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ABSTRACT

THE AROMA PERMEABILITY AND SOLUBILITY OF TWO CEREAL PACKAGE LINER MATERIALS AND THEIR RELATIONSHIP TO PRODUCT QUALITY

by

Susan Marie Braun Mohney

Permeability and Solubility studies were performed on two typical cereal package liners using d-limonene vapor as the volatile test penetrant.

Permeability coefficient ($\overline{P}$) values were found to be concentration dependent and the relationship between $\overline{P}$ and vapor concentration can be represented by an exponential equation. The glassine based structure exhibited between three to four orders of magnitude reduction in relative permeability as compared to the polyolefin structure, over the entire vapor concentration range studied. Solubility coefficient values were determined by an independent procedure, involving gravimetric analysis.

Additionally, a qualitative relationship was established between the limonene headspace concentration and sensory evaluation for a packaged fruit-flavored cereal product. Results from these studies indicate that the loss of volatile aroma moities may be due to sorptive and/or permeation mediated processes and both mechanisms must be considered in packaging a product where quality is associated with the retention of aroma compounds.

DEDICATION

This thesis is dedicated to my family in appreciation and thanks for their assistance and guidance through all my academic endeavors.

Also, to my husband for his patience and support throughout this work.

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INTRODUCTION

Volatile, low molecular weight organic compounds, represent important constituents of foodstuffs because of their influence on the characteristic odor and taste properties of a food. In general, protection against the loss of volatile aroma constituents from foodstuffs may be achieved through the selection and use of appropriate packaging materials. The intensity of the aroma of a packaged foodstuff thus depends, at least in part, upon: (i) the vapor pressure of the individual components of the total aroma; (ii) the interaction of these volatile organic moieties with non-volatile food components; and (iii) the aroma barrier characteristics of the package.

The solubility and transport properties of the aroma moieties-package system, is of major concern in the selection and use of plastic packaging materials for food packaging. Because of this inherent concern with plastic packaging materials and their wide utilization in food packaging, this work deals specifically with the interrelationship between mass transport and the shelf life of a product whose quality is associated with the retention of volatile aroma moieties.

The phenomenom of permeability can be considered a function of penetrant diffusion (D) and penetrant solubility (S) in the polymer matrix. The diffusion coefficient (D) is the rate which a penetrant molecule moves through the film and the solubility coefficient (S) describes the number of penetrant molecules permeating the barrier. For fixed or non-interactive gases the permeability coefficient ($\overline{P}$) is related to the two fundamental mass transfer parameters by (Crank & Park, 1968)

$$\overline{P} = D \times S \tag{1}$$

However, unlike the transport properties of non-interacting penetrants, for permeability involving organic penetrants and multilayer laminate structures, this simple relationship is not always applicable. For organic penetrants, the penetrant/barrier system can exhibit non-ideal diffusion and solubility properties due to the swelling of the polymer matrix by the sorbed organic penetrant (Crank, 1975; Berens, 1977; Bagley and Long, 1958; and Fujita, 1961). Thus, for such cases, diffusion, solubility and permeability data determined experimentally are necessary to completely describe the mass transfer and sorption behavior between organic vapors (i.e. aroma compounds) and a multilayer polymeric barrier structure.

Knowing the solubility of essential flavor ingredients in polymer structures typically used for food packaging is of paramount importance in avoiding the effect of "flavor scalping" or loss due to sorption. For example, d-limonene, a common flavor component present in citrus foods, has a relatively high solubility in polyolefins (DeLassus, 1985). Since aroma compounds such as d-limonene are normally present in low concentrations in a foodstuff, there is an increase in the potential for "lose" of the aroma constituents due to their absorption by the packaging materials (i.e. solubilization). DeLassus (1985) has alluded briefly to this phenomenom in his discussion of barrier layer location in multilayer structures. Further, knowledge of the diffusion coefficient (D) and permeability coefficient ($\bar{P}$) can provide information with regard to the time required to attain a steady rate of transmission and the steady-state permeation rate, for a specific penetrant/polymer system under some end-use application.

The studies reported here were undertaken to determine under well defined experimental conditions, the relationship of mass transport to the storage stability of a packaged fruit flavored cereal product, whose quality is associated with the retention of volatile aroma constituents. It is proposed that a selected volatile organic compound, or selected compounds contributing to product aroma be identified and the permeability and solubility of these moieties through the barrier films be determined. Such a constituent (or constituents) should be selected, based upon their contributions, to perceived product quality. d-Limonene, a compound present in the products aroma profile, was selected as the probe aroma compound to be monitored, because of its recognizable sensory characteristics and its ease of analysis.

Seperate studies were performed involving permeation and sorption measurements of d-limonene vapor to evaluate the barrier properties of two typical cereal package liners, namely a high density polyethylene/sealant[1] laminate structure and a wax/barrier/glassine/barrier/wax structure. The specific objectives included developing an accurate and reproducable method of measuring the permeability of d-limonene vapor through the selected packaging films and evaluating the effect of d-limonene partial pressure on the permeation rate. The solubility of d-limonene vapor in the respective film samples was also determined using a gravimetric technique, at a series of penetrant concentration levels.

Sensory analysis was carried out to evaluate the effectiveness of the glassine based structure in providing the necessary protection from loss of aroma. A qualitative relationship between d-limonene headspace concentration and perceived product quality was developed by packaging cereal product of varying d-limonene concentration in the glassine based structure. After allowing the system to equilibrate, the packaged product was evaluated by sensory analysis and

[1] Sealant is a polyblend of EVA, Surlyn and Polybutalene.

the amount of d-limonene in the headspace quantified.

In summary, the major objectives of this study were to:

(1) Evaluate the quality of a fruit-flavored cereal product undergoing loss via aroma permeation and/or sorption,

(2) Determine the aroma barrier properties of selected packaging liner materials to d-limonene vapor,

(3) Determine the effectiveness of the package liner materials for use under the specified d-limonene concentration levels and conditions of storage,

(4) Evaluate the effect of permeant concentration on the permeation constant of the respective film structures (concentration dependency),

(5) Determine the solubility of d-limonene in the respective film structures,

(6) Compare the barrier properties of the HDPE based structure and the glassine based structure as a function of d-limonene vapor concentration,

(7) To establish a qualitative relationship between d-limonene headspace concentration and sensory evaluation, and

(8) Indicate the mechanism responsible for the loss of volatile aroma constituents.

LITERATURE REVIEW

THE USE OF BARRIER MATERIALS

Preservation of food from environmental hazards is of major concern in food packaging. Oxygen, moisture, light and organic flavor compounds are to name but a few of the variables important in maintaining the quality of a product. Adverse conditions such as temperature, humidity, contamination, and adsorption of off odors may reduce the quality of even the finest products.

There is a definite movement towards the use of barrier plastics for food packaging applications. A recent survey (Hamilton, 1985) predicts a 72% annual growth rate over the next 12 years in the use of barrier films. Such growth is expected to occur based on:

- "New packaging manufacturing processes that will allow barrier plastics to be commericialized,"
- "New barrier and adhesive resins for use in sophisticated coextrusions", and
- "Increasing consumer acceptance of plastics for food packaging."

In the past, food packaging has been concerned primarily with problems associated with the transmission of oxygen, carbon dioxide and water vapor through the polymer structures (Manathunya, 1976; Gyeszi, 1971). Standard test methods were available to determine the transmission rates for these permeants (ASTM E96-66, ASTM D3985-81). More recently, the transport of organic vapors through polymeric packaging materials has become of increasing importance and has been the subject of several recent investigations (Gilbert, et al., 1983; DeLassus, 1985; Hamilton, 1985; Baner, et al., 1986).

Food packagers rely on the package to protect food from potential changes in sensory qualities (Hamilton, 1985). Undesirable odors are likely to occur in storage and handling and can be transmitted to other goods. Since with many foodstuffs, there is no natural protection against the loss of aroma nor the take-up of foreign odors from the environment, this is generally achieved by the use of appropriate packaging materials.

MASS TRANSFER PARAMETERS

The rate at which a gas, vapor, or liquid will pass through a film sample is dependent on several factors (Giacin, 1983; Gilbert, et al., 1983). These factors may be controlled by the properties of the material (degree of crosslinking, cystallinity, and size of lattice area for molecular passage), the properties of the gas, vapor, or liquid (degree of volatility, the size and shape of the permeating molecule), and/or the degree to which interaction occurs between the permeant and the film sample forming the barrier. Environmental conditions such as temperature and relative humidity affect the rate of permeation as well. Other parameters to consider are the concentration gradient, thickness of laminate structure as well as the gauge of the individual laminate plies and the surface area exposed.

Migration, absorption/adsorption, wicking/delamination, package catalyzed reaction, swelling and/or delamination, are among the list of potential compatability problems facing a product and its primary package (Giacin, 1986). Only recently has there been experimental evidence illustrating the importance of both permeability and solubility in understanding the behavior between penetrant/polymer interaction (Baner, 1986; DeLassus, 1985; Hernandez, 1984).

Crank & Park (1968) describe the Permeability Coefficient ($\overline{P}$) as the product of Solubility and Diffusion ($\overline{P} = D * S$); where:

Permeability ($\overline{P}$) is a measure of the ease with which a gas or vapor can pass through a polymeric structure, as a function of the end use application,

Solubility (S) is that which adheres to the matrix of a polymer film structure causing changes to occur in the physical as well as mechanical properties (i.e. swelling, bowing, molecular separation), and

Diffusion (D) refers to the rate at which a permeant is transmitted from a volatile (or high) vapor phase surface area, through to a non-volatile (or low) surface area [path length (cm^2)/time (sec)]. In other words, the rate which a molecule travels in the process of diffusion.

For gases, such as oxygen, a linear relationship exists between penetrant concentration and the permeability coefficient (independent of concentration). Results obtained from tests performed at high or low levels of penetrant concentration allow for extrapolation in estimating the results for other concentrations. This is not necessarily true for aroma permeability. As pointed out by Hamilton (1985) "Many equate aroma protection to oxygen permeability but this relationship is at best tenuous".

Zobel (1982) reported that "in many organic vapour/packaging film combinations, the permeability coefficient is strongly dependent upon concentration. This effect occurs because the vapour interacts with and swells the polymer, increasing the permeation rate. When exposed to certain saturated vapours, this effect can be so extreme as to cause distortion of the film, resulting in very high permeation rates limited principally by the rate at which the vapour is removed from the surface of the film."

Zobel (1982) also noted that "much of the published work has involved the use of saturated solvent vapours.

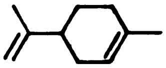
Whilst these data are useful in estimating how well a packaging material will withstand accidental high-level contamination, it is not valid to use such data to estimate permeation rates at the very much lower levels of vapour encountered in typical retailing situations, whether from foreign contaminating odours or from the flavour components within the package."

For cereal product containing volatile aroma constituents, vapor is absorbed onto the surface layer of the film and will either pass through to the other side or adhere to the matrix of the polymer film. That portion trapped within the matrix of the film may cause the film to swell. Permeability data in conjunction with solubility data are therefore integral parts of any study involving the storage stability of a product whose quality is related to the retention of aroma constituents.

Berens (1978) presented a detailed review of a sorption method for measuring the sorption and diffusion of small molecules in polymers. In the case of polyolefin structures (i.e. High Density Polyethylene, a non-polar polymer) swelling was observed when subjected to a non-polar substance such as d-limonene (DeLassus, 1985). When swelling takes place, diffusion, permeability and solubility change.

d-Limonene

d-Limonene, a hydrocarbon which occurs in essential oils, has recognizable odor properties (lemon) which can be monitored by sensory and gas chromatographic (G.C.) methods. Hydrocarbons contain only the elements hydrogen and carbon (Hart & Schuetz, 1978). d-Limonene, an unsaturated hydrocarbon contains double bonds. When two double bonds are present, the compounds are called alkadienes, or more commonly, just dienes. d-Limonene is characterized (Weast, et al., 1985 - 1986) by the following:

Structural Formula: 

Molecular structure = $C_{10} H_{16}$

Molecular Weight = 136.24

Density = 0.842 g/ml

Boiling Point = 178 °C

Melting Point = -74.3°C

Molar Density = 6.17 x 10-3 gmole/ml at 25°C

Soluble in: Ethyl Alcohol, Diethyl Ether

Vapor Mole fraction in equilibrium with pure liquid = 1.9 x 10-3 at 25°C

Among the essential oils, d-limonene constitutes over 90% of orange oil (fruit). "Essential oils are mixtures of various volatile organic substances along with some non-volatile waxy materials." The term "oil" does not refer to any chemical characteristic but rather implies these substances are insoluble in water and soluble in non-polarsolvents" (Amerine, et al., 1965).

METHODS OF ANALYSIS

The loss of odor/flavoring components were first studied in the forties and fifties through means of direct gravimetrical analysis for products packaged in plastic lined containers (Becker, et al., 1983).

Research and technology have developed more effective methods to analyze the chemical nature of various aromas within the last two decades. Although aroma/flavor research has been under investigation for many years it has not been until recently that methods have been developed to quantitatively measure barrier properties of polymeric films to a variety of organic penetrants (Zobel, 1982; Gilbert, 1983; Murray & Dorschner, 1983; Murray, 1985).

The majority of published studies have used the method developed by Barrer (1939). In studies involving an organic substance, a constant saturation vapor pressure is exposed to one side of a test film, while a vacuum is maintained on the other side so as to generate permeation. This is refered to as the Absolute Pressure Method.

Here the Absolute Pressure Method is one of three quantitative procedures used to obtain diffusion data of organic vapors in semi-permeable membranes. The other two procedures include the Quasi-Isostatic Method and the Isostatic Method (Giacin, 1983).

