual flavor fractions in foods will be required in the future.

THE USE OF SENSORY EVALUATION

In sensory evaluation, human observers or panelists act as the analytical tool. Depending on the type of investigation, the panelists can be grouped into three types, namely: (i) highly trained experts; (ii) laboratory panels; and (iii) large consumer panels. Highly trained experts evaluate quality, and large consumer panels are used to determine consumer reaction to a product. Sensory tests performed by fairly large panels are valuable in predicting consumer reactions. Evaluations by experts and trained laboratory panels can be useful for control purposes, for guiding product development and improvement, and for evaluating quality. The trained panel can be particularly useful in the assessment of product changes, for which there is no adequate instrumentation (Larmond, 1977). Amerine et al. (1965) and Larmond (1977) have provided general guidelines for the selection and training of panelists.

The use of sensory evaluation to monitor flavor change or deterioration during a shelf-life study requires careful planning and a thorough understanding of the sensory evaluation; physical and chemical composition of the product; formulation; processing and packaging treatments;

storage conditions; projected storage life; anticipated sensory changes; experimental design; and sensory evaluation procedures (Dethmers, 1979).

Both analytical and affective sensory methods may be used to determine the shelf-life of a food/beverage product (Prell, 1976). The method selected will be determined by the purpose of the test. This may include the extension of shelf-life by a change in processing, formulation, or packaging; establishment of the shelf-life of a new product; or determination of the shelf-life of an existing product.

Preference/acceptance tests are affective tests based on a measure of preference or acceptance. In these tests, samples are considered unacceptable when a sample obtains an average panel score of 3.5 based on a seven point scale (Gacula and Kubala, 1975), or when various deteriorative changes in a freshly packed product accumulate, such that the market quality would be judged lower than excellent or that a taste panel would consider the quality to be at the limit of acceptability.

Discriminatory tests are used to determine whether a difference exists between two samples. This type of testing requires trained or experienced panelists (Larmond, 1977). It is considered limited at the point when a difference between test and control samples can be detected by trained panelists (Van Arsdel, 1969; Jul, 1969) or when the percent of correct judgments in a triangle test comparing stored and control samples ranges between 70-80 percent (Guadagni,

1957). The use of this procedure is limited to experiments where a control sample can be maintained with a negligible change over time and to studies where the number of treatments is small (Gacula and Kubala, 1975).

Descriptive tests require trained panelists and are used to determine the nature and intensity of the difference. If a comparison of results from Profile Descriptive Analysis, before and after storage, indicates changes in character or intensity of the flavor, the samples are generally deemed unacceptable (Dethmer, 1979).

ENVIRONMENTAL EFFECTS ON STABILITY OF FLAVORS

Few researchers have been working in this area. Durr et al. (1981) investigated the influence of the behavior of d-limonene and other aroma components on the sensory quality of orange juice during filling and storage. Significant losses of d-limonene, neral, geranial, ortanal, and decanal from orange juice in carton packages were found. However, these investigators concluded that the main quality parameter for shelf-life was the storage temperature.

Hatzidimitriu et al. (1987) reported that some multilayer packaging films lost their barrier properties with respect to the permeation of organic vapors at higher relative humidities.

Wartenberg (1982) compared the quality of orange juice when packaged in aseptic packages and glass bottles (with and without headspace) during 6 months of storage. For the first 5 months of storage, juice in glass bottles and carton packages not having a headspace showed little difference in the decomposition of ascorbic acid. The loss of ascorbic acid was higher in the carton packages with headspace. During the first 5 months of storage, sensory changes were greater in the glass bottles than in either of the carton packages. There was no difference bewteen the carton package with headspace and that without headspace.

Granzer (1982) also reported on the quality of orange juice in two carton packages designed to have a high barrier against oxygen ingression. The material composition of the packages was the same as used in Wartenberg's (1982) study. Deterioration of color and loss of ascorbic acid occured during the first year of storage. These changes were said to be due to the influence of oxygen.

PRODUCT/PACKAGE INTERACTION

Most of the potent flavorings in citrus flavored products are highly lipophilic and can potentially interact with the hydrophobic polymers used in the packages.

Much of the research in this area has focused primarily on the permeability of plastics to gases and water vapor

(Lasoski, 1960; Karel et al., 1963; Masi and Paul, 1982). Standard methods are readily available in the literature for measuring the permeability of plastics (ASTM D 1434-82; ASTM E 96-80). The gas and moisture protection requirements of various foods are also well documented (Quast and Karel, 1972; Labuza, 1981). Another interaction that has received considerable attention has been the migration of package components into food (Crompton, 1979; Kashotock et al., 1980; Crosby, 1981).

The loss of flavor components due to sorption by plastics is also important and must be considered. Salame and Temple (1974) reported that a 1% loss of an aroma component to packaging results in a quality change that is detectable by human olfactory senses. The emphasis in aroma sorption has so far been on the sorption of citrus aroma components by plastics (Durr et al., 1981; Mannheim et al., 1987; Shimoda et al., 1984).

The absorption of d-limonene and specific flavorings into the polyethylene lining of packages has been reported by Hatzidimitriu et al., 1987; Ikegami et al., 1987; Kwapong and Hotchkiss, 1987; Mannheim et al., 1987; and Shimoda et al., 1987.

In 1981 Durr et al. studied the storage of orange juice packaged in polyethylene lined cardboard and glass. It was found that a loss of approximately 40% of d-limonene by absorption onto the polyethylene layer of the soft packages occurred within 6 days of storage. The sensory differences

of the juices from the two packages was not detectable until after 27 days of storage at 20°C. After 62 days, the glass-bottled juice was described as stale and musty. The soft-packed juice was similarly described as stale and musty after 90 days. Linalool, octanal, decanal and neral showed a similar decrease in both packages.

Marshall (1985) investigated the absorption of d-limonene by various polymers. He indicated that loss of d-limonene into sealant layers between the juice and the polyvinylidene chloride (PVDC) barriers of various permeabilities ($\bar{P}$ = 0, 1, 4, and 8 cc oxygen @STP/m^2 atm day) was directly related to the thickness of the polyethylene or polypropylene sealant layer rather than the oxygen permeability of the film.

Hatzidimitriu et al. (1987) reported the permeation rates (at 23°C) of several organic compounds found in composite films at 0% and 75% relative humidity (RH). Ethylene/vinyl alcohol copolymer and nylon combinations exhibited superior barrier properties compared to polyethylene terephthalate-glycol (PET-G) and polyvinylidene chloride (PVDC) laminations even at elevated RH, provided that moisture barrier films were also present in the laminate construction.

Shimoda et al. (1987) revealed that the absorption of flavor compounds into the inner layer of films depended on the number of carbon atoms and molecular structure of the flavor compounds, flexibility of the structure, and the

position of functional groups on the ring compounds. The study showed that higher levels of sorption were observed in crystallized polypropylene pouches than in high density polyethylene ones, particularly for d-limonene and mycrene. The authors proposed that the higher levels of sorption were due to the difference in molecular structure between plastic materials. In addition, density, geometrical isomerism, polarity, crystallinity and steric hindrance of the structure of the polymer films should also be taken into consideration for the mechanism of sorption (Brown et al., 1973; Peterlin, 1975; Kreituss, 1981; Ng et al., 1985).

Mohney et al. (1986) investigated the solubility and permeability of limonene vapor in two cereal package liners. They concluded that this was a necessary consideration when estimating the storage quality of a packaged fruit-flavored cereal product, since the quality was related to the retention of aroma constituents within the package headspace.

Although previous researchers had demonstrated flavor sorption by packaging materials, to the best of our knowledge, no studies have been reported describing the relationship between the sensory quality of the product and the absorption of flavor compounds by packaging materials. Even less is known about consumer acceptance for a product after a determined period of storage.

MATERIALS AND METHODS

PRODUCT AND MATERIALS

A fruit flavored cereal product, whose quality depends on the retention of volatile aromatic constituents, was chosen for this study. The product, supplied by the cereal manufacturer, was packaged in two commercial package liner systems. Product evaluated thorough this study came from the same production lot, which was shipped (August 7, 1987) to the School of Packaging, Michigan State University, two days after the production run.

The two package liner systems used in this study were a high density polyethylene/ethylene vinyl acetate (HDPE/EVA) coextrusion, and a high density polyethylene/ethylene vinyl alcohol/Surlyn (HDPE/EVOH/Surlyn) coextrusion. Hereafter, these films will be referred to as the HDPE and EVOH structures respectively, thorough this thesis. The composition and physical properties of the two liners are listed in Table 3.

In addition to the packaged cereal, samples of the liner materials were also obtained from the product supplier and were stored in a desiccator over $CaSO_4$ (0% relative humidity) at ambient temperature (23^{o}C). The roll stock liner material samples were used as controls in the thermal

Table 3. Composition and physical properties of the two liner systems. [a]

Physical Property	EVOH	HDPE
Description	HDPE/EVOH/Surlyn HDPE 1.70 mil Tie 0.15 mil EVOH 0.20 mil Tie 0.15 mil Surlyn Blend 0.40 mil	HDPE/EVA
Caliper [b]	0.0026	0.0020
Yield [c]	11,200	14,663
WVTR [d]	0.25	0.23
O_2 Transmission [e]	0.15	N/A

(a) data obtained from product supplier.

(b) unit, inches.

(c) unit, in^2/lb.

(d) WVTR, the water vapor transmission rate, units in grams/100 in^2/24 hrs.

(e) unit, cc/100 in^2/24 hrs.

distillation analysis for sorbed volatiles, for comparison with the liner materials which had been contacted with the product for up to twelve months storage. Roll stock liner samples were also used in permeation studies, to determine the permeability constants for d-limonene in the respective liner structures.

EXPERIMENTAL METHOD

STORAGE STABILITY

Eight pallet loads, each pallet load contained sixty six shipping containers with twelve 11 oz. cereal boxes per shipping container and a total of 6,336 boxes of cereal, were received from the supplier. Four pallet loads of product were packaged in the high density polyethylene (HDPE) based liner and the other four pallet loads of product were packaged in the ethylene vinyl alcohol (EVOH) based liner. The individual pallet loads were identified with respect to the liner structure and stored in the School of Packaging storage room at temperatures ranging from 21^{o}C (70^{o}F) to 26^{o}C (80^{o}F) and 50% relative humidity, thoroughout the study. The storage environment maintained good ventilation and no foreign flavors were detected within 350 square feet of the storage room.

Each pallet load was shrink-wrapped and loaded on wood pallets to minimize the influence of ground temperature and moisture. There was about one foot between each pallet load. The cereal packages were set in the storage room for at least three days, to allow the volatile aromas within the liner structures to equilibrate, before the initiation of the headspace concentration analysis.

SAMPLING PLAN

A random sampling plan was developed by Mr. Dennis Young of the School of Packaging, Michigan State University, and was employed in this study. This program was designed to use individual random numbers to represent the location of boxes of product within cases and tiers, under the condition that the orientation and stacking pattern of the cases was well defined. In this sampling plan, random numbers were generated by a computer program. The random number is comprised of a three digit number. The hundredth number represented the tier number, the tenth number the case number, and the last number the box number, which is counted clockwise from the manufacturer's joint for the container from which the sample was withdrawn. For example, the code number indicates 231 means that the sample was pulled from the first box in the third container from the second tier of the pallet load. The random number was then affixed to the

box chosen from the pallet load, according to the sampling plan. The storage location of any package can be traced by this random number in order to examine factors relating to aroma loss during storage.

The product was shipped in eight pallet loads, with each pallet load having six tiers. Every tier was composed of eleven cases, each containing twelve individual cereal boxes arranged in four by three order. The stacking pattern of the pallet load is illustrated in Figure 2.

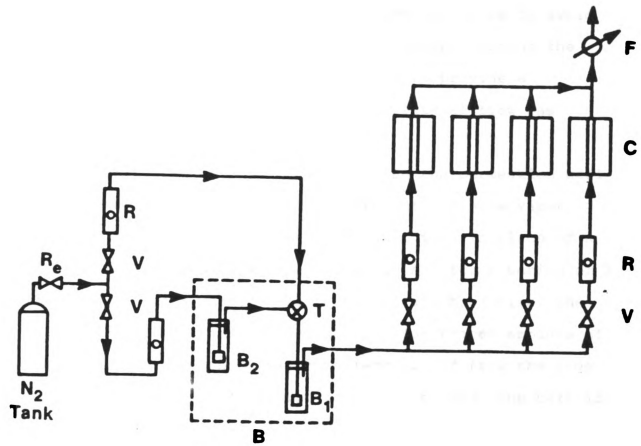
Sampling was done monthly over a period of nine months, followed by one additional sampling after twelve months storage. Sampling monthly was designed to sort products in both liner structures, by using a horizontal split of the three tiers of product starting from the top of a pallet load. Each month, three hundred and thirty (330) individual cereal packages were sampled from each liner structure. Five (5) packages were used for the quantitative analysis of d-limonene headspace concentration and the thermal distillation/desorption of d-limonene from the liners. Seventy five (75) packages were prepared for the triangle testing, while the remaining two hundred and twenty five boxes of cereal (250) were sorted for consumer preference testing.

PERMEATION STUDIES

The permeation studies were carried out by employing a Quasi-Isostatic method to determine the transmission rate of d-limonene through the two liner structures. The transmission rate is defined as that quantity of vapor passing through a unit area of the parallel surfaces of a plastic film per unit time, under specified conditions of test. This procedure is referred to as "Quasi-Isostatic" because the test compartments are maintained at an essentially constant total pressure of one atmosphere. It is, however, an accumulation procedure where permeant collects, as a function of time.

A schematic diagram of the permeation test apparatus is presented in Figure 3. A constant concentration of permeant vapor is produced by bubbling nitrogen gas through the liquid permeant. This is carried out by assembling a vapor generator consisting of a gas washing bottle, with a fritted dispersion tube, containing the organic liquid. Vapor concentration (ppm) in nitrogen is expressed throughout on a weight per volume basis. The permeability studies were carried out at temperatures ranging from 21.1^{o}C (70^{o}F) to 26.7^{o}C (80^{o}F) and approximately 0% relative humidity.

To obtain a low vapor concentration, the permeant vapor stream is mixed with another stream of pure carrier gas (nitrogen). Before being directed to the permeation cell, the vapor stream was passed through a glass reservoir as a



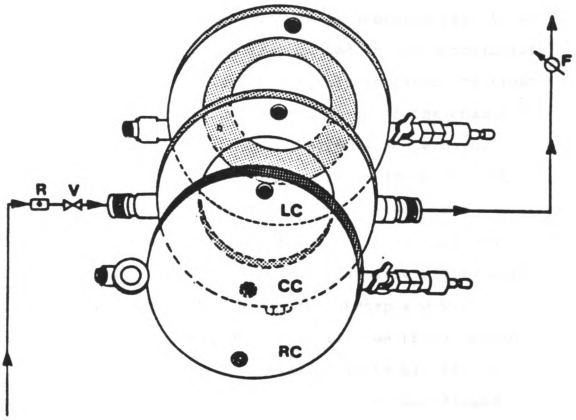
B = Water Bath
B_1 = Glass Mixing Device
B_2 = Glass Vapor Generator
R_e = Regulator
V = Needle Valve
R = Rotameter
C = Cells (Double Chamber)
F = To Waste and Gas Flow Bubble Meter
T = Three Way Valve

Figure 3. Schematic of Quasi-Isostatic Permeation Test Apparatus

system was mounted in a constant temperature water bath, maintained at 1°C above ambient temperature so as to avoid condensation after the permeant vapor passed through the glass reservoir. Flow meters were used to provide a continuous indication that a constant rate of flow was maintained.

Prior to the initiation of each run the permeation cell is cleaned to be sure that it is free of limonene vapor. This is achieved by mounting a sheet of foil in place of a film sample and allowing the system to set for a period of 2 to 3 days, under closed conditions. After which time, the headspace of each chamber is measured for traced amounts of residual limonene which may have leached off from the side walls of the cell. If any limonene is detected, the cell is disassembled and heated in a 43°C (110°F) oven for 3 to 4 days and then re-evaluated. This procedure is performed following each permeation test and repeated until the system is clean.

The permeability of the respective films was determined under identical conditions, so as to compare their relative barrier properties. Duplicate runs on the same film type are carried out simultaneously in specially designed permeability cells. Figure 4 provides a detailed view of the permeant cell system. Each permeability cell, constructed of stainless steel or aluminum, is comprised of two cell chambers and a hollow center ring. Both cell chambers and



PV = Permeant Vapor
R = Rotometer
V = Needle Valve
o = Sampling Ports
LC = Left Cell
CC = Center Cell
RC = Right Cell
F = To Waste and Gas Flow Bubble Meter

Figure 4. Permeant Cell System

the center ring are equipped with an inlet and outlet valve and a sampling port. The cell volume is approximately 50 cc.

In operation, test films are mounted in the permeability cell so that the center ring effectively isolates the right and left cell chambers. Hermetic isolation of the chambers from each other and from the atmosphere is achieved by compression of overlapping Viton "O" rings (from Detroit Ball Bearing Company) on the film sample. Viton is a fluorocarbon elastomer which is resistant to attack and swelling by most organic vapors. For the permeability cell with the lower center cavity from the atmosphere was achieved through compression of the film against a smooth metal face which resulted in a metal/film/metal seal. A constant concentration of permeant vapor is then flowed continuously through the high concentration (center) chamber of the permeability cell at a flow rate in the range of 25 to 35 cc/min.

The increase in penetrant level in the low concentration cell chambers is determined by gas chromatographic analysis. At predetermined time intervals, a 0.5 mL aliquot of headspace is removed from the low concentration cell chambers with a gas tight syringe (Hamilton no. 1750, side port type) and injected directly into the gas chromatograph for quantitation. A constant total pressure of one atmosphere is maintained in both the upper and lower cell chambers by replacing the smaple volume removed with an equal volume of pure nitrogen. Samples are removed a number

of times over the period of test and an array of time vs. area response values recorded.

To determine the permeability coefficient, the increase in penetrant quantity in the lower concentration cell chambers was plotted as a function of time and the resultant transmission profile related to the permeability of the film sample. The time interval during which the permeability data was evaluated to obtain a steady state rate of transmission was determined by graphical analysis of the time versus area response values. In all cases, the data was evaluated statistically by linear regression analysis to obtain the best straight line fit.

D-LIMONENE HEADSPACE CONCENTRATION ANALYSIS

Quantitation of d-limonene concentration in the headspace of a package was carried out by a gas chromatographic analysis. Prior to headspace analysis, the cereal boxes were opened and a square shaped gum sheet (1.27 cm. x 1.27 cm. x 0.1 cm.), which had an adhesive surface on one side, was affixed to the liner structure by using the adhesive side. This provided a sampling septum for headspace gas chromatographic analysis. A 0.5 mL aliquot of headspace was removed from the package headspace with a gas tight syringe (Hamilton no. 1750, side port type) and injected directly into a gas chromatograph (GC) for quantitation.

syringe (Hamilton no. 1750, side port type) and injected directly into a gas chromatograph (GC) for quantitation.

A Hewlett Packard Model 5890A gas chromatograph, equipped with a dual-flame ionization detector (FID), was used for this analysis. The GC conditions were as follow:

Column: 2-4081 Fused Silica Capillary SUPELCOWAX 10
60 Meters, 0.25 mm. ID, 0.25 um. df (Supelco, Inc., Bellefonte, PA).

Carrier Gas: nitrogen at 40 psi.

Temperature (^{o}C): injector, 200.
oven, 75.
detector, 275.

Retention Time for D-Limonene (min.): 13.65.

A standard curve of response vs. limonene concentration was constructed prior to analysis from standard solutions of known limonene concentration. This allowed the determination of the linearity and sensitivity of the method. Solutions used for calibration were prepared by dissolving known quantities of d-limonene in ethyl acetate. Peak responses were obtained by injecting the various concentration of d-limonene into the gas chromatography. Calibration data are detailed in Appendix A. D-limonene headspace concentration levels in the respective cereal box liner structures were determined for five individual randomly sampled boxes, and the values averaged.

THERMAL DISTILLATION/DESORPTION TEST

The amount of d-limonene sorbed by the respective package liner structures was determined by the thermal distillation/desorption method. Following d-limonene headspace analysis, liners were removed from the package and cleaned throughly to make sure no cereal residue remained. Liners were cut into small pieces (2.54 cm. x 2.54 cm.) and weighed on an analytical balance. The liner pieces were then added to 65 mL septa seal vials. The filled vials were gas flushed with nitrogen before sealing with a teflon-lined silicon septum and aluminum crimp cap. Vials were then heated for one hour at 90^{o}C. After one hour, the vial was removed from the oven, a 0.5 mL aliquot of headspace was taken from the vial with a heated syringe (Hamilton no. 1750, side port type), and injected directly into gas chromatograph for quantitation.

The amount of d-limonene sorbed by the liners was determined by reconstitution into the following equation:

$$Q = S \times A \times V \times 1/V_t \times 1/W_t \qquad (1)$$

where, S = the calibration factor from standard curve (gm/A.U.).

A = d-limonene area response (A.U.).

V = volume of the vial (mL).

V_t = volume of the injection (mL).

W_t = weight of the liner (gm).

Q = the quantity of d-limonene absorbed (gm of d-limonene/gm of liner).

SENSORY EVALUATION

Sensory evaluation was carried out using two tests, the triangle test and the preference test.

TRIANGLE TEST

The purpose of using the triangle test was to determine if a difference existed between the sensory quality of the product in the two liner structures, as a function of storage time.

In this test, twenty five (25) voluntary panelists (12 male and 13 female), ranging in age from 24 to 60 years, were selected on the basis of their previous experience with the test product and their sensitivity to the changing concentration of d-limonene in the package. The latter was established in preliminary screening studies. Panelists were scheduled every month to participate in the triangle test, shortly after analytical experiments were completed. The testing laboratory was located in the School of Packaging. It contained all the requirements needed for conducting sensory evaluation tests (Larmond, 1977). Panelists were

asked to refrain from smoking, wearing perfume, drinking, chewing gum, and eating for at least 30 minutes prior to testing. If a panelist was ill at his/her scheduled time, the person was allowed to skip the test.

On each day of testing, panelists were individually shown the testing room, explained the nature and procedure of the test, and asked to sign a consent form stating their willingness to participate in the sensory test (Appendix B). Paneliststst were blind-folded to avoid making any decision by observing a difference in the liners' opacity. A tape recording of instructions was prepared to standardize the testing condition. Three coded samples, two identical and one different, were presented simultaneously to a panelist with the help of an operator. Control and experimental treatments were systematically varied so that each was presented in odd and identical sample positions an equal number of times. Panelists were asked to identify which of the three samples presented differed from the other two. A copy of the triangle test questionnaire developed by Larmond (1977) and employed in this test is presented in Appendix B. Analysis of the results was based on the probability that if there was no detectable difference, the odd sample would be selected by chance one-third of the time. Tables for rapid analysis of triangle test data developed by Roessler et al. (1948) were used in this study to determine whether a

significant difference existed between test liners, over twelve months of storage.

PREFERENCE TEST

A preference test was used to give an indication of consumer's preference for the cereal products packaged in the two liner structures. The preference test was carried out by two hundred and fifty (250) untrained college students, ranging in age from 18 to 25 years. Participation was strictly voluntary.

The test took place in the standard sensory evaluation laboratory in the Department of Food Science and Human Nutrition at Michigan State University. The testing area was equipped with eight (8) individual booths constructed along a wall which divided the preparation area from the panel room. Partitions had been built between the booths to eliminate distraction and prevent communication among the panelists.

During the test, two samples each containing a different liner were simultaneously presented to the panelists. Panelists were asked to evaluate each sample and marked their preference accordingly on a nine-point hedonic scale (Appendix B). Descriptive terms ranged from "like extremely" to "dislike extremely".

Hedonic scale ratings were later converted to numerical scores ranging from "like extremely" (9) to "dislike extremely" (1). The mean scores from each treatment were then analyzed by using the Student's t-test. Results were analyzed to determine panelists' degree of liking between the two package liners.

RESULTS AND DISCUSSION

PERMEATION STUDIES

The results of the studies on the permeation of d-limonene vapor through the HDPE and the EVOH based liner structures, are summarized in Tables 4 and 5. Representative transmission rate profile curves for the respective film structures are presented graphically in Figures 5 and 6, where the total quantity permeated is plotted as a function of time.