The Absolute Pressure Method incorporates an apparatus where no gas other than the permeant in question is present. A pressure differential, provides the driving force for permeation between two chambers. Here, the permeation rate is determined from the change in pressure on the volume of the low pressure chamber of the cell.

Zobel (1982) developed an isostatic method for measuring the permeability of packaging films to organic vapors at low penetrant concentrations and described a modification of the procedure which incorporated an adsorption/desorption cycle (Zobel, 1984, 1985). In the Isostatic Method, both chambers of the permeation cell are maintained at atmospheric pressure. The gas which permeates through the film and into the lower chamber of the cell system is swept to a detector system by use of an inert carrier gas. Quantitative measurement, by means of gas chromatographic (G.C.) analysis, are then employed to determine the presence of a partial pressure differential or a concentration gradient between the two cell chambers. Hernandez (1984) and Baner, et al. (1984, 1986) have employed both isostatic and quasi-isostatic test methods in evaluating the diffusion of organic penetrants through barrier films.

The Quasi-Isostatic Method is a modification of the

Isostatic Method. Murray & Dorschner (1983) developed an accumulation method for determining the permeability of organic vapors through barrier films and in a more recent publication, Murray (1985) expanded on this procedure and reported a number of examples for which the test apparatus was employed to determine the "relative permeation rates" of organic vapors through barrier structures.

Three related procedures which are based on the Quasi-Isostatic method are (Giacin, 1983):

(1) In this process, the system is maintained at atmospheric pressure. One chamber of the test cell allows for a continuous flow of permeant vapor while the other portion(s) of the cell system contains the gas or vapor which has permeated through the test material. Samples are withdrawn from each of the concentration chambers of the cell system at predetermined time intervals and injected into the G.C. for quantitative measure. From the concentration data, the film permeability can then be determined.

(2) In this technique the penetrant gas or vapor thoroughly purges the upper chamber of the cell which is then closed. G.C. analysis is used to monitor the gas concentration in both the upper and lower chambers initially, and throughout the permeation run at predetermined time intervals.

Permeability can be determined from the difference in pressure between the cell chambers or from concentration data.

(3) In this method the lower chamber of the permeation cell is filled with a liquid above which is maintained permeant vapor at a constant partial pressure. The vapor permeating into the upper chamber is then monitored as a function of time until the permeation rate reaches a steady state. In most cases, the concentration of permeant in the upper chamber is determined by G.C..

Odor/flavor quantification is most commonly obtained through means of Flame Ionization Detector (FID) systems, such as that used in G.C. analysis. "Ionization detectors operate on the principle that the electrical conductivity of a gas is directly proportional to the concentration of charged particles within the gas." (Giacin, 1983) "The effluent (flowing out or forth) gas from the column is mixed with hydrogen and burned in air or oxygen." "The FID responds to virtually all organic compounds. The lack of response to air and water make an FID especially suitable to headspace analysis of aqueous samples."

Gas Chromatography(GC), Gas Chromatography/Mass Spectrometry(GCMS) and High Pressure Liquid Chromatography (HPLC) methods are frequently utilized in mass transport studies. Separation and identification of several hundred to thousands of components naturally occuring in aromas may be accomplished by such methods. It is possible to correlate the quality of a food product based upon permeation and sorption values with that relating to sensory evaluation.

Recently, DeLassus (1985) described the transport of d-limonene vapor through a series of polymer films typically used in food packaging. Permeability ($\overline{P}$) was determined from experimental data, diffusivity (D) was calculated from a derived equation, and the solubility coefficient (S) was calculated from the equation $\overline{P} = D * S$ using measured values of $\overline{P}$ and D.

In this study, limonene was used as the penetrant vapor, with argon as the carrier gas. Measurement was made through means of a Photoionization Detector. Five films, of different structures, were evaluated. The data showed that as the test temperature increased, the permeability and diffusivity values rose, while a decrease in the solubility coefficient was observed.

The permeability ($\overline{P}$) of a Saran^R film was found to be up to four orders of magnitude lower than that determined for a polyolefin structure. However, little difference was noted with regard to the solubility coefficient values.

Theoretical analyses (or modeling) were applied to two product/package systems; Package System (1), a rigid 6 oz. polypropylene (PP) container and Package System (2), a thin-walled LDPE package. Orange juice was contained in each of these containers. A summary of DeLassus's findings are described below.

Pkg. System (1): The initial quantity of d-limonene in the container (i.e. 0.09 gm) was determined to be well above its saturation in either water or sugar water therefore the contents would provide a concentration pressure gradient of d-limonene.

Information on the vapor pressure of d-limonene at two specific temperatures of interest (25^oC and -5^oC) was obtained from the literature. Permeability of d-limonene and the solubility coefficient values were estimated from theoretical analysis to determine the steady state rate of diffusion at each temperature.

In calculating the potential loss of d-limonene due to sorption, the values obtained were higher than the initial amount of d-limonene in the product.

Application of the expression,

$$D = \frac{L^2}{7.2 * t_{1/2}}$$

[Where: D = diffusivity; L = film thickness; and $t_{1/2}$ = the time required to reach half of the steady state rate], indicated that the time to reach a steady state rate of diffusion was very long, being on the order of 10^3 to 10^5 days. Therefore, DeLassus concluded that for the rigid

Polypropylene container, all important losses of d-limonene were sorptive.

As previously noted, the solubility values were essentially the same for both polymers. The permeability of the Saran^R polymer is much lower than the PP, therefore virtually all of the d-limonene pressure drop will be across the barrier layer, Saran^R.

When adding a layer of Saran^R to the inside wall of the PP container, the permeability barrier is significantly improved. Thus, the PP layer becomes temporarily isolated from sorption, reducing the sorption capacity of the container.

Pkg System (2): DeLassus's results suggest that for the thin-walled LDPE package, a very significant loss due to permeation would occur within one day. Losses due to sorption however, would not be as severe when compared to the permeation barrier requirements. The author proposed that the permeation rate of d-limonene through the LDPE package could be reduced by as much as 10^{-6} g/day by adding a barrier layer of Saran^R to the LDPE structure. Placement of the barrier material in the overall structure is not as critical a factor in this package system. Presumably, the sorption loss in the LDPE layer would occur quickly as compared to several months for loss to be detected in the barrier layer. Applying the barrier film to the skin layer between the LDPE and the contents would reduce sorption in

LDPE to approximately zero.

Conclusions: "A barrier layer would help both the rigid container and the thin-walled container. Sorption is controlled in the rigid container. Permeation is controlled in the thin-walled container." If the quality of a product, based on its aroma characteristics can not be maintained, "it makes little difference if a molecule is lost by permeation to the enviornment or by sorption in the package wall".

AROMA

Defining odor is a difficult task. If one were to establish that odor is "that which can be smelled" then the question remains "by whom?". Since it is impossible to deine odor in physical terms it has been suggested that it be defined in terms of "phenomenolgy"[2].

Sagarin (1954) proposed a phenomenological definition: "Odor is the property of a substance that is perceived, in the human and higher vertebrates, by inhalation in the nasal or oral cavity; that makes an impression upon the olfactory area of the body; and that, during and as a result of such inhalation, is distinct from seeing, hearing, tasting, or feeling, and does not cause or result in choking,

[2] The scientific investigation or description of phenomena.

irritation, cooling, warmth, drying, wetting or other functions foreign to the olfactory area. A phenomenological definition places the responsibility on the individual."

Odor can also be defined in "physiological"3 terms: "sensations perceived from responses of the olfactory nerve or first cranial nerve" (Amerine, et al., 1965).

The physiological significance of an odorous substance is that it can easily stimulate appetite. Because odors may attract or repel consumers, the food industry is cognizant of its importance. The task of producing, increasing, or maintaining aroma is not the responsibility of the food technologists alone but also includes those involved in the preparation, processing, packaging and storage of foodstuffs.

Odor: Characteristics & Molecular Structure

The detection of odor occurs when molecules of volatile substances reach the olfactory receptors at the top of the naval cavity. All known odorous substances are gases having a high vapor pressure and boiling below 300°C (Amerine, et al. 1965). Odor is perceived from molecules having neither too low nor too high a molecular weight. Odor intensity increases with increasing molecular weight, however, "the characteristic odor of a chemical compound (which is

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[3] pertaining to the functions of living organisms.

specific for that compound) decreases with molecular weight in a homogeneous series" (Amerine, et al, 1965). Compounds having a molecular weight greater than 300 are characteristically odorless, according to Stoll (1957). "This is particularly due to the low volatility of such compounds and partially to differences in structure" (Amerine, et al., 1965).

Research on aromas is difficult due to associated complexities. An enormous variety of organic materials exist each having its own structural significance (aliphatic, aromatic, saturated and unsaturated hydrocarbons, etc...).

Molecules of quite dissimilar structure may have similar odor properties. Amoore (1952) stipulated "that the odorous properties of any compound depend on its volatility and on the size, shape, and electronic status of its molecule." "Double bond and ring structures are associated with odor." "The quality and intensity of odor are influenced by the position of the double bond in the molecule, the distribution of electrons, resonance or induction of the molecule (particularly in the 5- or 6-membered rings), and the kind of group adjacent to the osmophore. [Osmophore refers to a chemical entity which confers odor on an otherwise odorless compound. Strong osmophores include phosphorus, arsenic, sulfur, selenium, chlorine, and bromine (Amerine, et al., 1965).] In general, molecules with greater adsorption capacity are more odorous" (Amerine, et al., 1965).

Rigid molecules of specific shape have been found to be more effective olfactory stimuli than flexible molecules. Odor may be attributed to the internal attractive forces of the compound and by the size and shape of the molecule. Odor may also be influenced by the polarity and form of the molecules (DeLassus, 1985; Amerine, et al., 1965).

Cyclic or polycyclic compounds (rigid structures) are more odorous than aliphatic compounds (less rigid structures). "When the stereoisomerism is the result of a ring, the kind of odor and their intensity vary. Optical isomers generally have very similar odors. The odor of cis and trans - isomers is very distinct but their intensities are about the same (Amerine, et al., 1965).

When performing research where odor is of prime importance, a volatile organic compound (or compounds which contribute to product aroma) should be identified prior to the initiation of work. Such a consitiuent (or constituents) should be selected based on contribution to perceived product quality. In monitoring the behavioral characteristics of odorous substances, a sample must be isolated under controlled conditions.

Sensory Analysis (selecting panelist)

Observation based on past research shows that the sense of smell is more highly developed than the sense of taste (Parker & Stabler's 1913). The human sense of smell is the best way by which to initially detect the quality of a food product, but unfortunately odors cannot be measured quantitatively by the nose. In conducting experiments it is difficult for normal individuals to indicate differences associated with odorous substances.

For sensory evaluation to be significant, a panel should consist of either six highly trained judges or fifty untrained judges. Semi-trained judges may also be used if at least ten to fifteen individuals are able to differentiate and identify a set of samples (Filadelfi, 1985; Hamilton, 1985).

Although not always possible to find, highly trained experts are more useful in evaluating quality. Metzner (1943) noted that a connoisseur is not necessarily more sensitive to stimuli but instead attributes his or her skill to knowledge of what signs to look for and how to interpret them.

If threshold tests are selected then judges must have the ability to detect specific properties (semi-trained or trained individuals). Laboratory panels are generally used as qualified judges in studies involving human perception of food attributes. Threshold refers to the "value which gives the limiting concentration at which an odor is still just perceived" (Amerine, et al., 1965). Consumers are seldom trained and presumably react similar to an untrained laboratory panel.

Consumers, normally unfamiliar with taste tests, are generally influenced by appearance. Many times color changes are accompanied by undesirable change in odor. Therefore, objectives should be established (initially) and well understood by all subjects involved in sensory evaluation. Food attributes, such as color and texture should not distract panelists when performing odor evaluations on products.

Many precautions should be followed when doing taste panel work. Panel members should avoid such things as coffee, mints, smoking, perfume, and any other substances which may interfer with the odor of interest, at least 30 minutes prior to the test (Filadelfi, 1985).

Hammer (1951) found that sensitivity increases throughout the day if no lunch is acquired. Furchtgott and Friedman (1960) found that a mild degree of hunger lowers the olfactory thresholds - but only slightly and not in all individuals. In physiological terms, research indicates that appetite is affected by odor. After meals, Mancioli (1921) observed a decrease in olfactory insensitivity which was attributed to excessive stimulation of the olfactory region (during eating). Olfactory sensitivity may be due to alcohol, sugar, and amphetamine (10 mg) (Amerine, et al., 1965). By including tannic, tartaric, or acetic acid with a meal preserves after eating acuity.

Kuehner (1954) pointed out that extreme variations in sensitivity may occur in an individuals response and found it necessary to "standardize" a subject from day to day. With some compounds the age of a panelist may effect the olfactory threshold (Fortunato, 1958; Fortuneto and Niccolini, 1958).

The ability to smell is limited by a fatigue factor causing interference in the detection of similar odors, but rarely affects the detection of dissimilar odors. Interference may be caused by several factors (Amerine, et al., 1965) including: fatigue, obstructed nasal passages, partial anosmia (loss of the sense of smell), brain lessions, or injured olfactory. In addition, it is possible for one odor to overwhelm another.

Fatigue tends to set-in and remain more so in sniff studies than in sight, sound, or taste evaluations (Amerine, et al., 1965). In certain cases, loss of the sense of smell may be beneficial providing it's a different odor than that being evaluated.

Sensory rooms should be ventilated, have odor free air, good lighting, and partitioning between individuals. Odors move downwind, thus in certain situations, some odors could be detected from a distance causing erroneous conclusions.