Permeation can be described in terms of its component parts, the diffusion coefficient (D) and the solubility coefficient (S) by Equation (2).

$$\bar{P} = D \times S \qquad (2)$$

The diffusion coefficient is a measure of how fast molecules move in a film, and the solubility coefficient is a measure of how many molecules can dissolve in a film. As shown, the permeation behavior of the respective films had, as predicted by theory, an initial induction period followed by a non-steady state rate at diffusion, which preceded a steady state transmission rate. For the low penetrant concentrations used in this study, it was considered

Table 4. Permeability Data for the HDPE Based Liner Structure

Run Time (min.)	Total Quantity of Limonene Permeated [a] ($gm \times 10^{-6}$)
0	0.00
15	0.60
30	1.25
45	3.59
60	28.71

Limonene Vapor Concentration (gm/mL, ppm) = 6.6 $\pm$ 0.2

Lag Time (min.) = 35 $\pm$ 2

Permeability Coefficient (gm/m^2. day. 100 ppm) = 5.86 [a]

(a) Value is the average of duplicate runs.

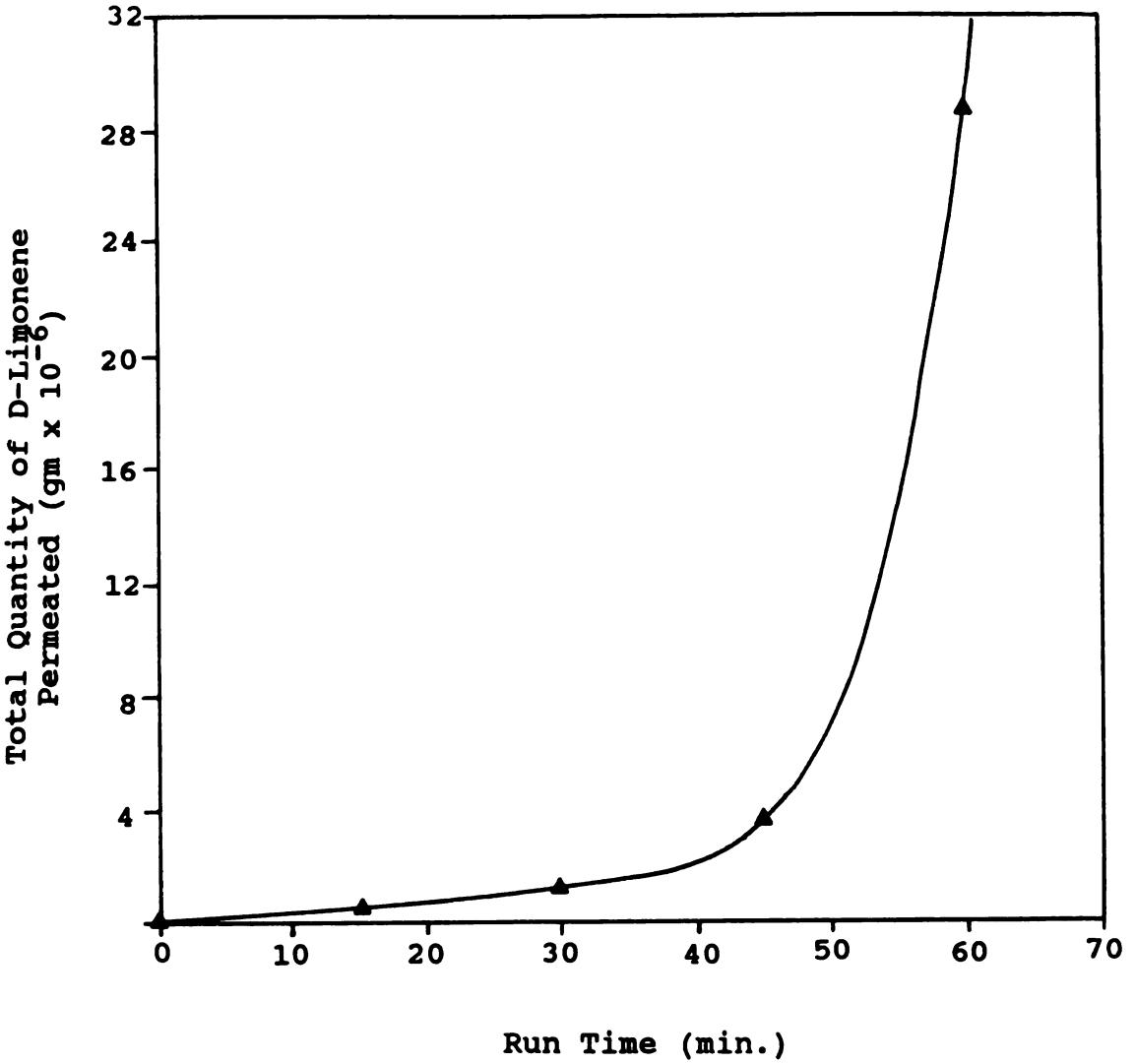


Figure 5. Permeation of d-limonene through the HDPE based liner structure at 23°C and 0% RH.

Table 5. Permeability Data for EVOH Based Liner Structure

Run Time (min.)	Total Quantity of Limonene Permeated [a] ($gm \times 10^{-6}$)
0	0.00
10	0.11
20	0.22
35	0.57
60	2.21
70	2.93
80	3.41
90	3.96
100	4.73
110	5.22

Limonene Vapor Concentration (gm/mL, ppm) = 6.6 $\pm$ 0.2

Lag Time (min.) = 95 $\pm$ 5

Permeability Coefficient (gm/m^2. day. 100 ppm) = 0.34 [a]

(a) Value is the average of duplicate runs.

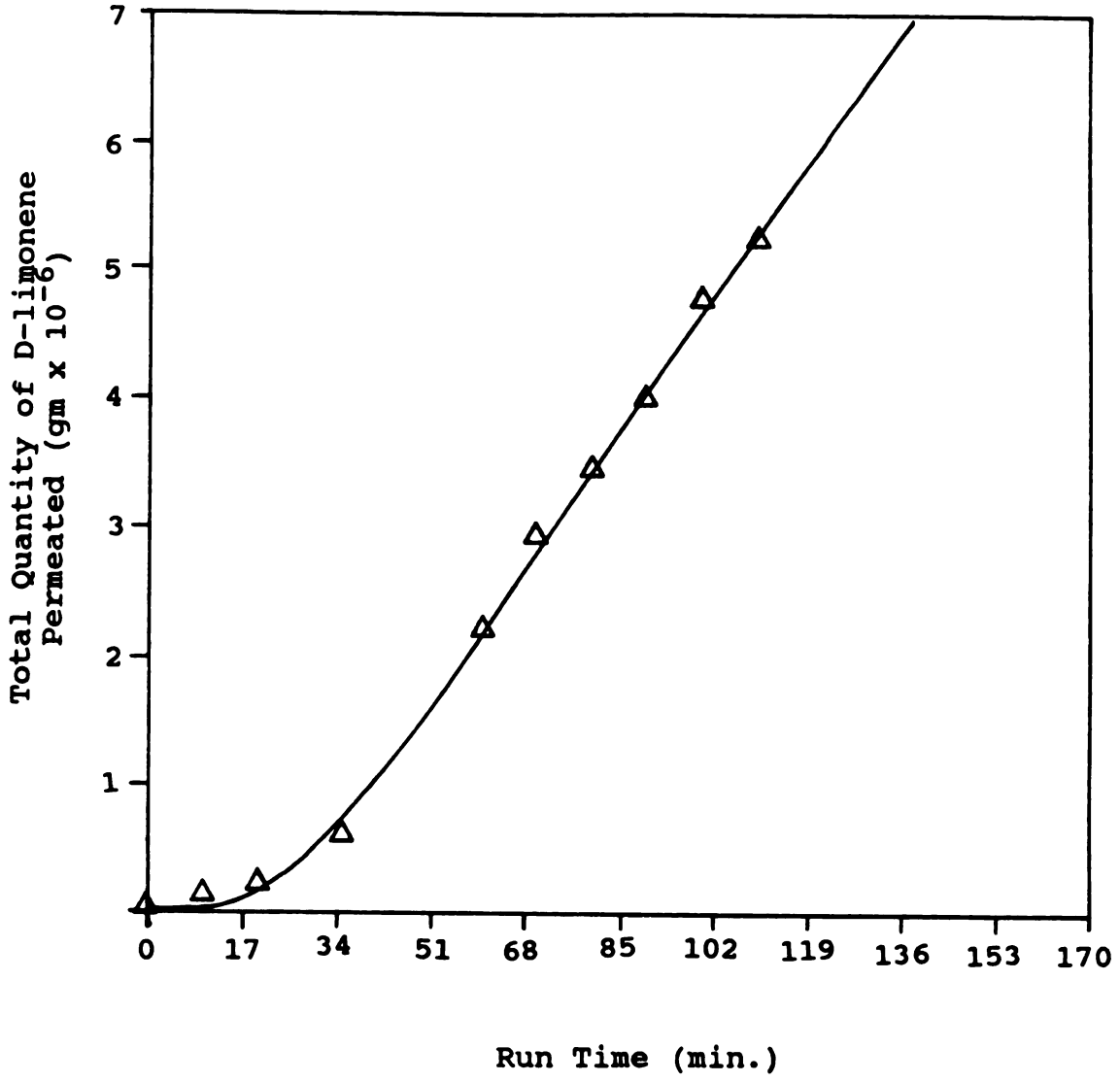


Figure 6. Permeation of d-limonene through the EVOH based liner structure at 23°C and 0% RH.

appropriate to assume that the diffusion process was Fickian. From the transmission data, the permeability constant can be calculated by using the standard methods (Barrer, 1939; Crank and Park, 1968), with a normalization of the units of the permeability constant to 100 ppm (gm of permeant/mL of nitrogen) permeant concentration difference across the film.

As shown in Tables 4 and 5, the averaged permeability coefficient of the HDPE based liner structure is almost 22 times higher than the permeability coefficient of the EVOH based liner structure. The lag time and the permeability coefficient values for the HDPE based liner structure obtained in this study were found to be in good agreement with the values reported by Mohney et al. (1987). These results support the hypothesis that the EVOH liner structure possesses much better barrier properties with regard to the retention of d-limonene within the cereal package, than does the HDPE based liner structure.

D-LIMONENE HEADSPACE CONCENTRATION

The results of monitoring d-limonene headspace concentration levels in the two cereal package liner structures over 12 months of storage are summarized in Table 6 and presented graphically in Figures 7 and 8, where headspace concentration is plotted as a function of storage

Table 6. D-limonene headspace concentration levels in two cereal package liner systems during 12 months of storage at 23°C and 50% RH.

Storage Time (months)	Average d-limonene concentration[a] (gm/mL, ppb)	
	HDPE liner	EVOH liner
0	-	-
2	0.24±0.21	6.04±0.37
3	0.07±0.15	4.23±1.12
4	0.04±0.07	3.00±0.16
5	N.D	3.08±0.17
6	N.D	4.09±0.10
9	N.D	3.54±0.64
12	N.D	1.45±0.33

(a) Values represent the means of five replicates.

(b) N.D means not detectable.

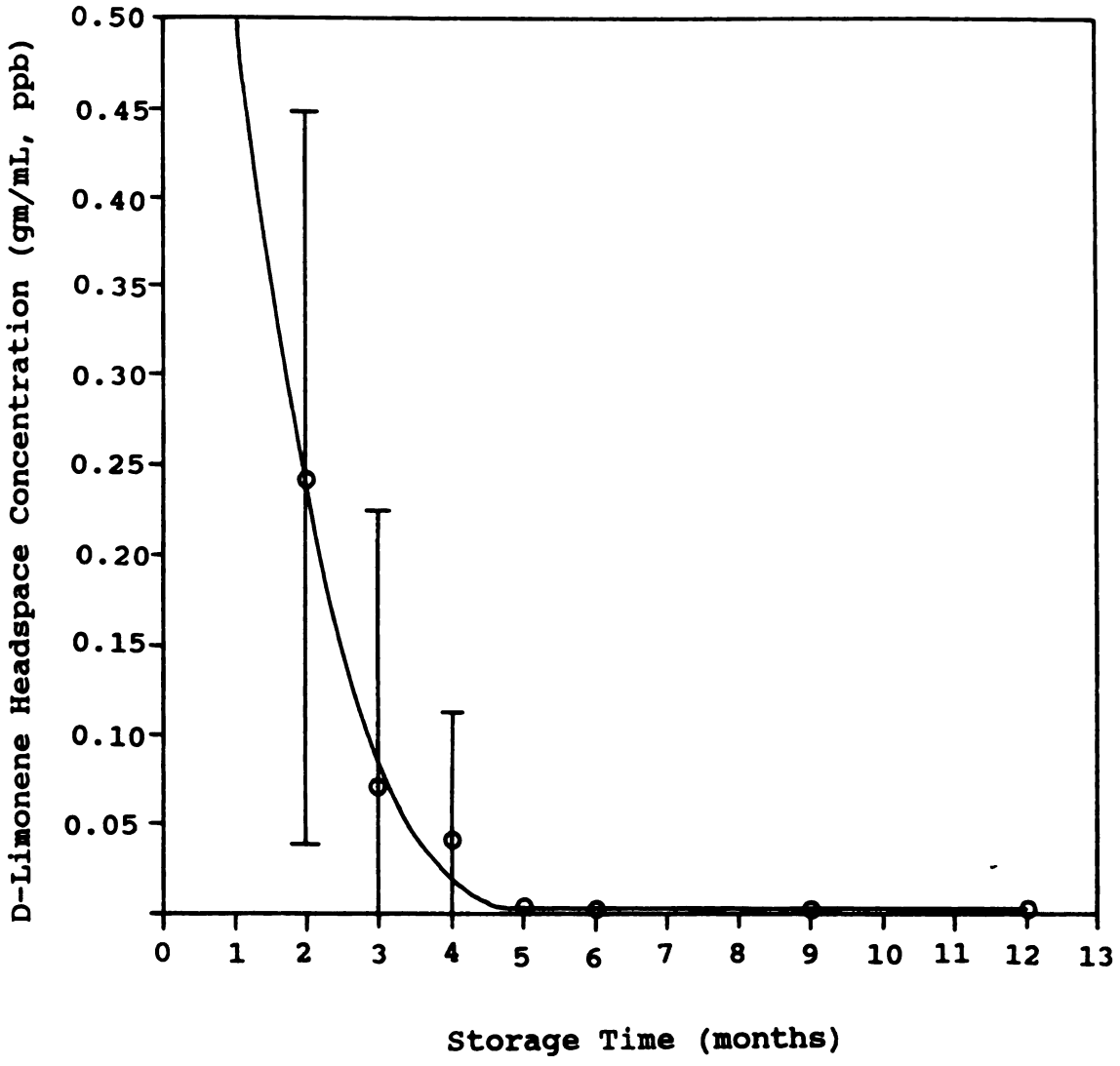


Figure 7. D-limonene headspace concentration levels in the HDPE based cereal package liner structure during 12 months of storage at 23°C and 50% RH.

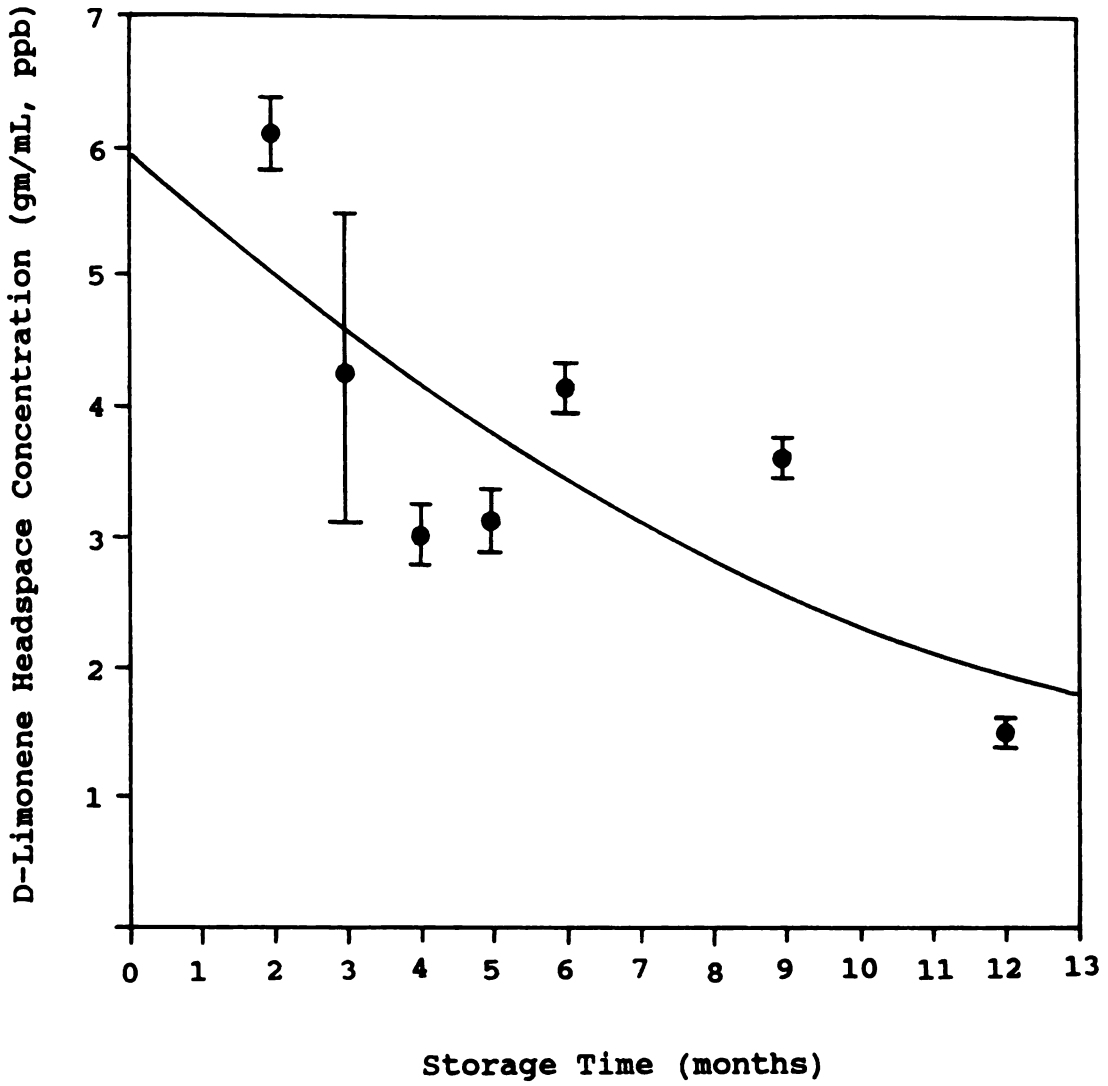


Figure 8. D-limonene headspace concentration levels in the EVOH based cereal package liner structure during 12 months of storage at 23°C and 50% RH.

time. The headpace concentration levels for the respective liner structures are superimposed in Figure 9 for comparison.

At the time the cereal product was received from the manufacturer, the gas chromatograph was inoperable and therefore, the initial d-limonene levels were not recorded. However, headspace analyses were completed from the second month to the ninth month of storage, followed by one analysis after the twelfth month of storage. Data for the d-limonene headspace analyses performed are tabularized in Appendix C.

As shown in Figure 7, the headspace concentration of d-limonene in the EVOH liner structure decreased at a fairly constant rate over the course of the study. However, a rapid loss of d-limonene in the headspace of the HDPE liner structure was observed over the first 4 months of storage, with the concentration of d-limonene being below the level of detectability for the remainder of the study.

As shown in Table 6, the standard deviation for the third and fourth months' measure of the amount of d-limonene remaining in the headspace was found to be higher than the means for the HDPE based liner. A trace of the storage location of the cereal boxes used in the third and fourth months of testing showed that only boxes taken from cases stored in the middle tier of a pallet, where one or two sides of the case were exposed to air, had a detectable amount of d-limonene remaining in the headspace of the

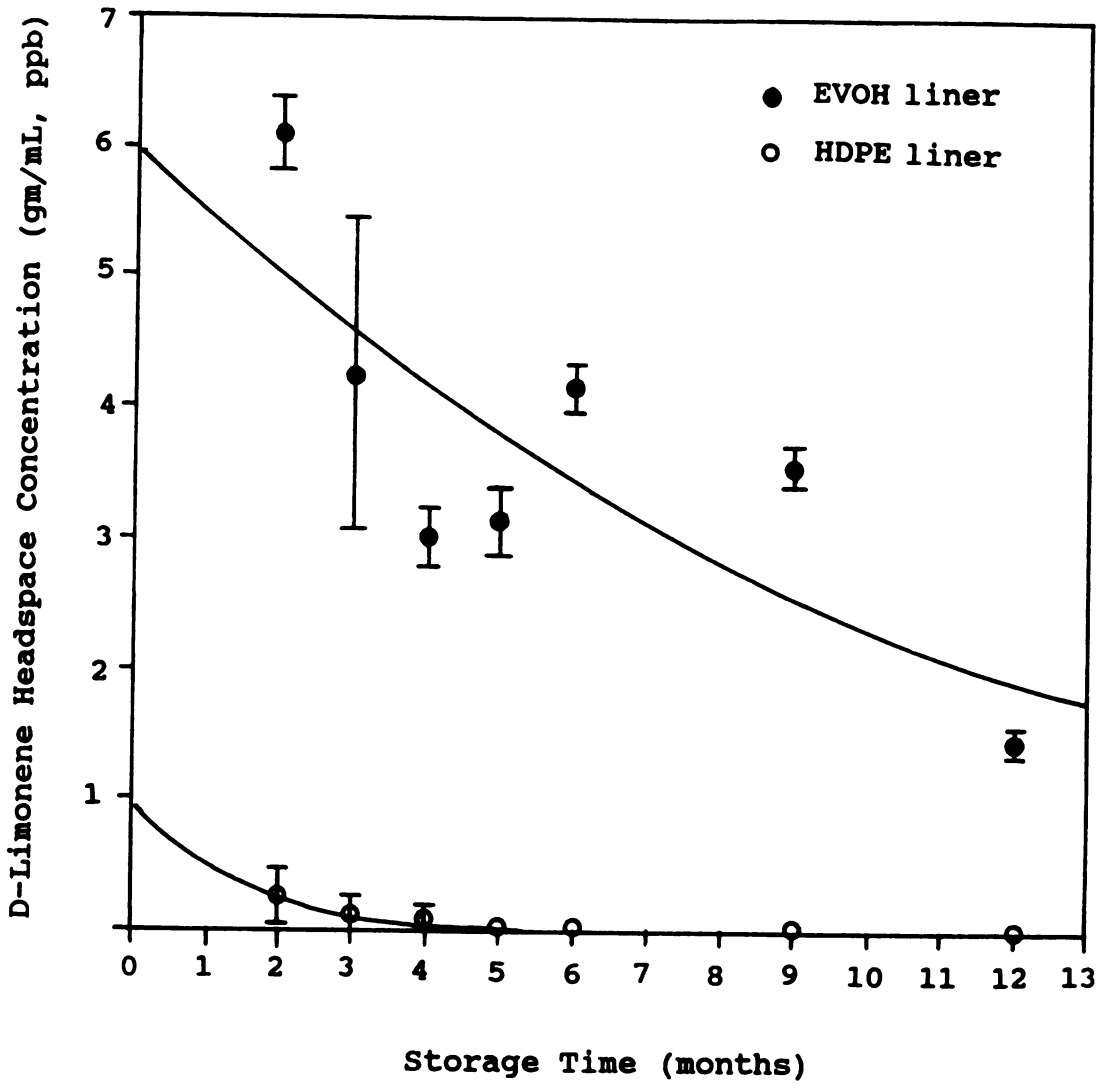


Figure 9. D-limonene headspace concentration levels in two cereal package liner structures during 12 months of storage at 23°C and 50% RH.

package. Boxes withdrawn from cases located in the top or bottom tier of a pallet, where two or more sides of the case were exposed to air, showed a below detectable amount of d-limonene in the headspace of the package (Appendix C).

A one-way analysis of variance (ANOVA) was performed to test the time effect on the loss of d-limonene from the EVOH based liner structure (Appendix C). It was found that the storage time had a positive effect on the reduction of d-limonene headspace concentration in the EVOH based liners ($P < 0.05$).