The period set aside for sniffing should also be controlled. The time of day, number of samples per test period, frequency of tests per day (and/or per week), and time allotment per sample, are all factors to consider (Filadelfi, 1985).

Interference may arise if care is not exercised in selecting the appropriate medium for test specimens. The material selected must maintain and not react with the quality of a particular product (Filadelfi, 1985; Harte, 1985). The container opening should be wide enough to allow a subject to sniff an adequate quantity of the odor upon first opening the sample. Thus the type and ease of opening of a container is also of great importance.

An adequate and simple technique for odor (threshold studies) determination is through sniffing. This technique is popular, inexpensive, and in most cases easy to perform with large numbers of subjects. Means of expressing the intensity of the stimulus vary.

Analysis involving new or improved packaged products may be evaluated through means of scoring tests. Large consumer groups are necessary to determine consumer reaction to new or improved packaged products. This type of test is also valuable for quality control, storage stability, screening of intensity levels, and measuring panel characteristics (reproducibility).

In detecting a difference between two items, a pairedstimuli procedure is followed (Harte, 1982). A similar study, involving three samples, is known as a triangle test. Here one of the three samples is identified as being different.

A test more effectively applied by untrained consumers refers to Hedonic scaling (Amerine, et al., 1965). Judges express the degree of liking by selecting a point on a scale ranging from extreme disapproval to extreme approval. Values obtained are treated by rank analysis or analysis of variance.

Sensory panels may base their judgements on an acceptance or preference basis (Amerine, et al., 1965). In accepting a product, the panelist shows a willingness to use or eat a product. Where as, preference relates to a greater degree of acceptance of one product over another.

Sensory stimuli makes it possible to recognize certain foods and choose food in accordance to our needs. It also initiates appropriate responses in establishing digestion, promotes satiety, and makes it possible to anticipate the pleasure of eating (Amerine, et al., 1965). Odor is often the key to consumer acceptance of foods (Hamilton, 1985).

Detecting a difference in taste is seemingly an easier task than with odor. Measurement of the odor threshold, which directly relates to loss of quality can be a difficult and lengthy task (depending on the product and type of organic compound).

Odor quality is retained more precisely than odor intensity (Amerine, et al., 1965). Moncrieff (1957) termed odor-intensity as "the ratio of the olfactory threshold determined after sniffing the undiluted substance, to the threshold determined after sniffing the diluent". In other words, the more diute a sample, the less smell detected, and the lower the odor-intensity [full strength/diluent].

The human sense of smell is the best means by which to initially detect the quality of a food product, but unfortunately these odors cannot be measured quantitatively by the nose. Therefore, sensory tests are correlated with chemical measurement in the determination of a products quality and/or its shelf life (DeLassus, 1985; Wyatt, 1985; Zobel, 1985; Amerine, 1965).

MATERIALS AND METHODS

MATERIALS

Analytical grade d-limonene, obtained from Eastman Kodak Company (Rochester, N.Y. 14650), was used throughout this study. The films which were evaluated included two typical cereal package liners, namely a High Density Polyethylene/Sealant laminate and a Wax/PVOH[4]/Glassine/PVOH/Wax structure. Throughout the remainder of this thesis, the d-limonene will be refered to simply as limonene, the High Density Polyethylene/Sealant Laminate liner will be referred to as the HDPE base structure and the Wax/PVOH/Glassine/PVOH/Wax liner will be referred to as the glassine base structure. The composition of the two film structures are as follows:

* HDPE BASE STRUCTURE

(1.9 mil Thickness)	POUND/3000 ft^2
Total weight	33.5
HDPE	27.9
Sealant	5.6

* Obtained from supplier of film.

---

[4] PVOH refers to Polyvinyl alcohol.

* GLASSINE BASE STRUCTURE

(2.2 mil Thickness)	POUNDS/3000 ft^2
Total weight	38.3
Wax	9.0
PVOH (polyvivyl alcohol)	
Coating	2.4
Glassine	26.9

* Obtained from supplier of film.

Film samples were stored in a desiccator over $CaSO_4$ desiccant (0% relative humidity) at ambient temperature (23 C) prior to testing. The product chosen for evaluation involved a fruit flavored cereal, whose quality is associated with the retention of volatile aroma constituents. The product was purchased, as fresh as possible, from Michigan State University stores.

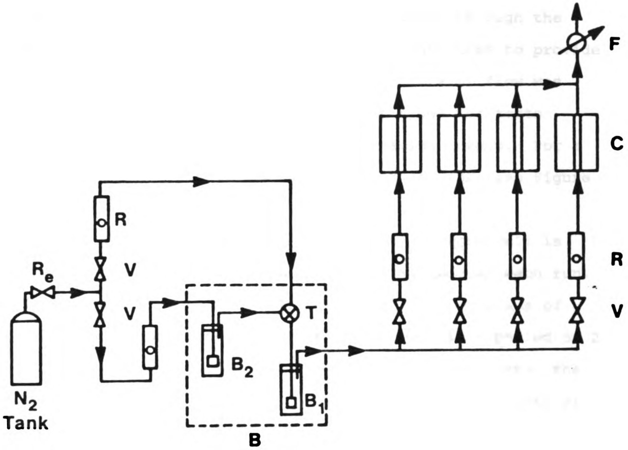
EXPERIMENTAL METHODS

Permeation Measurements

The transmission rate, as determined by a Quasi-Isostatic method, 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 refered to as "Quasi-Isostatic" because the test compartments are maintained at an essentially constant total pressure of 1 atmoshpere. 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 1. 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. The apparatus was designed to have the capability of controlling penetrant concentration through a broad range of levels. The effect of limonene partial pressure on the permeation rate and permeability coefficient was determined over a concentration range of 0.4 to 3.6 ppm (HDPE based) and from 1.5 to 4.8 ppm (Glassine based) for the respective film structures. 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 means of dampening perturbations. The vapor generator system was mounted in a constant temperature water bath,



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 1. SCHEMATIC OF QUASI-ISOSTATIC PERMEATION TEST APPARATUS

maintained at 1^{0}C above ambient temperature so as to avoid condensation after the permeant vapor passed through the glass reservoir. As shown, flow meters were used to provide a continuous indication that a constant rate of flow was maintained. A micro-flow meter was utilized for tests performed at the low permeant concentration levels. For a better illustration of the permeation apparatus, see Figure 2.

Care is taken to ensure that the permeation cell is free of limonene vapor prior to the initiation of each run. 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 trace 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 baked in a 43^{0}C (110^{0}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 3 provides a detailed view of the Permeant Cell System. Each permeability cell,

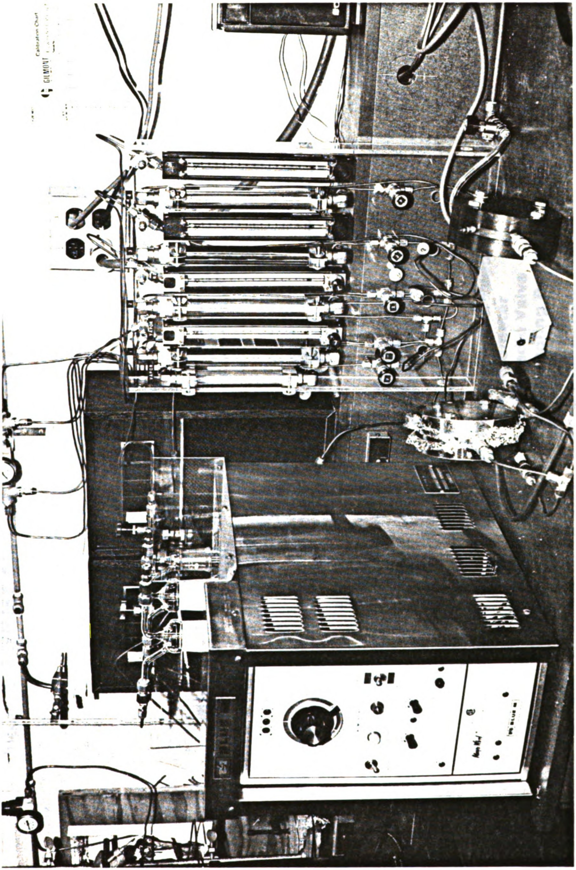
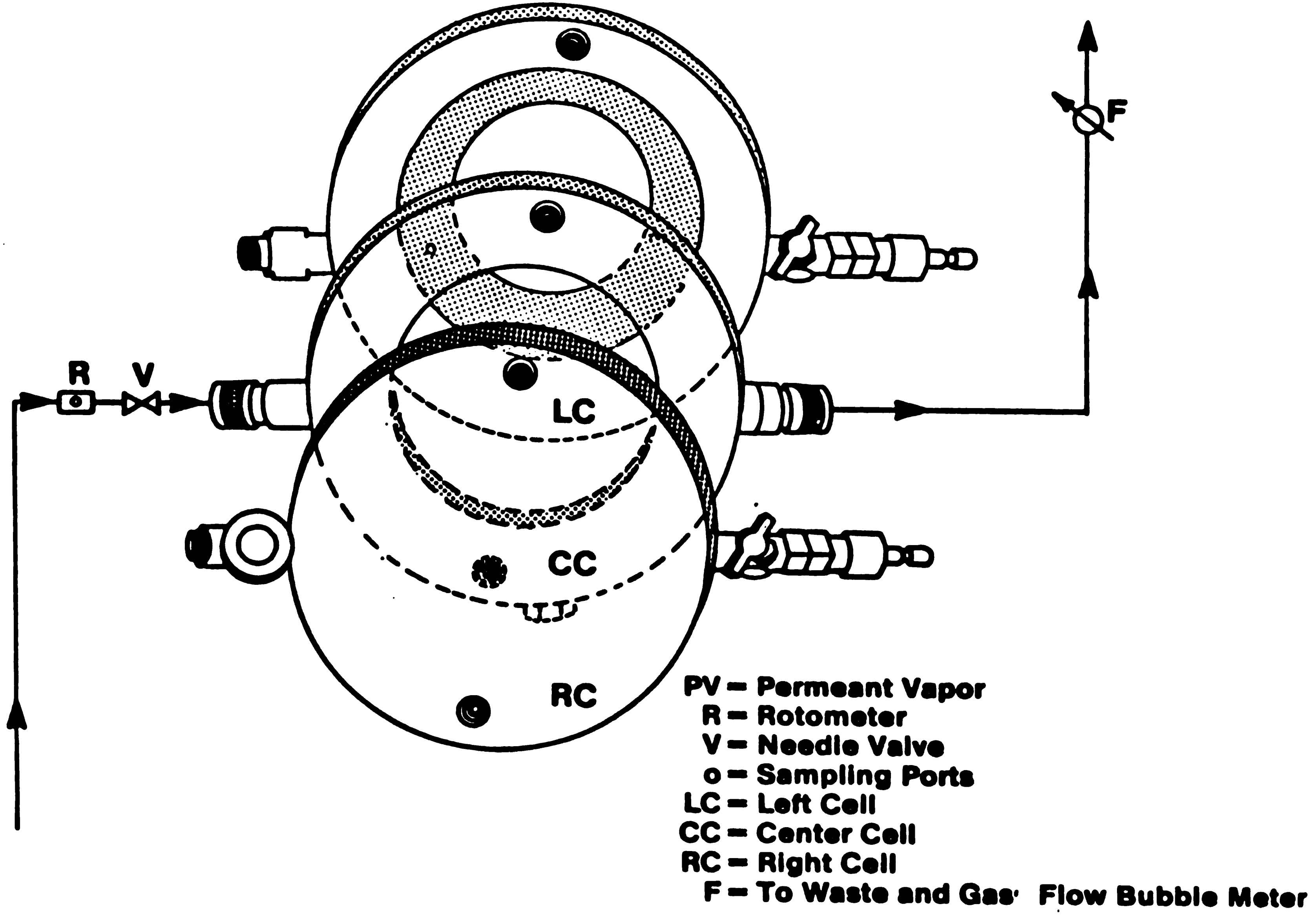


Figure 2. Quasi-Isostatic Permeation Test

Figure 3. **PERMEANT CELL SYSTEM**



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

constructed of stainless steel or aluminum, is comprised of two cell chambers and a hollow center ring. Both cell chambers and the center ring are equipped with an inlet and outlet valve and a sampling port. An assembled cell is shown in Figure 4. Unless otherwise stated, the low concentration cell chambers each have a volume of 50 cc, and the volume of the center cavity is approximately 90 cc. Tests were also performed utilizing permeability cells having a smaller volume for the center cavity (50 cc)(see Appendix A). In this case, the low concentration cell chamber volumes remained at 50 cc. A comparison of these volumes is shown in Figure 5 for the center chamber of the two permeability cells utilized.

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 volume, isolation of the cell chambers from each other and from the atmosphere was achieved through compression of the film against a smooth metal face which resulted in a metal/film/metal seal.