An assessment of the two liners with regard to their ability to retain d-limonene was made (Appendix C). It was found that the EVOH liner was a better barrier to flavor than the HDPE liner ($P < 0.05$).

D-limonene headspace concentration levels were observed to be dependent on storage location within the pallet stacking pattern. A linear regression method was employed to analyze the relationship between the storage location of cereal boxes, and the corresponding d-limonene headspace concentration measured for the cereal packages. It was found that samples pooled from cases which had two or three sides exposed to air had lower d-limonene levels in the headspace than samples from the middle cases, having only one side exposed to air (Appendix C). However, the results of the studies were found to be statistically insignificant ($P > 0.05$) due to the limited number of paired sample groups. The observation might still be valuable to explain,

in part, the broad range of standard deviations for the d-limonene concentration levels obtained, particularly for the HDPE liner.

SORPTION OF D-LIMONENE BY LINERS

The results of analyses to quantify the levels of d-limonene sorbed by the two liner structures during storage are presented in Table 7. As shown, the quantity of d-limonene sorbed by the EVOH liner structure was significantly higher than that sorbed by the HDPE liner structure. For better illustration, the results of these studies are presented graphically in Figures 10, 11, and 12, where the levels of sorbed limonene are plotted as a function of storage time. The high level of d-limonene sorbed by the HDPE liner, shown in the fifth month of storage, was found to be associated with the storage location of the boxes in the pallet stacking pattern (Appendix D).

Figure 13 illustrates an ideal transmission model of penetrant across a monolayer barrier polymer film. In this figure, the permeant concentration in the polymer film progresses from the start of exposure until steady-state. Shortly after exposure, the film has a high concentration of permeant near the exposed surface. The permeant has not however, penetrated very far into the film. With time, the

Table 7. Sorption concentration levels of d-limonene by two cereal package liners during 12 months of storage at 23°C and 50% RH.

Storage Time (months)	Average quantity of d-limonene Sorbed [a] (gm/gm liner, ppb)	
	HDPE liner	EVOH liner
0	-	-
2	-	-
3	14.39±2.68	110.21±10.99
4	15.59±2.00	90.10±1.88
5	22.10±2.53	69.05±9.84
6	9.64±0.81	47.30±6.29
9	N.D	16.54±3.46
12	N.D	7.92±1.58

(a) Values represent the means of five replicates.

(b) N.D means not detectable.

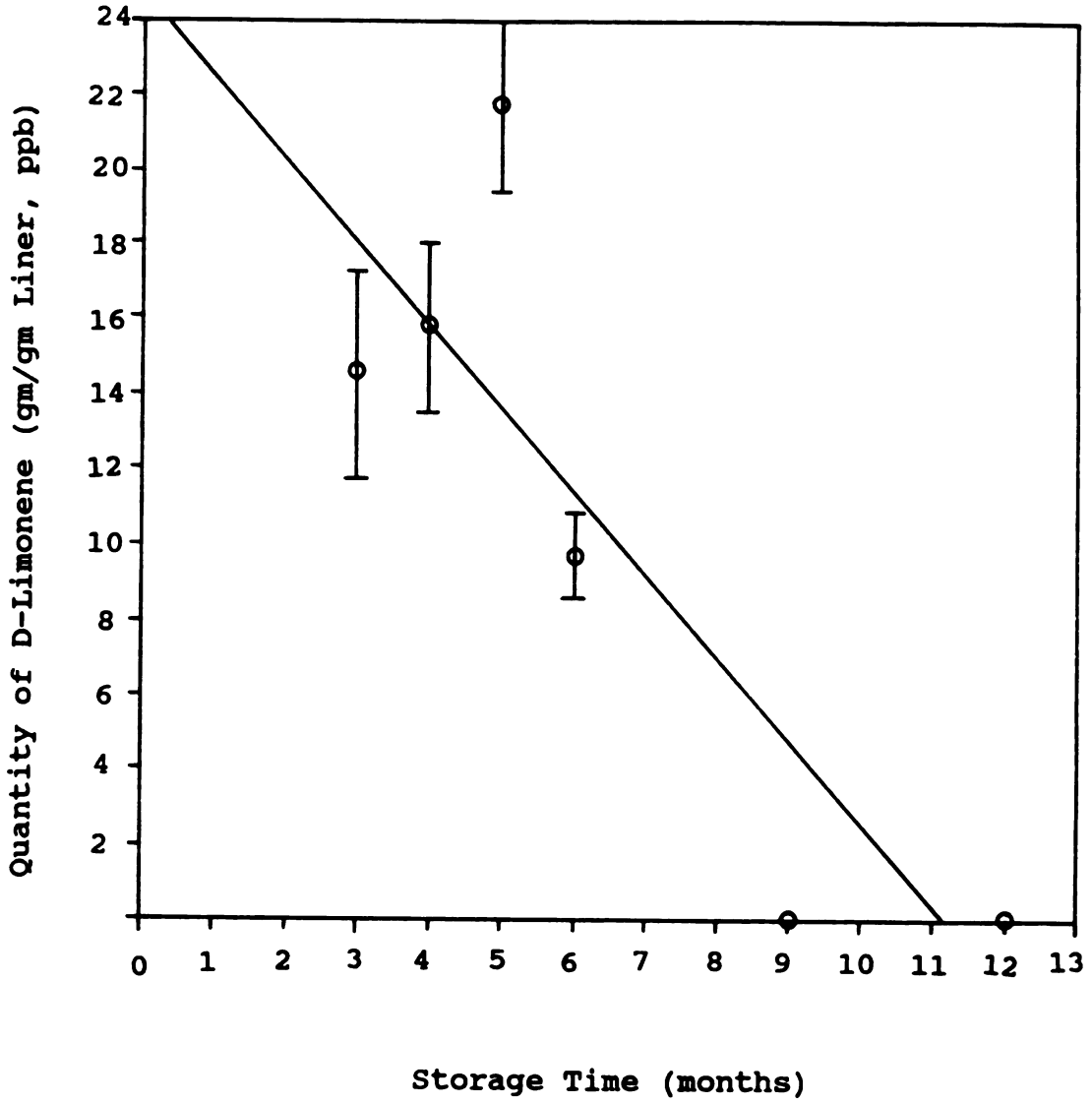


Figure 10. Sorption concentration levels of d-limonene by the HDPE based cereal package liner structure during 12 months of storage at 23°C and 50% RH.

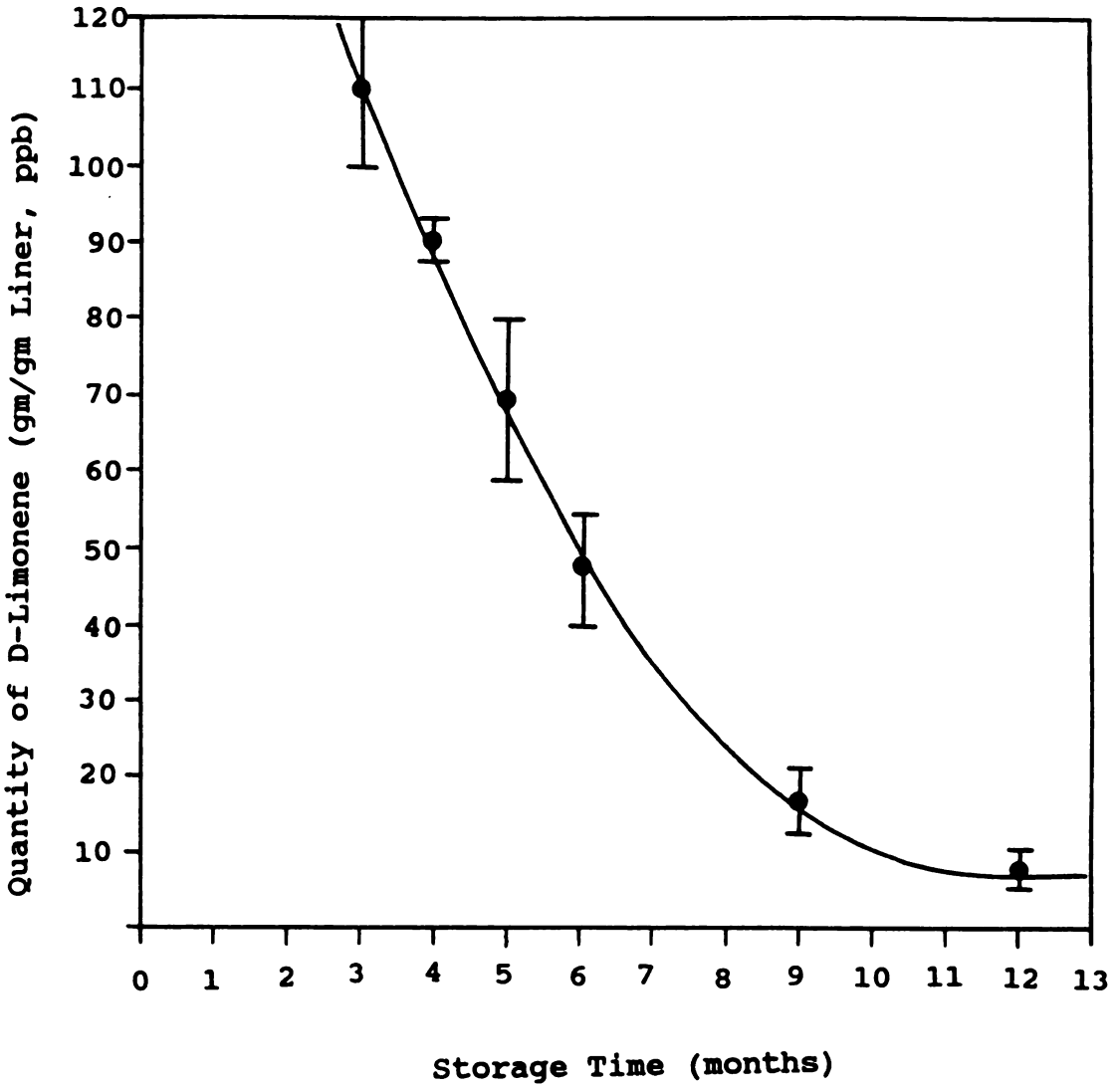


Figure 11. Sorption concentration levels of d-limonene by the EVOH based cereal package liner structure during 12 months of storage at 23°C and 50% RH.

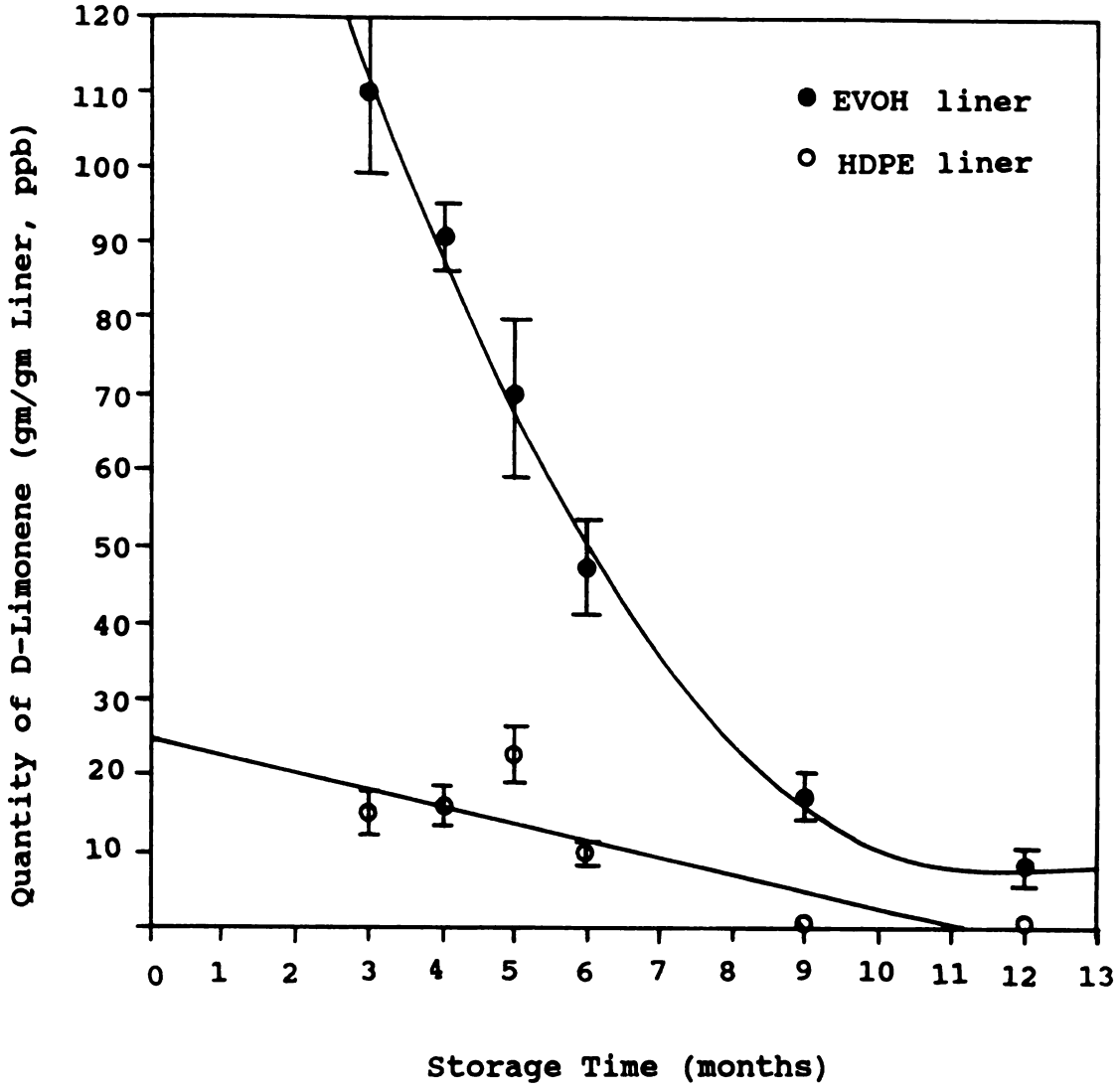


Figure 12. Sorption concentration levels of d-limonene by two cereal package liner structures during 12 months of storage at 23°C and 50% RH.

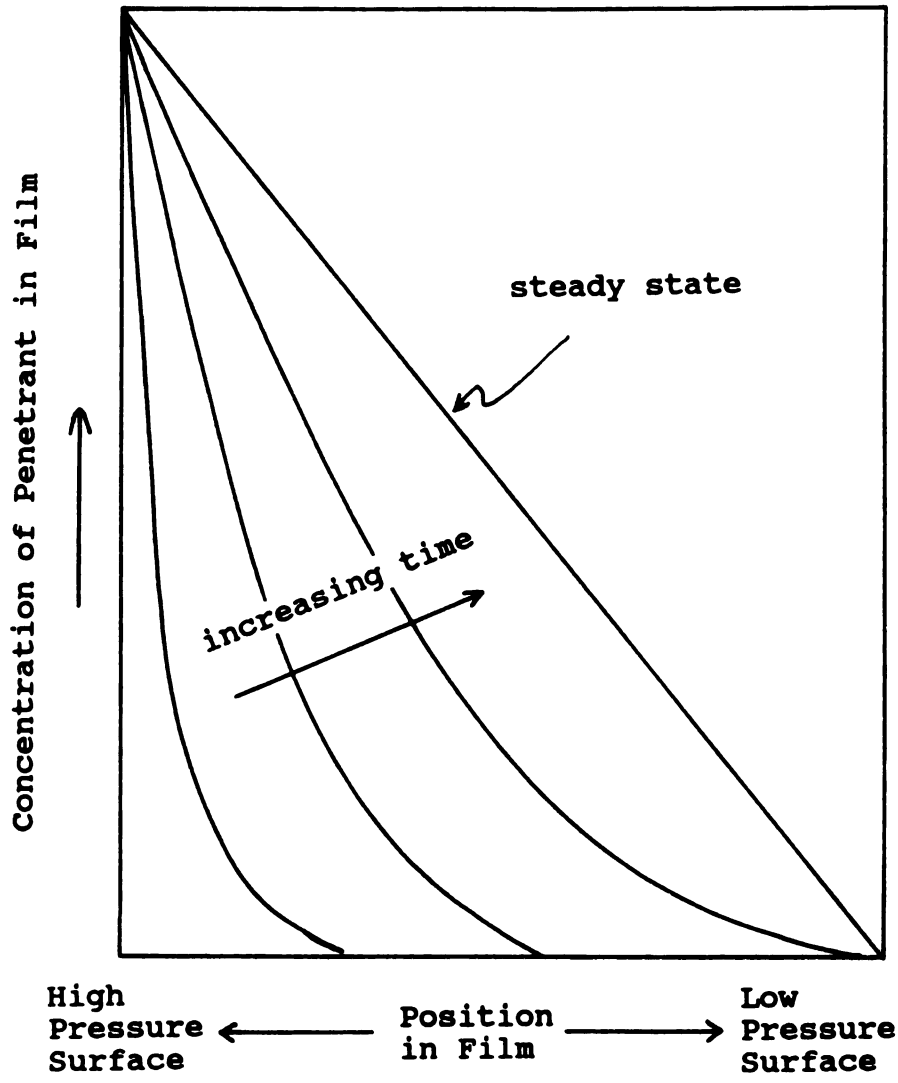


Figure 13. Concentration profile of a penetrant in a polymer film as a function of time.

DeLassus and Marcus (1986)

surface concentration does not change, but the penetration depth increases. Finally, at steady-state, the concentration profile is a straight line that drops uniformly across the film. The area under the curve is proportional to the quantity absorbed (DeLassus and Marcus, 1986).

Today, a monolayer barrier polymer film is less commonly used, and a multilayer structure would typically be fabricated and used in designing packages. In the multilayer structure a thin barrier layer would be combined with thicker layers of a less expensive, mechanically tough polymer. For example, in this study, the 2.6 mil thick EVOH based liner structure is a multilayer lamination comprised of HDPE/EVOH/Surlyn, where the EVOH barrier layer (0.5 mil) is placed between 1.70 mil thick HDPE and 0.4 mil thick Surlyn blend.

The permeation process for large, organic molecules in polymer films differs from the permeation process for small gas molecules in polymer films (DeLassus and Marcus, 1986). For small gas molecules, the diffusion coefficients are large, and the solubility coefficients are small. This means that few molecules are moving in a film; however, they are moving quickly. For large, organic molecules, like d-limonene, the diffusion coefficients are small, and the solubility coefficients are large. This means that many molecules are moving in a film; however, they are moving slowly. These differences have an important consequence for food package design. For good flavor retention, a multilayer

barrier container should have the barrier structure as the inside layer (DeLassus and Marcus, 1986). This is illustrated by considering the Saran coated oriented polypropylene laminates described by DeLassus and Marcus (1986). Such a structure has two 10 mil skin layers of polypropylene and a 2 mil center layer of Saran copolymer. If this structure was used to package a product which contained methyl salicylate, the sorption in the interior polypropylene layer would be great. This is depicted in Figure 14 (A). The concentration profile in this layer would be nearly constant because the activity gradient would tend to be across the barrier layer in much the same way, as described by DeLassus et al. (1986), that temperature drop is across an insulator and voltage drop is across a resistor. While the permeability coefficient was maintained the same, switching the barrier layer position in the laminate would result in the level of sorption to be quite different. This is shown in Figure 14 (B). As illustrated in this Figure, a lower permeant concentration gradient would be expected to be seen in this structure. This means that if the barrier were placed at the inner layer of the multilayer structure, the barrier behavior would be enhanced, with respect to respective losses.

DeLassus and Hilker (1987) further described a model to explain the mass transfer of permeants such as flavor, aroma, and solvent molecules across a multilayered structure, as a function of the location of the barrier

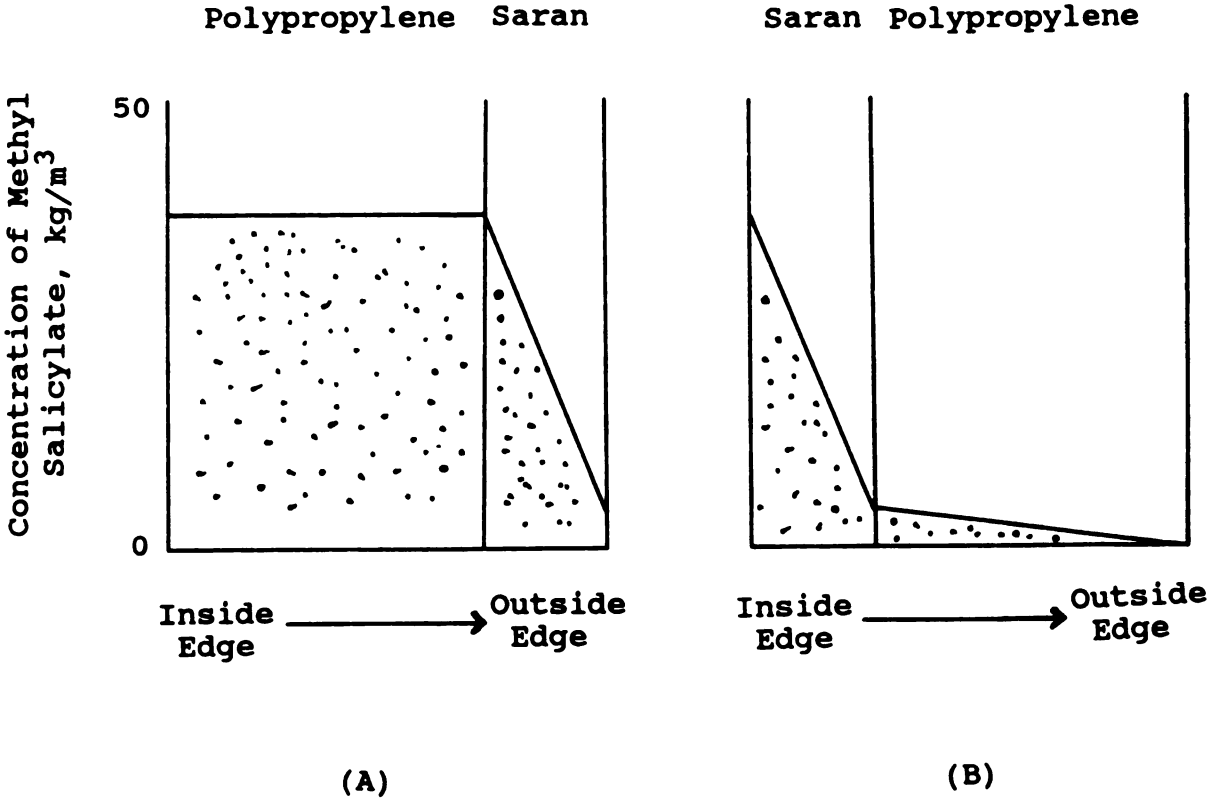


Figure 14. Concentration profiles of methyl salicylate at 25°C in two hypothetical multilayer walls at steady-state.

DeLassus and Marcus (1986)

layer. The movement of low molecular weight molecules depends on the concentration profile of the permeant across the respective layers of the laminate structure, the solubility of the permeant in the respective layers of the lamination, the composition of the barrier layer, the thickness of each layer of the lamination, and the location of the barrier layer with respect to the penetrant phase. The equation can be described as following:

$$\Delta M \text{ (sorb)} = 0.5 \; S \times \bar{P} \times L \text{ (penetrated)} \times A \qquad (3)$$

where, ΔM is the quantity of permeant that will cross a film during the time to reach steady-state of permeation; S is the solubility coefficient, which can be calculated from Equation (2) by substitution of a known $\bar{P}$ and a known D; $\bar{P}$ is the permeability coefficient; L is the penetrating depth of the film when permeation reaches steady-state; and A is the film area.

The solubility of a permeant in a polymer layer depends on the chemical affinity of sorbed molecules to the structure of the layer (Ikegami et al., 1987), the molecular weight of the permeant (Schimoda et al., 1987), and the density of the barrier layer (Schimoda et al., 1984).

In this study, where the EVOH barrier layer was placed as the middle layer of the multilayer structure, a modified transmission profile model, based on the concept of DeLassus and Marcus (1986) can be utilized to explain the

transmission and sorption of d-limonene through both liner structures.