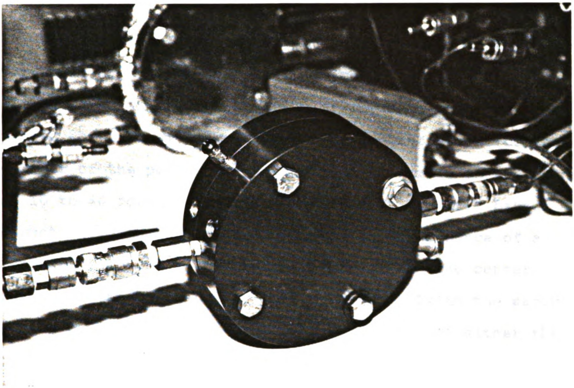


Figure 4. An Assembled Cell System

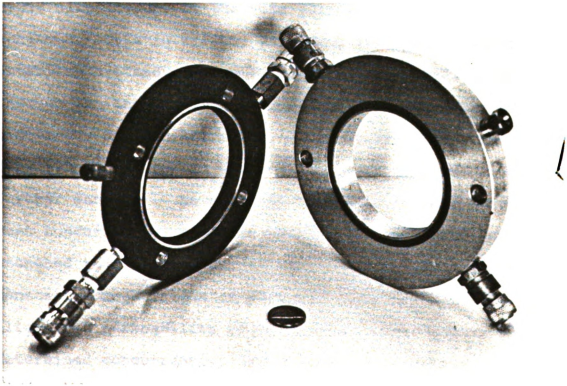


Figure 5. Comparison of Cell Volumes

In use, the films to be tested are mounted in the permeability cell and the cell assembled. Unless otherwise stated, 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 10 to 40 cc/min. Initial studies with the HDPE based structure revealed a problem related to maintenance of a constant limonene vapor concentration within the center cavity of the permeability cell, particularly in the early stages of the diffusion process. Adjustment of either the center cell cavity size or the rate of permeant flow, however, eliminated this problem and allowed for a more representative collection of data. By increasing the flow rate of the penetrant vapor through the center chamber, rapid displacement of the void volume was successfully achieved. This in effect, decreased the time necessary to establish a steady concentration prior to actual permeation through the test material. Therefore, in two cases of limonene vapor concentration, a higher flow rate ranging from 130 to 140 cc/min was employed (see Appendix A for further details). As shown in Figure 1, to perform multiple runs concurrently, a series of four (4) cells can be attached to a dispensing manifold which allows delivery of a constant concentration of permeant vapor to each cell. This allows the permeability of up to eight film samples to be determined concurrently, under identical conditions.

The increase in penetrant level in the low concentration cell chambers is determined by gas chromatography analysis with flame ionization detection. At predetermined time intervals, an aliquot (500 µl) 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 sample 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 evaluate the concentration dependency of the diffusion process, permeation runs were carried out at several penetrant concentration levels. The transmission rate (P) and permeability constant ($\bar{P}$) values were determined from the resultant transmission data.

To determine the diffusivity and permeability values, 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 lag time (Θ) value is obtained experimentally as the intercept on the time axis of the steady rise portion of the penetrant-time plot and the apparent lag time diffusion coefficient (D_{lag}) determined

(Barrer, 1939) by:

$$D_{lag} = l^2/6\theta \quad (3)$$

where: D_{lag} = apparent lag time diffusion coefficient (cm^2/sec)

l = total film thickness (cm)

θ = lag time (sec)

The lag time diffusion coefficient for laminate structures is considered an apparent diffusion coefficient value, being a composite of the diffusivity properties of the respective individual laminate layers. Due to the complex nature of the glassine base liner material, an apparent diffusion coefficient was not determined for this structure.

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.

Sorption Measurements

Sorption measurements were carried out on a Cahn-RG Electrobalance by the continuous flow method (Cahn Instruments Inc., Cerritos, CA). The electrobalance and sample tube were maintained at a constant temperature of 21.5 + 0.5°C. A schematic diagram of the test apparatus is shown in Figure 6.

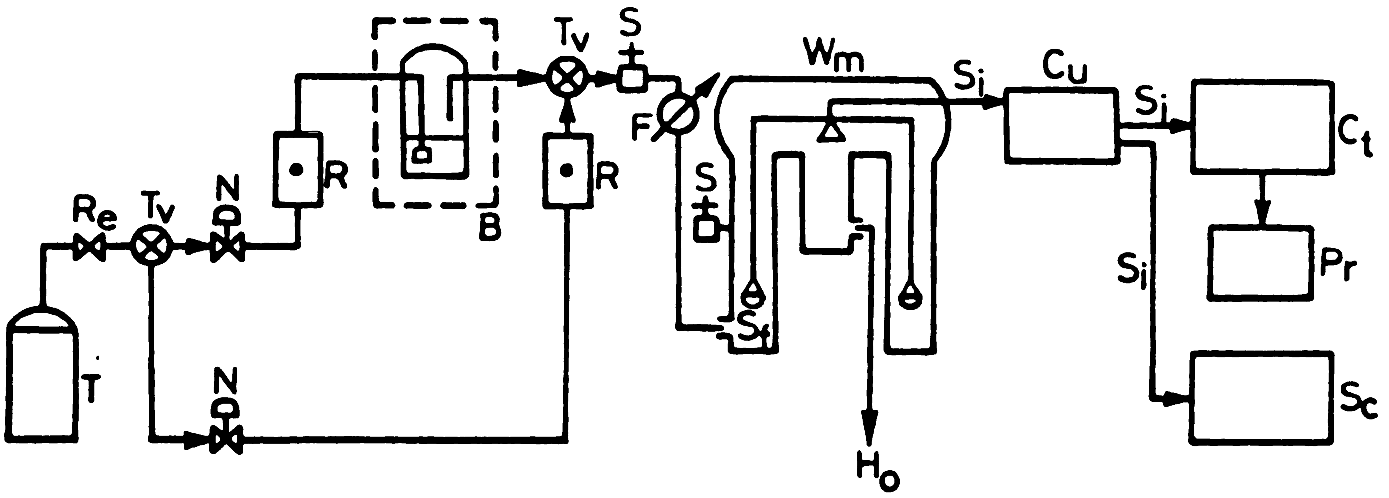
As shown, the polymer film sample is suspended directly from one of the arms of the electrobalance and a constant concentration of penetrant vapor is flowed continually through the sample tube (hang-down tube), such that the polymer sample is totally surrounded by the vapor. A constant concentration of penetrant vapor is produced by employing a vapor generator system, similar to that described above. The level of limonene concentration found in the glass hang down tube is dependent on the amount of nitrogen gas flowing over the liquid phase (limonene) and on the amount of nitrogen gas selected for mixing. The equilibrium sorption and solubility coefficient values of limonene in the films were evaluated within a vapor concentration range of 0.3 to 7.0 ppm for the HDPE based structure and between 1.5 and 7.3 ppm for the Glassine based structure.

The test system, as designed, allows for the continuous collection of sorption data from the initial time ($t = 0$) to the time the system has equilibrated (steady state conditions), as a function of penetrant concentration.

The penetrant vapor surrounding the test film, is quantitatively measured by a G.C. procedure. Using a gas tight 500 μl syringe, a portion of the vapor within the sample holding facility is removed and injected into the G.C.

Figure 6.

SCHEMATIC DIAGRAM OF SORPTION/DESORPTION APPARATUS



B - Water bath, generation of permeant
Vapor phase diluted in Nitrogen
C_t-Computer terminal
C_u-Control unit
F - Gas flow bubble meter
H_o-Hood
N - Needle valve
P_r- Printer
T - Nitrogen tank

R - Rotameter
R_e-Regulator
S - Sample port
S_f-Sampling film
S_c-Strip chart
S_i-Electrical input/output signal
T_v-Three way valve
W_m-Cahn electrical balance

Since the measurement of the concentration of limonene vapor is highly dependent upon the sampling technique, one syringe was used throughout the solubility study, over the entire range of vapor concentrations.

The microbalance (W_m), along with the stripchart recorder (S_c), are easilly calibrated using a standard set of weights (Figures 7 & 8). The arm of the electrobalance, opposite the sampling film chamber (S_f), contains a reference sample (foil) similar in weight to that of the test film sampled. The reference sample may also be refered to as a control chamber, in that the foil is in an odor free environment. For a sample mass of approximately 26 mg, the sensitivity of the system is + 5 μg.

At the beginning of this work, large fluctuations were seen in the concentration of limonene as a result of limonene adhering to the syringe between samples. Apparently, not all of the limonene was flushed out of the syringe between samples; thus trace amounts were still present. To eliminate error, a penetrant saturated syringe was employed. The syringe was filled with limonene vapor prior to and in between each series of samples, so as to maintain saturation of the syringe. The lowest concentration level of limonene vapor is initially analyzed, followed by increased increments over the entire range of vapor concentrations.

To reduce potential error, the first two samples are

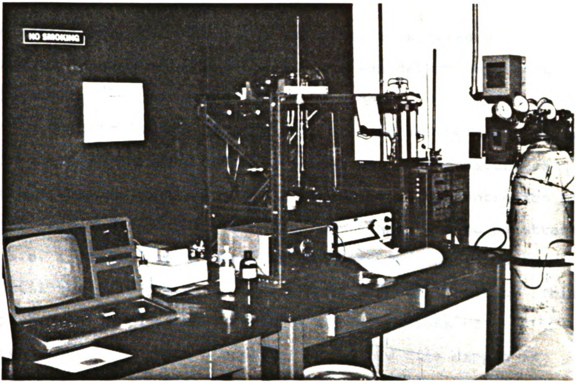


Figure 7. Sorption Apparatus (Overall View)

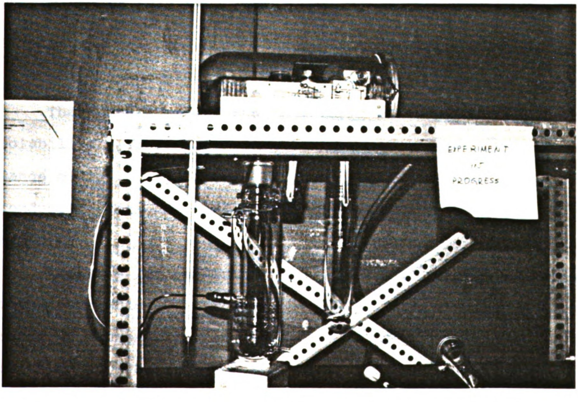


Figure 8. Sorption Apparatus (Close-up View)

disposed of. This minimizes the difference between replicate samples. An average value was determined of at least five consecutive sample injections.

In the analysis of each film structure, the test sample is initially weighed and then placed within the saturated glass chamber containing the limonene vapor concentration of interest. The gain in weight of the sample due to penetrant (i.e. limonene vapor) sorption is monitored continuously until the system attains steady state or equilibrates. This procedure is repeated at several concentrations of penetrant. For each concentration, a new film sample is utilized. The relationship between penetrant vapor concentration, the equilibrium sorption concentration and the solubility coefficient for the film structures were determined by this technique.

Analytical

The temperature of the room where Permeability & Solubility measurements were made was maintained within a range of 21.1^{o}C (70^{o}F) and 26.7^{o}C (80^{o}F). All tests were conducted under dry conditions, essentially 0% relative humidity.

Analysis for penetrant concentration was based on a gas chromatographic (GC) procedure. In all cases, a standard curve of response vs. penetrant concentration was constructed from standard solutions of known concentration to determine the linearity and sensitivity of the method. Solutions used for calibration were prepared by dissolution of known quantities of d-limonene in ethyl acetate. Peak responses were obtained starting with injection of the lowest concentration and gradually increasing. The penetrant concentration specified for each study was determined by reference to the calibration curve.

Two Hewlett Packard gas chromatographs, Models 5830A and 5890A, equipped with dual flame ionization detection (FID), were used for these analyses. The GC conditions are as follows:

MODEL #5830A

Column, 6 ft. x 1/8 in. O.D. stainless steel packed with 5% SP2100 on 100/120 mesh Supelcoport (Supelco, Inc., Bellefonte, PA); Carrier Gas, helium at 30 ml/min.; Temperature ^{o}C: injector 200, column 175, detector 350, to give a retention time of 1.14 minutes for limonene.

MODEL #5890A

Column, same as above; Carrier Gas, nitrogen at 40 psi; Temperature ^{o}C: injector 200, oven 150, detector 250, to give a retention time of 0.78 minutes for limonene.

All injections are direct on-column at a constant volume of 500 µl. A standard calibration curve was constructed for each gas chromatographic employed. These calibration curves compensate for detector response drift and aid in determining the linearity and sensitivity of the detector (see Appendix C for calibration curves and further details).

Sensory Analysis

Cereal product, of known limonene concentration, was packaged in commercial, 15 oz. packages fabricated from the glassine based structure and stored at constant conditions of temperature (23 C) and relative humidity (50%). At predetermined time intervals, the packaged/product combinations were removed from storage and evaluated both qualitatively (sensory analysis) and quantitatively (gas chromatographic analysis). Prior to initiating the storage studies, a bead of silicon rubber is affixed to the package liner to provide a sampling septum. After allowing the system to equilibrate, the concentration of limonene in the package headspace is determined by removal of a 0.5 ml aliquot and injecting directly into the gas chromatograph for quantitation. Immediately following limonene quantification, the packages are opened and the product quality rated by at least six untrained panelists. The samples were evaluated initially and at three pre-determined storage intervals (3 months, 6 months and 9 months). An aroma evaluation form was provided for each panelist (see appendix D).