D-limonene is well known to have a high chemical affinity to polyolefins. According to DeLassus and Hilker's (1987) model, the flavor compounds in cereal would be sorbed rapidly by the interior HDPE layer in both liner structures evaluated in this study. DeLassus (1985) pointed out that the HDPE reaches a steady-state transmission rate quickly with the permeant, d-limonene. It takes only 2.6 hours for a 2.0 mil HDPE film to reach steady-state when d-limonene was selected as the permeant. Even if the thickness was increased to 20 mil, steady-state would be reached in only 10 days. The same results were observed by Mohney et al. (1987). The results of permeability studies have shown that the HDPE based liner is a poor barrier to d-limonene (Tables 4 and 5). Therefore, for the HDPE liner structure, it is anticipated that a high percentage of the d-limonene within the cereal package would be lost from the system within several months of storage, due to the permeation mechanism. This is demonstrated by the low concentration levels of d-limonene remaining in the headspace of the packages, and the low quantity of d-limonene sorbed by the HDPE based liner structure, over the storage time of the study. This model is shown in Figure 15 (B). In contrast, the high level of d-limonene concentration detected in the headspace of the EVOH based cereal packages, and the high amount of d-limonene sorbed by the EVOH based liner structure indicated that the

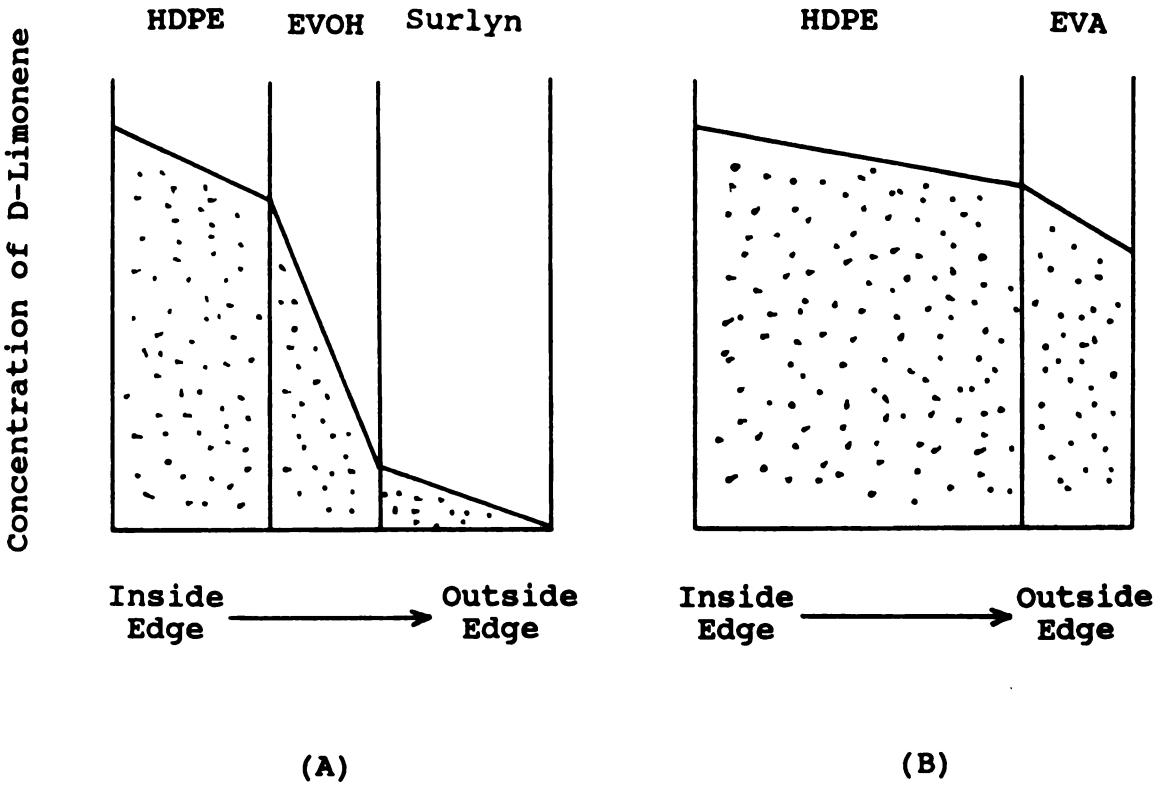


Figure 15. Hypothetical concentration profile of d-limonene at 25°C in two cereal liner structures at steady state of transmission.

transmission rate of d-limonene through the EVOH based structure was lowered due to the EVOH barrier layer. The model proposed to account for the results of headspace ananlyses and sorption studies involving the EVOH liner structure is illustrated in Figure 15 (A).

TRIANGLE TEST

The triangle test was used to determine if panelists could sensorially identify differences in aroma intensity between the two package liner systems as a function of storage time. These results are summarized in Table 8.

It was found that panelists could identify differences in d-limonene concentration intensity between the two cereal package liner structures at the confidence level of $P < 0.05$.

Months 5 and 6 in the triangle design seemed to be less significant ($P < 0.05$) than months 2, 3, and 4 ($P < 0.001$). This was probably due in part to panelists' fatigue during the last two testing months. Verification of this could be observed by the gradual shortening of testing time taken by panelists, by panelists' complaints, and by the truancy of panelists from their arranged testing time.

Table 8. Triangle test of cereal packaged in two liner systems during 12 months of storage at 23°C and 50% RH.

Storage Time (months)	Number of Panelists Identifying difference (N_c/N_t) [a]	Degree of difference (D) [b]
0	-	-
2	19/25 **	moderate (2.316)
3	17/25 **	much (2.706)
4	11/14 **	moderate (2.545)
5	11/18 *	moderate (2.545)
6	12/20 *	much (2.750)
9	11/20 *	much (2.681)
12	13/25 *	much (2.750)

(a) N_c is the number of judges who identified the odd sample correctly and N_t is the total number of judges.

(b) D is the mean which was obtained by multiplying the number of judges in each degree of difference with a numerical value given to that level (1=slight, 2=moderate, 3=much, and 4=extremely) and then dividing the summation by N_c.

* 5% significant level.

** 0.1% significant level.

CONSUMER PREFERENCE

Consumer preference was quantitatively measured and the results are presented in Table 9. Data showed that cereal packaged in the EVOH liner system was rated more acceptable than the same product packaged in the HDPE liner system ($P < 0.001$), even after 6 months of storage. This was due to the consumers' perception of a much higher aroma intensity in the EVOH liner packages than in the HDPE liner packages ($P < 0.001$). Cereal in an EVOH liner package was commonly rated by consumers in the "like moderately" category compared to the "like slightly" category for the product in the HDPE liner package.

It was found in the quantitation of consumer preference, that the degree of liking had a positive increasing relationship with the storage time ($P < 0.01$). For example, consumers felt that a longer storage time produced a more acceptable product. This information gives an important indication of the flavor quality of the product over the storage stability test.

Further analyses were conducted to locate the source of difference in the sensory preference. It was found that only the EVOH liner structure showed a negative relationship with storage time. Differences shown in the acceptability of consumer preference for products in the EVOH based liner structure were mainly due to consumers' changing attitudes over the storage time. The degree of acceptability of cereal

Table 9. **Consumer preference for cereal packaged in two package liner systems during 12 months of storage at 23°C and 50% RH.**

Storage Time (months)	Number of Panelists Identifying Stronger in Intenstiy (N_c/N_t) (a)	Degree of Difference (D) (b)	Acceptability (N_a/N_t) (c)	Degree of Preference (L) (d)
2	EVOH = 164/192 HDPE = 28/192	much (3.14)	EVOH = 133/192 HDPE = 59/192	EVOH = 6.47 (e) HDPE = 5.80 (f) t = 3.71 *
3	EVOH = 136/163 HDPE = 27/163	much (3.32)	EVOH = 110/163 HDPE = 53/163	EVOH = 6.72 (e) HDPE = 5.94 (f) t = 3.63 *
5	EVOH = 105/119 HDPE = 14/119	much (3.21)	EVOH = 86/119 HDPE = 33/119	EVOH = 7.13 (e) HDPE = 6.22 (f) t = 4.05 *
6	EVOH = 74/84 HDPE = 10/84	much (3.15)	EVOH = 61/84 HDPE = 23/84	EVOH = 7.06 (e) HDPE = 5.74 (f) t = 5.84 *
9	EVOH = 126/173 HDPE = 47/173	much (3.12)	EVOH = 109/173 HDPE = 64/173	EVOH = 7.11 (e) HDPE = 5.80 (f) t = 5.65 *
12	EVOH = 95/120 HDPE = 25/120	much (3.23)	EVOH = 83/120 HDPE = 37/120	EVOH = 7.01 (e) HDPE = 5.12 (f) t = 5.37 *

Table 9. (cont'd)

(a) N_c is the number of judges who identified stronger aroma intensity. N_t is the total number of panelists who participated in each test.

(b) D represents the mean which was obtained by multiplying the number of judges in each level of difference with a numerical value given to that level (1=slight, 2= moderate, 3=much, and 4=extremely).

(c) N_a is the number of judges who felt that they would purchase the cereal. N_t is the total number of panelists who participated in each test.

(d) L represents the mean which was obtained by multiplying the number of judges in each level of preference with a numerical value given to that level. In the 9-point hedonic scale, 9=like extremely and 1=dislike extremely respectively.

(e) Number represents "like moderately".

(f) Number represents "like slightly".

* 0.001% significant level.

packaged in the HDPE liner structure was seen to remain the same. This can be interpreted as people preferred the product packaged in the EVOH liner structure much more than that packaged in the HDPE liner structure.

CONCLUSION

The relative performance of two typical liner structures of a fruit-flavored cereal product, whose quality is associated with the retention of volatile aroma constituents, had been assessed by both qualitative (i.e. triangle test and consumer preference survey) and quantitative methods (i.e. d-limonene headspace concentration analysis and thermal distillation sorption test).

The results are summarized as follows:

(1) The d-limonene headspace concentration was found to be strongly time dependent. The EVOH liner structure had better barrier properties with respect to retaining aroma components within the packages, than the HDPE liner structure over the storage time considered.

(2) The amounts of d-limonene sorbed by the EVOH liner structure was significantly higher than by the HDPE liner structure over time. This was felt to be due to the differences in transmission rate of d-limonene in these two laminate structures.

(3) The sensorial difference between product packaged in the EVOH liner structure and the HDPE liner structure increased over time. However, it is felt

that, panelists' fatigue may be regarded in part for the differences to be less significant for the last two months' measurements.

(4) Consumers viewed the product packaged in the EVOH liner structure to be more acceptable than the same product packaged in the HDPE liner structure. Sensory responses showed that the degree of preference for only the EVOH lined packages increased over time. This indicated that consumers' preference was based on the intensity of the aroma constituents within the package.

The results from both the analytical measurements and the sensory evaluation support the hypothesis that the EVOH package liner structure is a better barrier than the HDPE liner structure in retaining the flavor quality of the fruit flavored cereal product.

APPENDIX

APPENDIX A

Standard Calibration

Table 10. Limonene/Ethyl Acetate Standard Calibration Curve Data as Measured by HP Gas Chromatograph Model #5890.

Initial Calibration: 8/10/1987

Area Response (A.U.)	Absolute Quantity (gm x 10^{-9})
0	0.00
75094	16.83
154500	33.65
264050	50.48
320620	67.30

Calibration Factor = 2.02 x 10^{-13} gm/A.U.

Recalibration: 10/17/1987

Area Response (A.U.)	Absolute Quantity (gm x 10^{-9})
0	0.00
49929	16.83
86731	33.65
161300	50.48
326020	67.30
435210	84.13

Calibration Factor = 1.98 x 10^{-13} gm/A.U.