RESULTS AND DISCUSSION

SORPTION STUDIES

The results of the studies on the equilibrium sorption of limonene by the HDPE base structure and the glassine based structure are summarized in Tables 1 and 2, where the equilibrium solubility (C_s) and the solubility coefficient (S) values are tabulated. For the HDPE based structure, the sorption diffusion coefficient (D_s) is also listed. To determine diffusion coefficient values, the ratio of the amount of penetrant vapor absorbed at any time (M_t) and the equilibrium sorption level at infinite time (M_∞) or saturation, is plotted as a function of time $[(t)^{1/2}]$. The diffusion coefficient can be determined from this graphical analysis by solution of Equation (4), for the diffusion of molecules through film (Crank, 1975).

$$D_S = \frac{0.049\ l^2}{t_{0.5}} \qquad (4)$$

Where $t_{0.5}$ is the "half-sorption time" or the time required to attain the value, $M_t/M_\infty = 0.5$. Shown in Figure 9 is a typical plot of M_t/M_∞ (relative weight gain) versus $t^{1/2}$ for limonene sorption by the HDPE based structure at a vapor

Table 1

Solubility Data For HDPE Base Structure As A Function of Limonene Vapor Concentration

Limonene Vapor Concentration(a)	Equilibrium Solubility(b)(e)	Solubility Coefficient(c)(e)	Diffusion Coeffiecient(d)(e)
0.3	2.2	7.6	---
1.5	10.3	7.6	4.3
2.6	18.7	7.3	4.9
4.2	32.1	7.6	5.9
6.4	62.4	9.7	8.4
7.0	116.2	16.6	12.7

Units expressed as:
(a)ppm, wt/v.
(b)g limonene/g polymer x 10-3.
(c)g limonene/g polymer * ppm limonene vapor x 10-3.
(d)cm2/sec x 10-10.

(e)Value is the average of at least two replicate runs.

Table 2

Solubility Data For Glassine Base Structure
As A Function of Limonene Vapor Concentration

Limonene Vapor Concentration(a)	Equilibrium Solubility(b)(d)	Solubility Coefficient(c)(d)
1.5	1.5	1.0
2.5	4.6	1.9
4.6	6.4	1.4
6.4	14.4	2.3
7.3	60.6	8.8

Units expressed as:
(a)ppm, wt/v.
(b)g limonene/g polymer x 10-3.
(c)g limonene/g polymer * ppm limonene vapor x 10-3.

(d)Value is the average of at least two replicate runs.

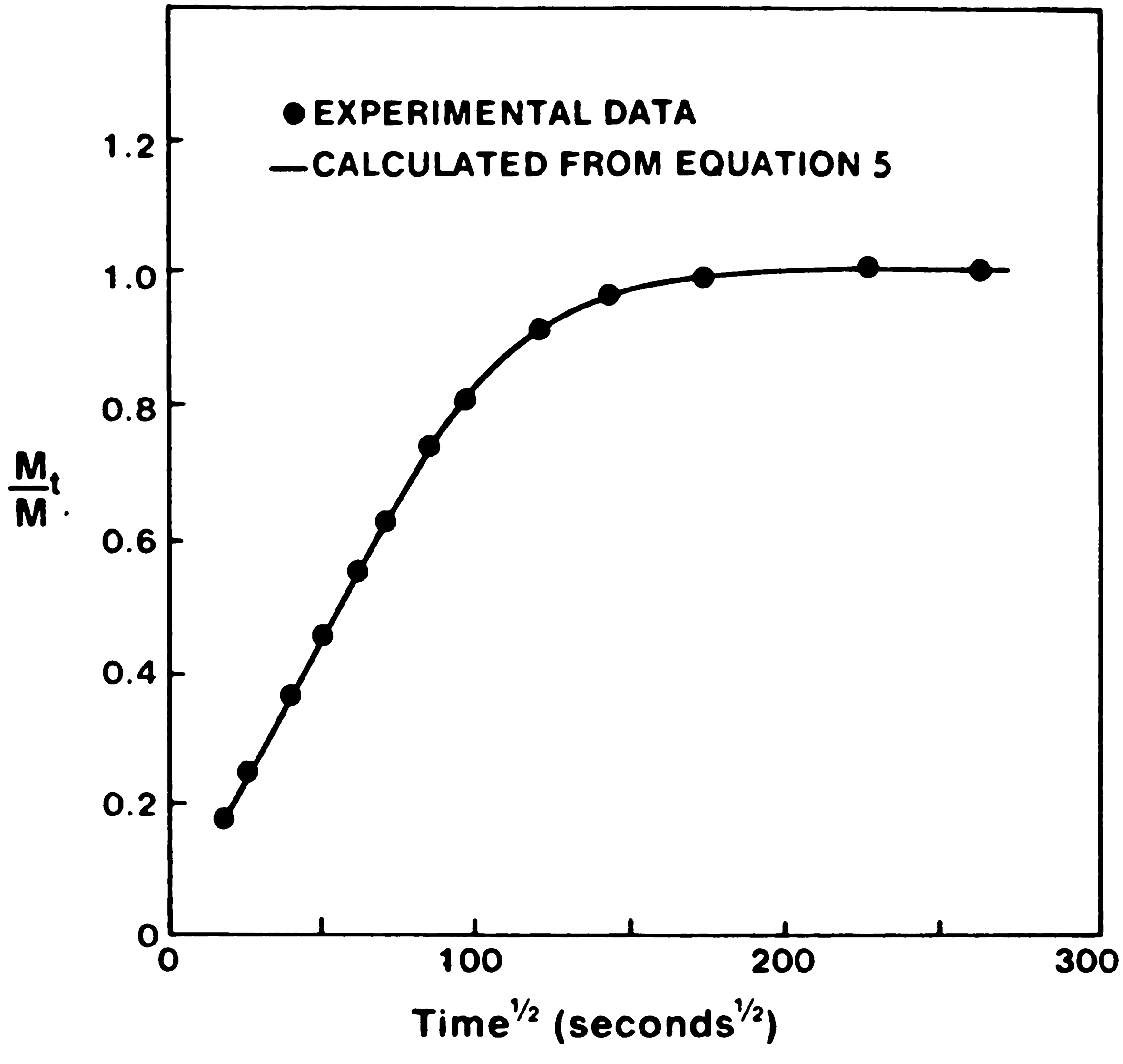


Figure 9. ABSORPTION OF D-LIMONENE IN HDPE BASE STRUCTURE AT 1.5 ppm AND 20.5 C

concentration of 1.5 ppm (wt/v). Superimposed in Figure 9 is the sorption profile obtained by solution of the sorption vs. time data fitting equation (Equation 5).

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\left[\exp\left(\frac{-D * \pi^2 * t}{l^2}\right) + \frac{1}{9}\exp\left(\frac{-9D * \pi^2 * t}{l^2}\right)\right] \qquad (5)$$

Equation 5 was derived from the equation,

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n + 1)^2\pi^2} \exp\left[\frac{-(2n + 1)^2\pi^2 Dt}{l^2}\right] \qquad (6)$$

by taking the first two terms.

As shown, good agreement was obtained between the experimental data and that calculated from the theoretical expressions. The general shape of the sorption curve supports the assumption that for the HDPE based structure the diffusion process followed apparent Fickian behavior (Fujita, 1961; Crank and Park, 1969) at the limonene vapor concentration level of 1.5 ppm. That is, the diffusion coefficient is not time dependent (Crank, 1975). Sorption profile curves were also determined for the HDPE based structure, at d-limonene concentration levels of 3.9 ppm, 4.1 ppm, 6.3 ppm, 6.6 ppm and 7.2 ppm. These curves are shown in Figures 10 through 14 respectively. For each limonene vapor concentration studied, the experimental and calculated results, following the same procedure as above, are presented. As shown, at the higher d-limonene vapor

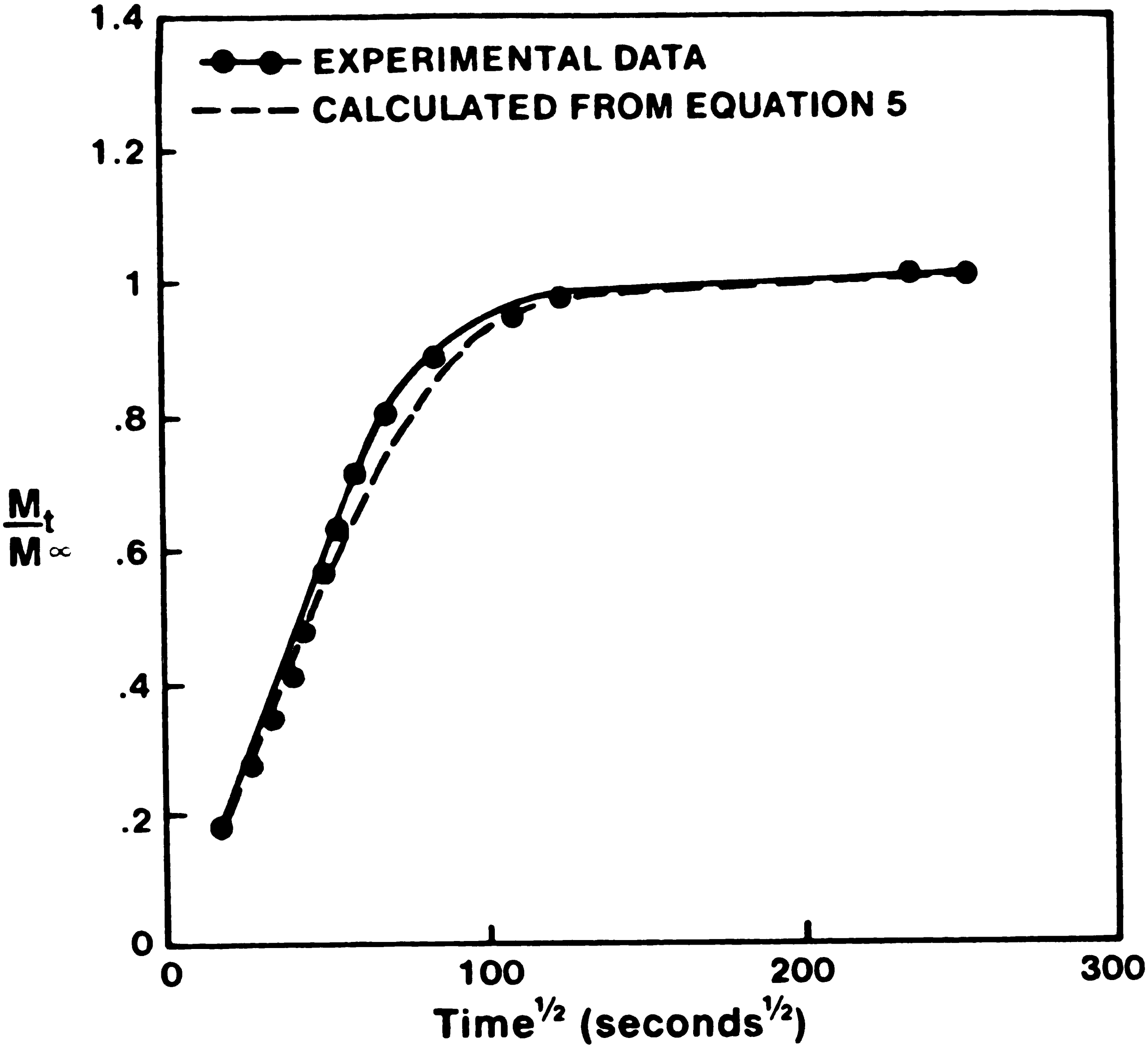


Figure 10. ABSORPTION OF D-LIMONENE IN HDPE BASE STRUCTURE AT 3.9 ppm AND 20.5° C

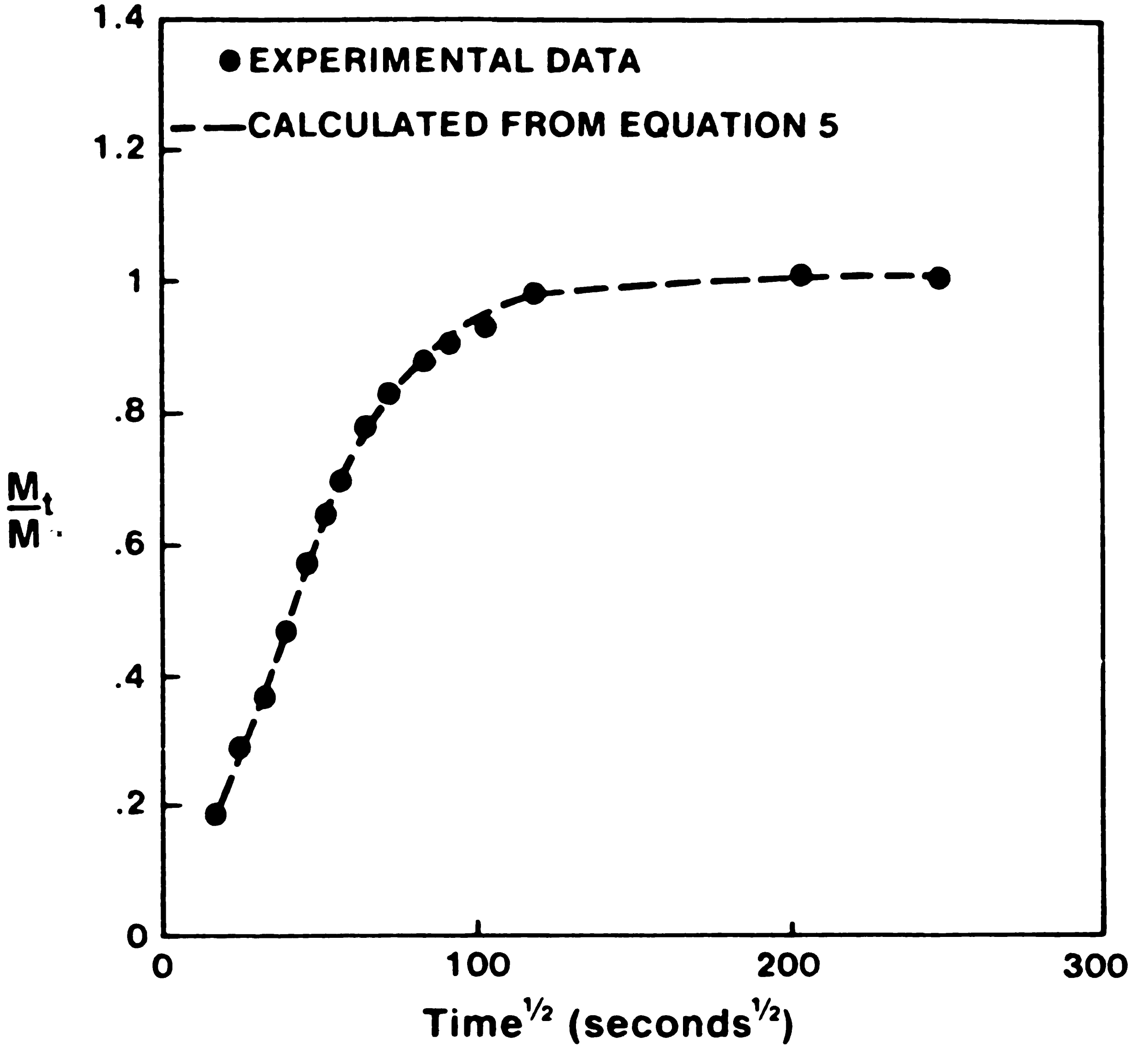


Figure 11. ABSORPTION OF D-LIMONENE IN HDPE BASE STRUCTURE AT 4.1 ppm AND 20.5 C

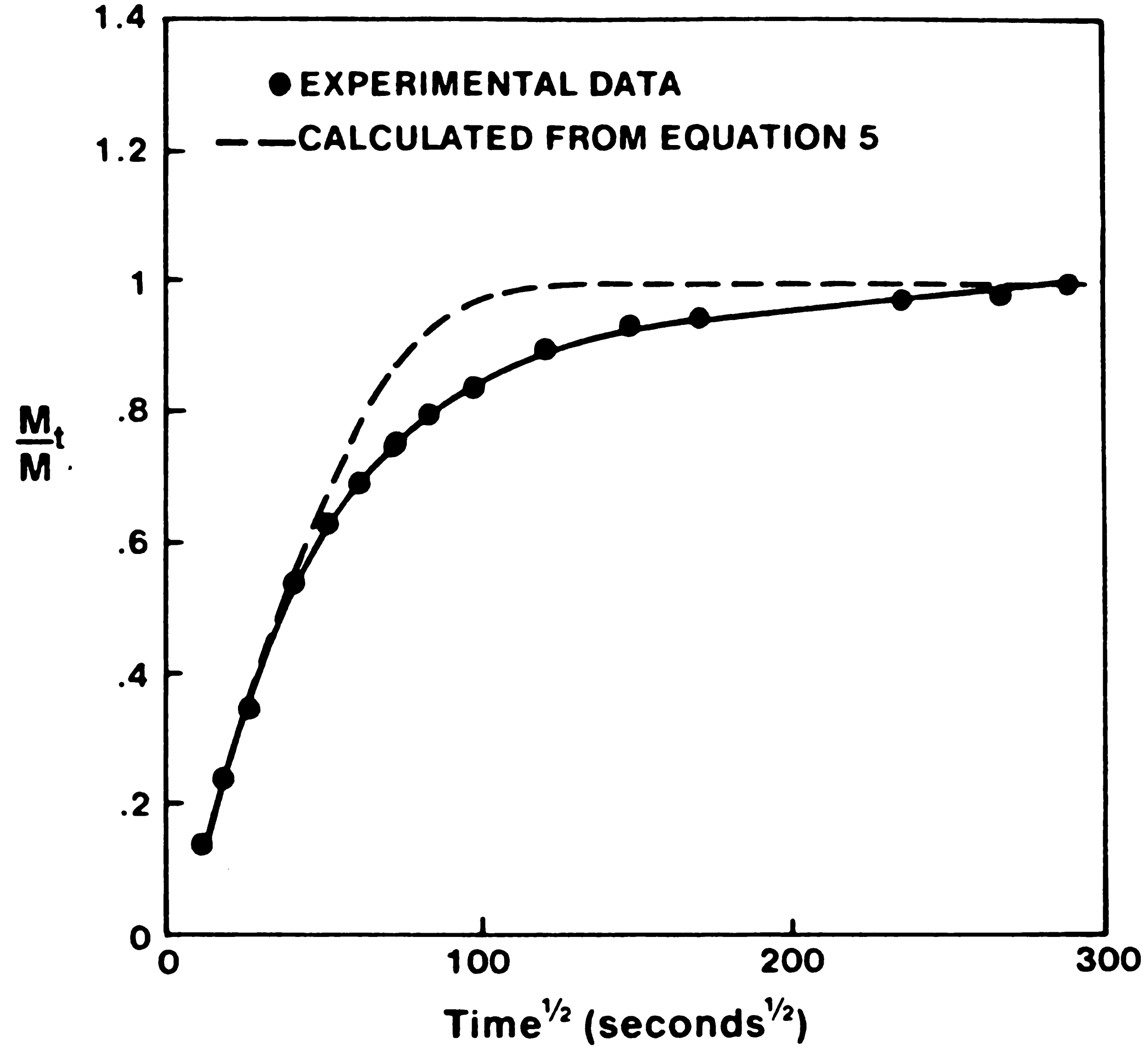


Figure 12. ABSORPTION OF D-LIMONENE IN HDPE BASE STRUCTURE AT 6.3 ppm AND 20.5 C

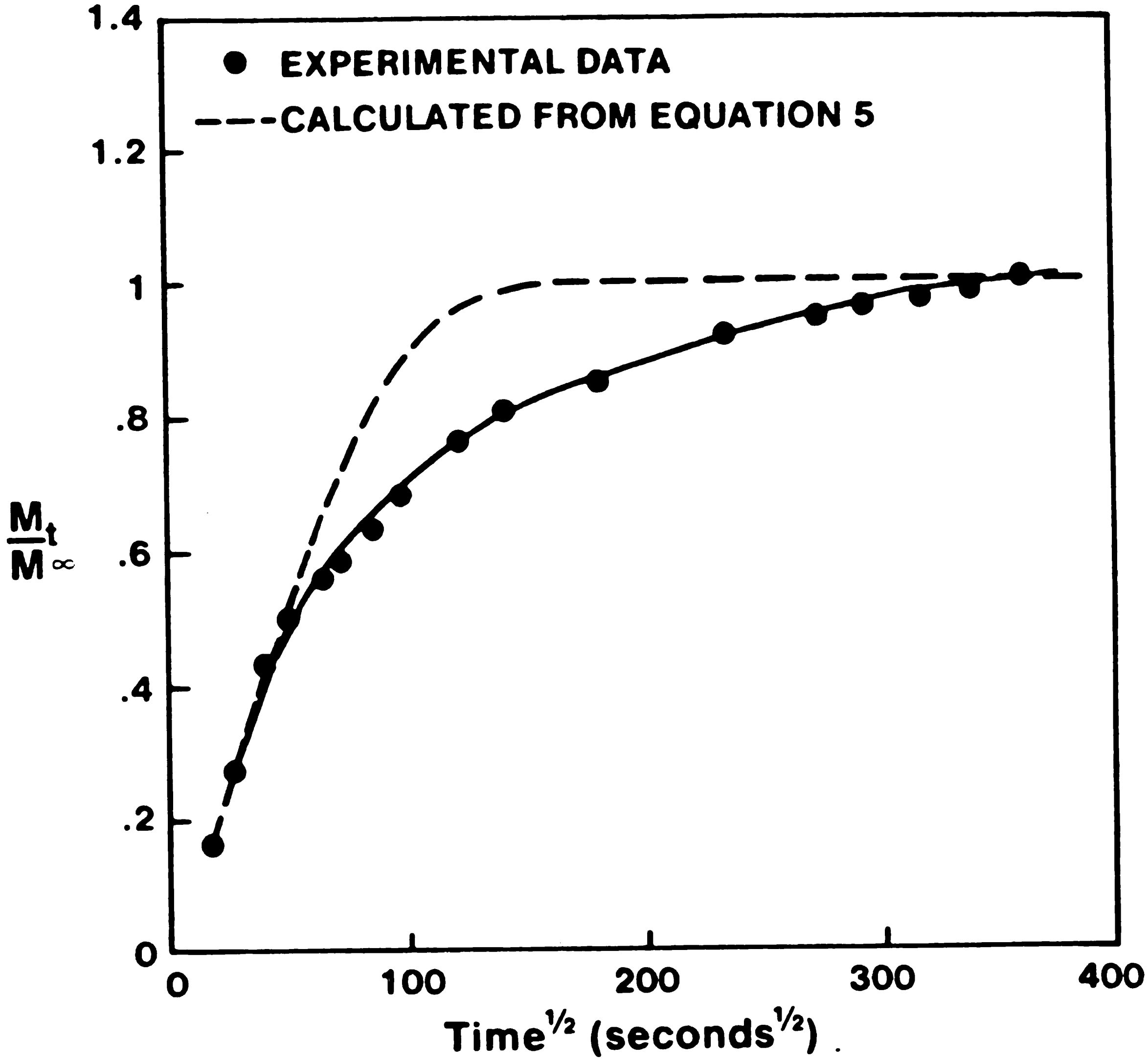


Figure 13. ABSORPTION OF D-LIMONENE IN HDPE BASE STRUCTURE AT 6.6 ppm AND 20.5° C

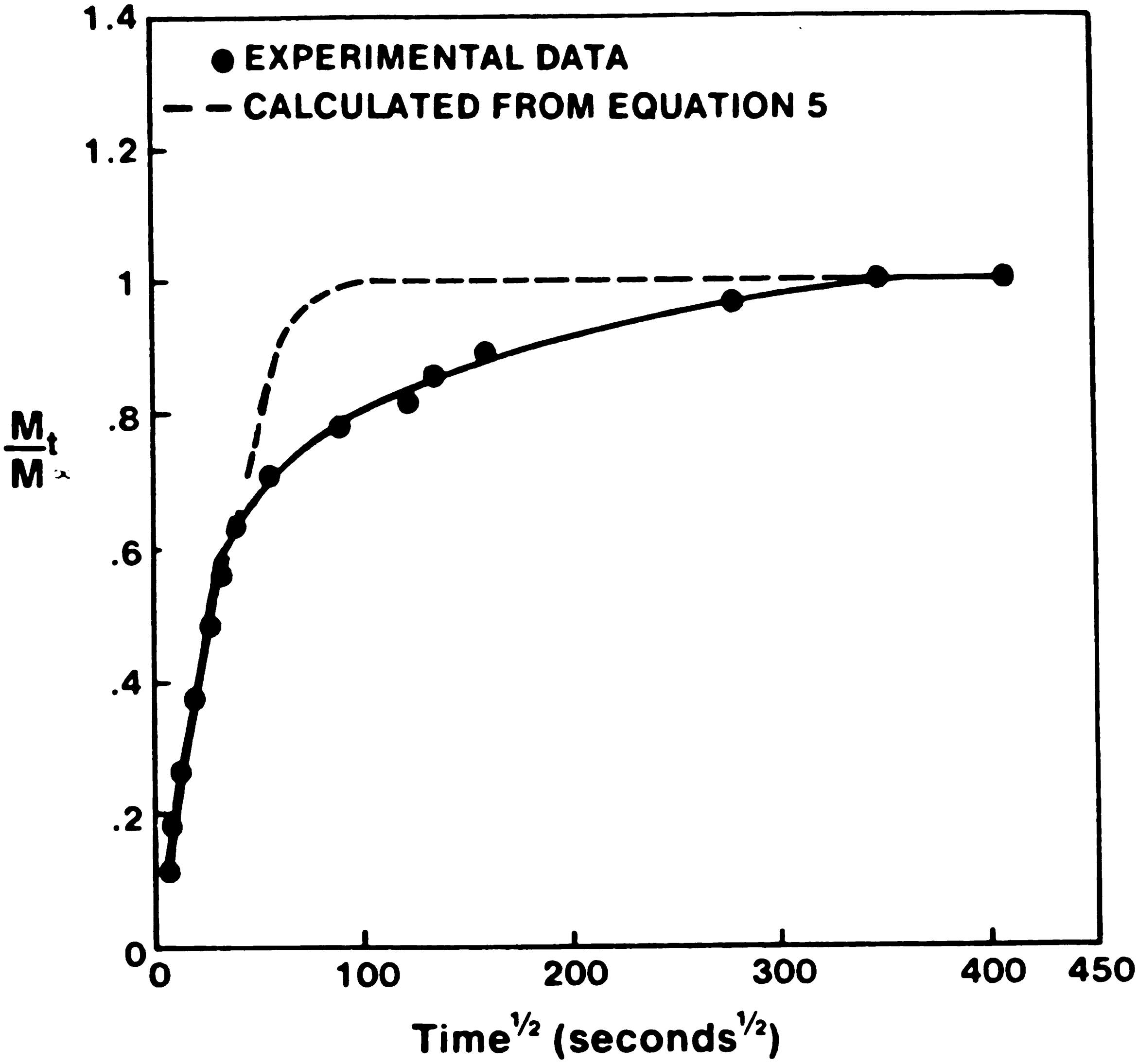


Figure 14. ABSORPTION OF D-LIMONENE IN HDPE BASE STRUCTURE AT 7.2 ppm AND 20.5° C

concentrations, there is apparently non-Fickian relaxation controlled sorption which results in additional sorption of the penetrant. A similar sorption process has been described by Berens (1977) for a vinyl chloride/polyvinyl chloride system and by other investigators (Bagley and Long, 1958; Fujita, 1961).