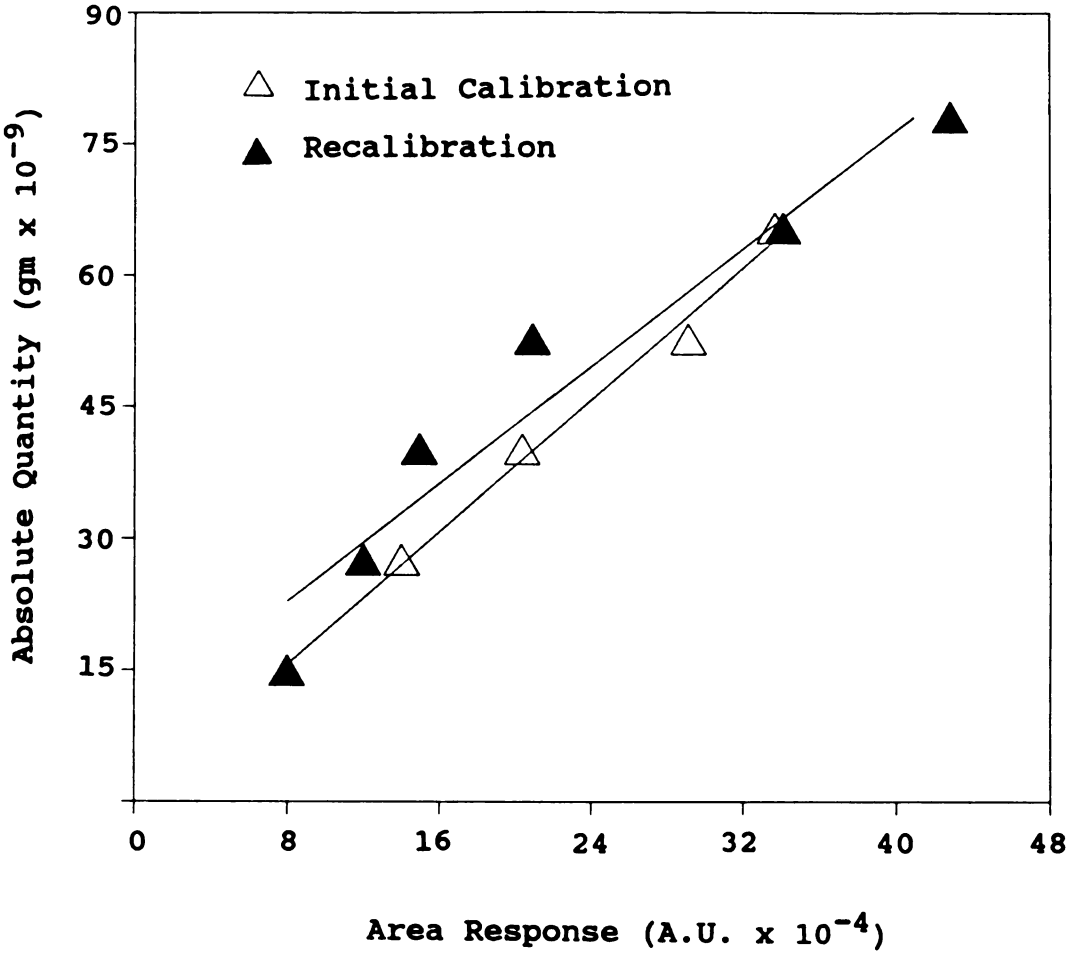


Figure 16. Limonene /Ethyl Acetate Standard Calibration Curve as Measured by HP Gas Chromatograph Model #5890.

APPENDIX B

Consent Form For Sensory Panel Members

Triangle Test Questionaire

Consumer Preference Questionaire

CONSENT FORM FOR SENSORY PANEL MEMBERS

School of Packaging
Michigan State University

Fruit Flavored Cereal Ingredients:

Rice, sugar, hydrogenated coconut and/or palm oil, corn syrup, salt, artifical color (includes yellow #5), natural and artifical fruit flavors.

The nature of the proposed study involves panelists comparing the sensory preference of a fruit flavored cereal product packaged in two commercial cereal liner systems as a function of storage time.

The product is a fruit flavored cereal product with predominant citrus flavoring which includes d-limonene as a major componene. D-limonene is a naturally occuring constituent of cold pressed orange and lemon oil which are used to provide the desired product aroma. Panelists will be asked to identify the presence of fruity flavor which includes d-limonene in the headspace of the cereal package as a function of storage time.

I_____ have read the above list of ingredients and find none that I know I am allergic to. I have also been informed of the nature of the study and the procedures which will be used during the sensory analysis.

I agree to serve on this survey panel, which is being conducted on this_____day of _____ 1988.

I understand that my anonymity will be protected during the reporting of results and that I am free to withdraw my consent and to discontinue participation in the panel at any time without panelity.

I understand that if I am injured as a result of my participation in this research project, Michigan State University will provide emergency medical care if necessary, but these and other medical expenses must be paid by my own health insurance program.

_____
Signature

_____
Date

NAME_____ DATE_____

PRODUCT_____

Test Procedure:

1. Two of these three cereal samples are identical, the third is different. In the order indicated, open one box of cereal at a time by tearing the liner. Then smell the sample. Identify the odd sample based on perceived aroma.

Code	Check odd sample
_____	_____
_____	_____
_____	_____

2. Indicate the degree of difference between the duplicate samples and the odd sample.

   Slight_____
   Moderate_____
   Much_____
   Extreme_____

3. Acceptability:

   Odd sample more acceptable_____
   Duplicates more acceptable_____

4. Check the degree of acceptability for the sample you have chosen in question 3.

   _____ like extremely
   _____ like very much
   _____ like moderately
   _____ like slightly
   _____ neither like nor dislike

3. Comments:

   Please describe the flavor and aroma you perceived and other factors which helped you to make your decision. If you have any suggestions for better evaluating the sensory qualities of the product, we welcome your comments. Thank you very much and enjoy your cereal!

NAME_____ DATE_____

PRODUCT_____

1. Evaluating the **aroma** in the cereal packages by opening the box of cereal on the **left** first, tearing the liner and smelling the sample. Check below which sample has the stronger **aroma**. (Do not taste samples!)

Code	Stronger in aroma
_____	_____
_____	_____

2. Check the degree of difference in odor between these samples.

Slight_____
Moderate_____
Much_____
Extreme_____

3. Which of these samples do you feel more acceptable?

_____	_____
_____	_____

4. Check how much you like or dislike each one.

	_____	_____
like extremely	_____	_____
like very much	_____	_____
like moderately	_____	_____
like slightly	_____	_____
neither like nor dislike	_____	_____
dislike slightly	_____	_____
dislike moderately	_____	_____
dislike very much	_____	_____
dislike extremely	_____	_____

5. Comments:

Please describe the flavor you perceived and other factors which helped you to make your decision. If you have any suggestions for better evaluating the sensory qualities of the product, we welcome your comments. Thank you very much and enjoy your cereal!

APPENDIX C

Headspace Analyses Data

Table 11. Data points of d-limonene headspace concentration analyses (area response obtained from GC reading).

Storage Time[b] (months)	D-limonene Area Response/Sample Code[a] (A.U./#)	
	HDPE liner	EVOH liner
2	618 (#132)	14627 (#359)
	1160 (#367)	14372 (#232)
	1182 (#167)	14146 (#128)
	0 (#007)	14875 (#058)
	0 (#047)	16738 (#192)
Mean=	592	14952
Standard Deviation=	524	926
3	0 (#370)	14416 (#395)
	0 (#365)	12320 (#214)
	907 (#251)	10881 (#048)
	0 (#326)	7932 (#036)
	0 (#084)	6845 (#003)
Mean=	182	10479
Standard Deviation=	363	2784
4	0 (#314)	7298 (#308)
	446 (#300)	7809 (#302)
	0 (#358)	7806 (#396)
	0 (#212)	7451 (#304)
	0 (#381)	6766 (#321)
Mean=	89	7426
Standard Deviation=	183	386
5	0 (#220)	8031 (#062)
	0 (#233)	8003 (#144)
	0 (#057)	7074 (#242)
	0 (#018)	7190 (#337)
	0 (#251)	7868 (#223)
Mean=	0	7633
Standard Deviation=	0	415
6	0 (#102)	10463 (#346)
	0 (#260)	9730 (#113)
	0 (#041)	10048 (#290)
	0 (#063)	10077 (#280)
	0 (#123)	10304 (#321)
Mean=	0	10124
Standard Deviation=	0	249

Table 11. (continued)

Storage Time (months)	D-limonene Area Response/Sample Code (A.U./#)	
	HDPE liner	EVOH liner
9	0 (#211)	11536 (#285)
	0 (#006)	7317 (#341)
	0 (#355)	8499 (#105)
	0 (#249)	9284 (#117)
	0 (#186)	7186 (#269)
Mean=	0	8764
Standard Deviation=	0	1588
12	0 (#057)	5185 (#097)
	0 (#012)	3312 (#257)
	0 (#370)	3328 (#286)
	0 (#224)	3103 (#275)
	0 (#232)	2992 (#145)
Mean=	0	3584
Standard Deviation=	0	811

(a) The code was generated from the random sampling plan. The hundredth number represents the tier number where the sample was withdrawn. For example, 231 means that the sample was pooled from second tier of the palletload.

(b) Samples were pooled from the top three tiers of the palletload at 2, 4, 6 months and from bottom three tiers at 3, 5, 9 months.

Table 12. Data points of d-limonene headspace concentration analyses (d-limonene headspace concentration [a]).

Storage Time (months)	D-limonene Headspace Concentration (gm/mL, ppb)	
	HDPE liner	EVOH liner
2	0.250	5.909
	0.469	5.806
	0.478	5.715
	0	6.010
	0	6.762
Mean=	0.239	6.040
Standard Deviation=	0.212	0.374
3	0	5.824
	0	4.977
	0.366	4.396
	0	3.205
	0	2.765
Mean=	0.073	4.233
Standard Deviation=	0.146	1.124
4	0	2.948
	0.180	3.155
	0	3.154
	0	3.010
	0	2.733
Mean=	0.036	3.000
Standard Deviation=	0.072	0.156
5	0	3.245
	0	3.233
	0	2.858
	0	2.905
	0	3.179
Mean=	0	3.084
Standard Deviation=	0	0.167
6	0	4.227
	0	3.931
	0	4.059
	0	4.071
	0	4.163
Mean=	0	4.090
Standard Deviation=	0	0.101

Table 12 (continued)

Storage Time (months)	D-limonene Headspace Concentration (gm/mL, ppb)	
	HDPE liner	EVOH liner
9	0	4.661
	0	2.956
	0	3.434
	0	3.751
	0	2.903
Mean=	0	3.541
Standard Deviation=	0	0.642
12	0	2.095
	0	1.338
	0	1.345
	0	1.254
	0	1.209
Mean=	0	1.448
Standard Deviation=	0	0.327

(a) Data obtained from multiplying the calibration factor (0.404 x 10-12 gm/a.u./mL) of standard solutions (d-limonene/ethyl acetate) by the area response from each GC injection.

Table 13. ANOVA Table for Headspace Analysis on Storage Time (Independent Variable) Versus D-Limonene Headspace Concentration in EVOH Liner System (Dependent Variable).

Source of Variation	SS	df	MS	F value
Treatments	59.21	5	11.84	35.88 *
Error	7.85	24	0.33	

* $F_{1-.01(5,24)} = 3.90$.

APPENDIX D

Sorption Analyses Data

Table 14. Data points of the thermal distillation sorption test.

Storage Time (months)	Quantity of D-limonene Sorbed (gm/gm liner, ppb)	
	HDPE liner	EVOH liner
3	13.86	101.51
	12.65	98.82
	10.98	103.66
	15.66	124.25
	18.80	122.79
Mean=	14.39	110.21
Standard Deviation=	2.68	10.99
4	18.21	92.10
	13.06	88.40
	14.09	87.34
	14.98	91.09
	17.63	91.57
Mean=	15.59	90.10
Standard Deviation=	2.00	1.88
5	25.21	55.92
	17.63	81.07
	21.54	75.35
	22.83	74.01
	23.27	58.91
Mean=	22.10	69.05
Standard Deviation=	2.53	9.84
6	8.78	42.50
	10.50	52.11
	9.22	57.15
	8.97	40.68
	10.71	44.06
Mean=	9.64	47.30
Standard Deviation=	0.81	6.29
9	N.D.[a]	18.71
	N.D.	20.35
	N.D.	14.15
	N.D.	10.98
	N.D.	18.51
Mean=	N.D.	16.54
Standard Deviation=	N.D.	3.46

Table 14. (continued)

Storage Time (months)	Quantity of D-limonene Sorbed (gm/gm liner, ppb)	
	HDPE liner	EVOH liner
12	N.D.	10.11
	N.D.	8.68
	N.D.	5.37
	N.D.	7.22
	N.D.	8.22
Mean=	N.D.	7.92
Standard Deviation=	N.D.	1.58

(a) N.D. means not detectable.

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