The M_t/M vs. $t^{1/2}$ curve for sorption of limonene by the glassine based structure, at a concentration level of 2.5 ppm, is shown in Figure 15. The data shows what appears to be a smaller relative amount of rapid sorption, followed by a slower approach to apparent equilibrium. In contrast to the apparent Fickian behavior of the HDPE based structure, the sorption of limonene by the glassine based structure appears to be more complex and showed a time dependency. While this phenomenon is not totally understood, it can be attributed to the rapid uptake of limonene vapor by the external wax layer followed by a slower approach to steady state due to diffusion through the PVOH barrier layer.

The results of the equilibrium vapor pressure measurements on the HDPE structure and the glassine structure are shown in Figure 16, where limonene solubility is plotted against vapor concentration for the respective films. Equilibrium solubility was determined by:

$$C_s = \frac{\text{weight of penetrant uptake at equilibrium}}{\text{weight of polymer}} \tag{7}$$

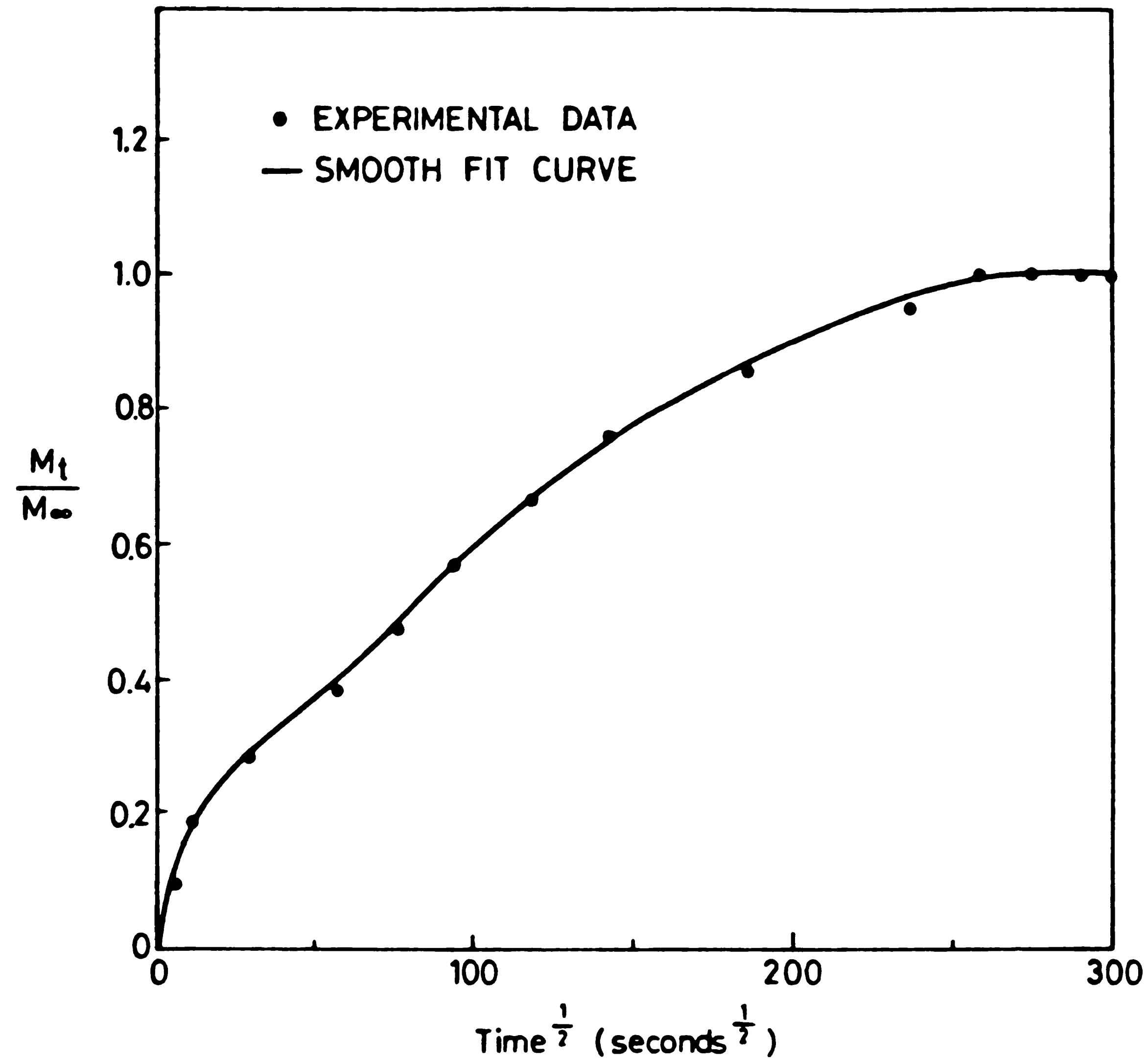


Figure 15. ABSORPTION OF D-LIMONENE IN GLASSINE BASE STRUCTURE AT 2.5 ppm AND 20.5°C

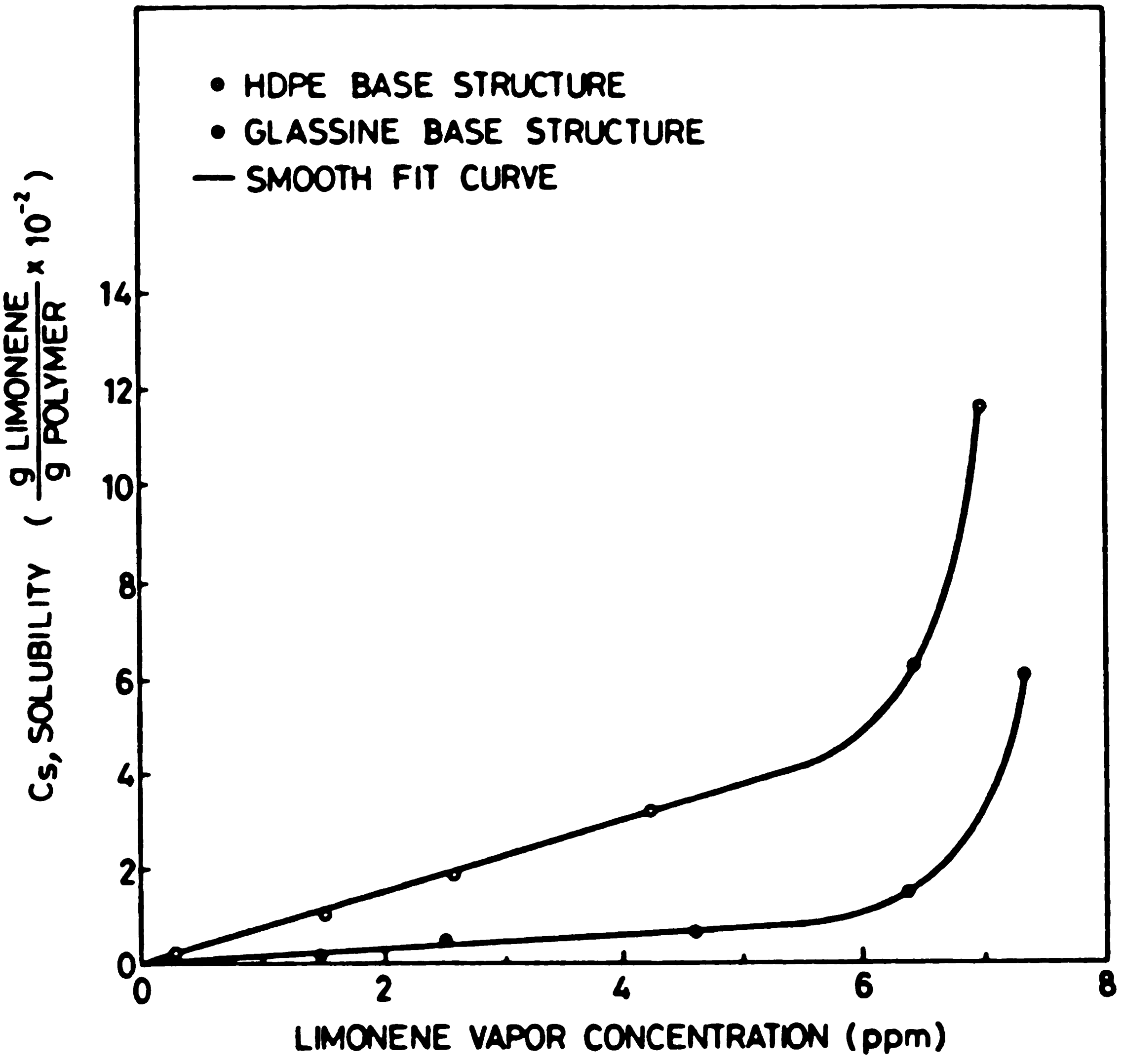


Figure 16. LIMONENE VAPOR SOLUBILITY IN HDPE BASE AND GLASSINE BASE STRUCTURES

As shown, over the lower portion of the concentration range studied, the data follow Henry's Law:

$$C_s = k\ C_v, \tag{8}$$

where C_s is the equilibrium solubility in g limonene/g polymer, C_v is the vapor concentration in ppm (wt/v) and k is a constant. According to Henry's Law the amount of limonene sorbed by the film structure should be directly proportional to the level of limonene vapor surrounding the film sample, at equilibrium. However, at vapor concentrations above 5.5 ppm deviation from Henry's Law is observed.

As shown, the limonene solubility in the glassine structure is substantially lower than in the HDPE structure, at the same limonene vapor concentration and temperature. Equilibrium distribution of limonene vapor between the fruit flavored cereal, and the packaging liner systems would result in a much lower limonene concentration in the glassine structure than in the HDPE structure. This can be of paramount importance in avoiding the effect of "flavor scalping" or loss due to sorption, for a product whose quality is associated with the retention of volatile aroma constituents.

Solubility coefficient values were determined from the equilibrium sorption data, where:

$$S = \frac{\text{weight of penetrant uptake at equilibrium}}{\text{weight of polymer * vapor concentration in ppm}} \qquad (9)$$

The results for the respective films are shown in Figure 17, where the S values are plotted against the relative limonene vapor concentrations. The solubility coefficient values over a limonene vapor concentration range of 0.3 to 5.0 ppm were essentially constant for the HDPE based structure with

$$S = 7.7 \times 10^{-3} \frac{\text{g limonene}}{\text{g HDPE structure * ppm limonene vapor}}. \qquad (10)$$

Above a limonene vapor concentration of 5.0 ppm, the solubility coefficient appears to be concentration dependent and must be determined for the specific concentration of interest. Similarly, the solubility coefficient (S) determined over the concentration range of 1.5 to 5.5 ppm for the glassine structure can be taken as essentially constant and estimated by linear regression analysis to give

$$S = 1.5 \times 10^{-3} \frac{\text{g limonene}}{\text{g Glassine struct * ppm limonene vapor}}. \qquad (11)$$

The data suggest that at the higher concentration levels, swelling may be induced, thus changing the structural characteristics of the liner materials. In the process of swelling, polymer relaxation occurs forcing the molecular bonds to expand. This increases the molecular space into which penetrant molecules may absorb. In general, the further apart the molecular bonds, the higher the penetrant solubility and the lower the barrier properties.

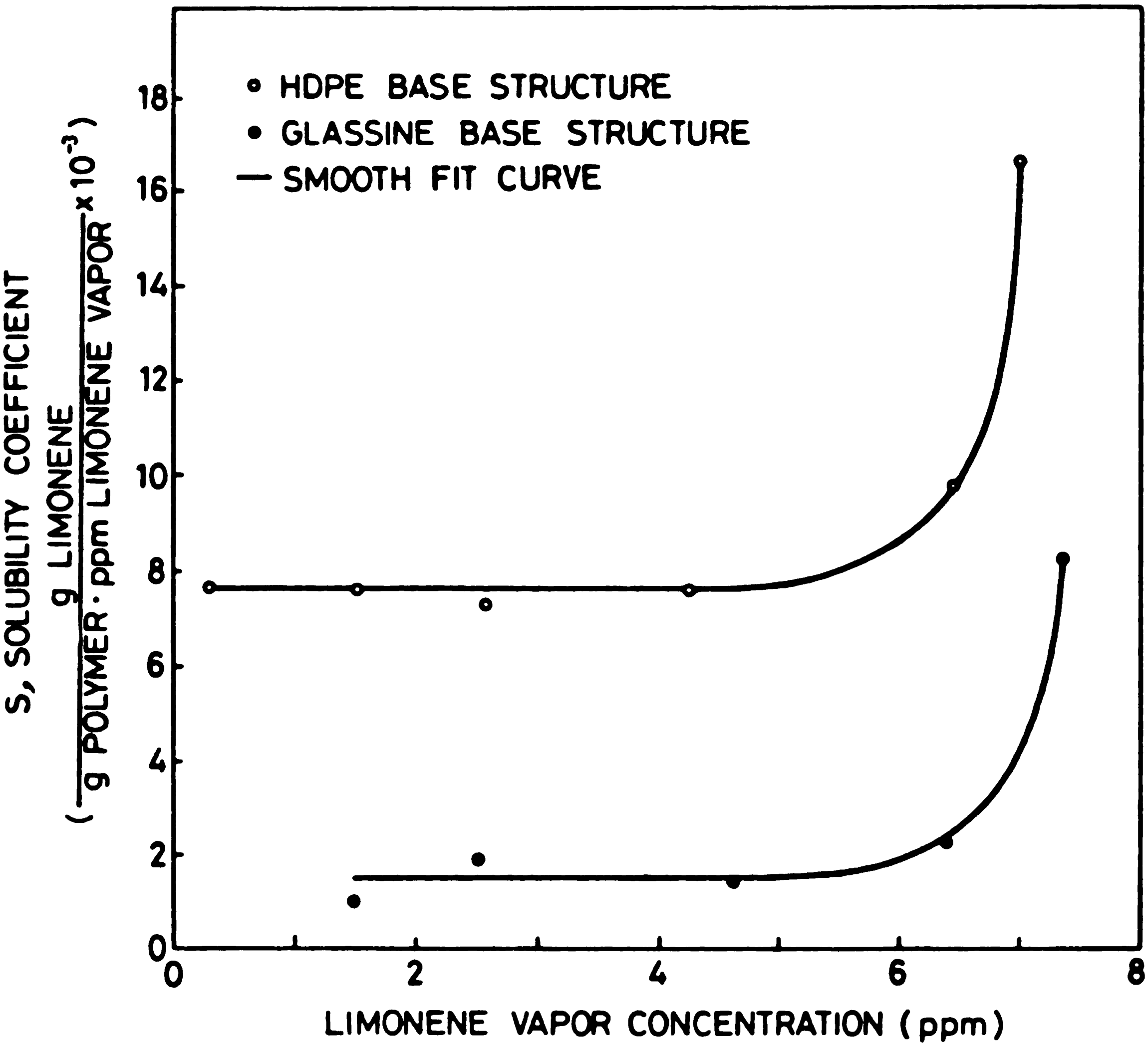


Figure 17. LIMONENE VAPOR SOLUBILITY COEFFICIENT OF HDPE BASE AND GLASSINE STRUCTURES

PERMEATION STUDIES

The results of the studies on the diffusion of limonene vapor through the HDPE and the glassine structures, as a function of penetrant concentration, are summarized in Tables 3 and 4. The data show, as anticipated, a concentration dependent permeability constant ($\overline{P}$) for the respective film samples, with $\overline{P}$ increasing with an increase in penetrant concentration. The concentration dependent permeability constant suggests penetrant/polymer interaction, or swelling of the polymer matrix by the sorbed limonene vapor, which can result in alteration of polymer chain conformational mobility and thus penetrant diffusivity. If there was no interaction between the penetrant and film, the permeability constant should remain constant over the entire range of penetrant concentrations investigated.

Representative transmission rate profile curves of the HDPE based structure, for the respective limonene penetrant levels investigated, are presented graphically in Figure 18, where the total quantity of limonene permeated is plotted as a function of run time. Figure 18 illustrates the effect of penetrant concentration on transmission rates and lag time values for the limonene/HDPE system. The transmission profile curves of the test film show an induction period, followed by a non-steady state rate of diffusion, after which a constant transmission rate is observed.

Table 3

Permeability Data for HDPE Base Structure As A Function of Limonene Vapor Concentration

Limonene Vapor(a) Concentration (ppm, wt/v)	Permeability(b)(c) Coefficient $\frac{\text{g * structure}}{\text{m2 * day * ppm}}$	Lag Time(b) (minutes)	Apparent(b)(d) Diffusion Coefficient cm2/sec x 10-10
0.4	72	132	4.9
1.0(e)	164(e)	93(e)	7.0(e)
1.3	106	126	5.2
1.9	158	105	6.2
2.6	351	91	7.1
3.1	417	76	8.7
3.6	589	73	8.9

(a) Limonene vapor concentraion (wt/v) gave an average deviation of +/- 6% during the course of the runs.
(b) Value is the average of at least two replicate runs.
(c) Average coefficient of variability, (σ/x) x 100, for P = 25%.
(d) Average coefficient of variability, (σ/x) x 100, for Dlag = 7%.
(e) Flow rate through high concentration cell chamber was 130 cc/min.

Table 4

Permeability Data for Glassine Base Structure As A Function of Limonene Vapor Concentration

Limonene Vapor Concentration(a) (ppm, wt/v)	Permeability Coefficient(b)(c) $\frac{\text{g * structure}}{\text{m2 * day * ppm}}$
1.5	0.03
2.5	0.08
3.6	0.25
4.3	1.50
4.8	1.97

(a)Limonene vapor concentraion (wt/v) gave an average deviation of +/- 6.4% during the course of the runs.

(b)Value is the average of at least two replicate runs.

(c)Average coefficient of variability, $(\sigma/x) \times 100$, for P = 32.4%.

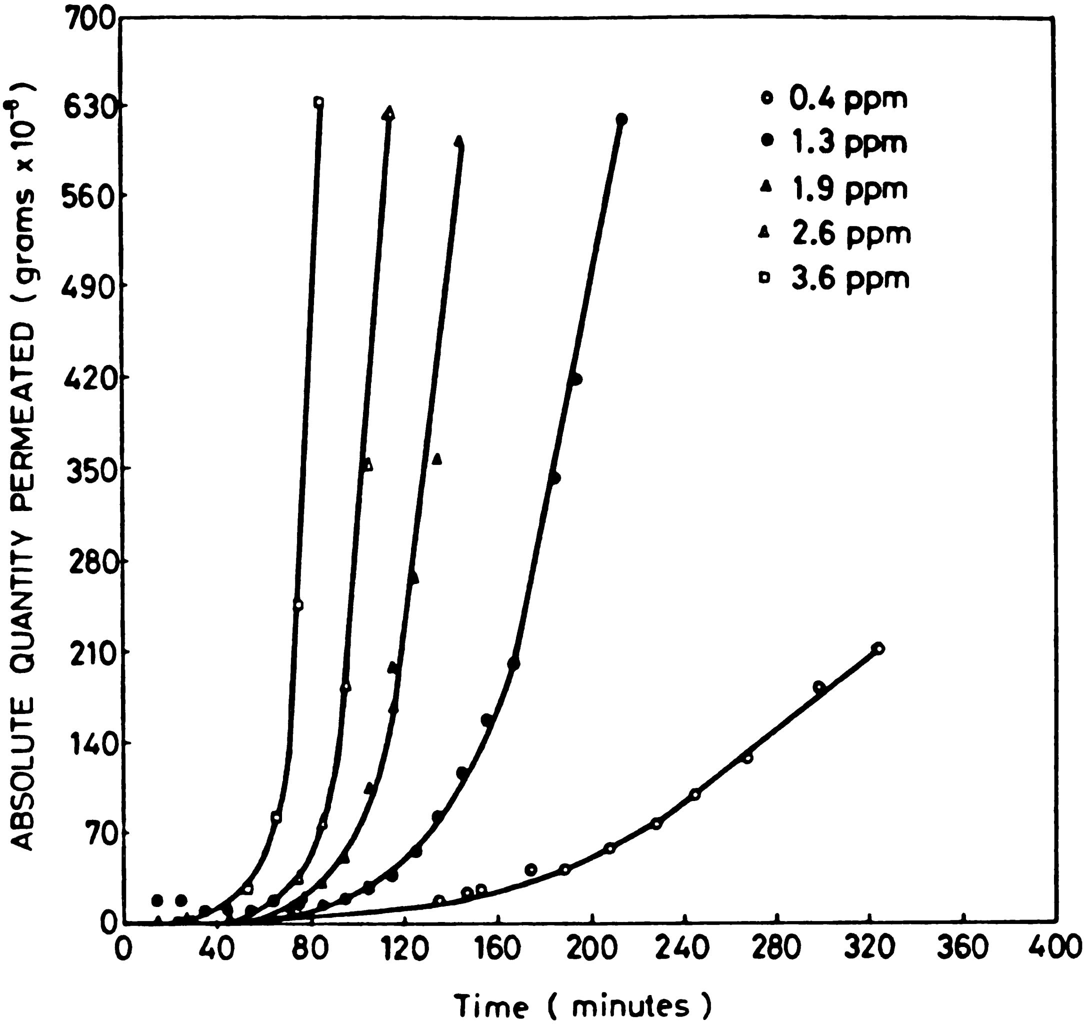


Figure 18. THE EFFECT OF VAPOR CONCENTRATION ON THE DIFFUSION OF LIMONENE THROUGH HDPE BASE STRUCTURE AT 23° C

As permeation begins to occur, the partial pressure or concentration gradient across the high concentration surface and the low concentration surface of the test film changes. As a result of this change in concentration gradient, the permeation rate of limonene, by the test film will be reduced. In an attempt to treat the data in a consistant manner over the entire concentration range investigated, a standard percentage of vapor permeating from the high concentration side to the low concentration side was selected, above which the data was not included in the analysis.

For example, permeability measurements were terminated when 12% to 14% of the driving force concentration was found to have permeated through the HDPE structure and into the low concentration chamber of the cell system.

From the transmission data, the permeability constant and lag time diffusion coefficient values were obtained by standard methods (Barrer, 1939; Crank & Park, 1968)(Appendix A). It is important to point out that the diffusion coefficient values for the HDPE structure were calculated from the transient state region of the permeation curves and may not necessarily represent the actual diffusion coefficient values at steady state. Therefore, whenever diffusion coefficient values are mentioned, the "apparent" values are presumed. As expected, the lag time values were found to be inversely related to the vapor driving concentrations.

Shown in Figure 19, are a series of typical transmission rate profile curves obtained for the glassine structure. The permeability of the glassine based structure was determined in a manner similar to that used for the HDPE structure. In this case however, permeability runs were terminated when 1% to 4% of the driving force concentration diffused through to the low concentration chamber of the cell system.

As was observed for the HDPE based structure, the transmission rate of limonene through the glassine based structure was also found to be concentration dependent. Due to the complex nature of the glassine structure, diffusion coefficient values were not determined.

It should be pointed out that for the glassine based structure, approximately ten days were required for the transmission rate to attain steady state, over the low limonene concentration range, as compared to a matter of hours for the HDPE based structure, at similar vapor concentration levels and temperature.

The relationship between limonene vapor concentration and the permeability coefficient ($\overline{P}$) for the HDPE based structure and the glassine based structure is shown in Figure 20, where log $\overline{P}$ is plotted as a function of penetrant concentration. It appears that, for both polymeric structures, the permeability coefficient increases

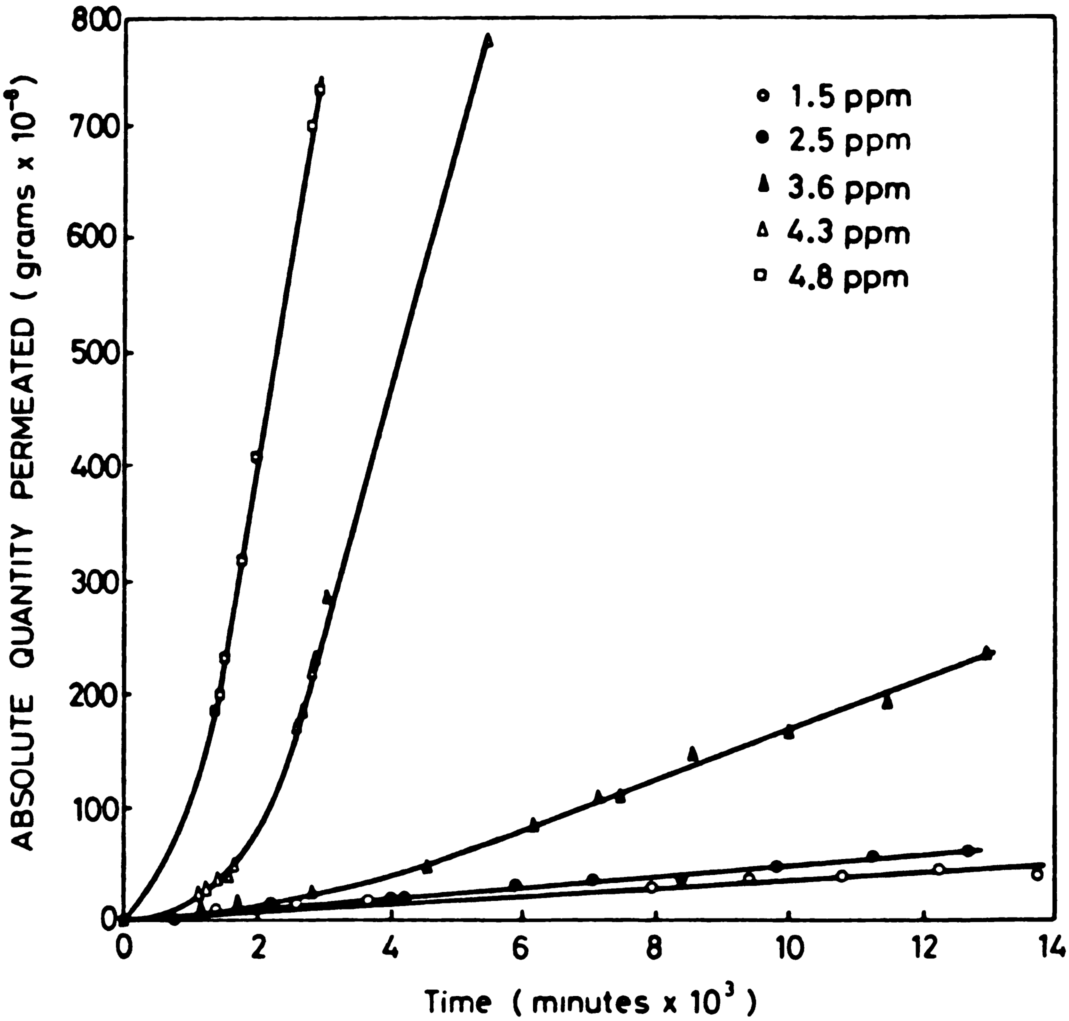


Figure 19. THE EFFECT OF VAPOR CONCENTRATION ON THE DIFFUSION OF LIMONENE THROUGH GLASSINE BASE STRUCTURE AT 23° C

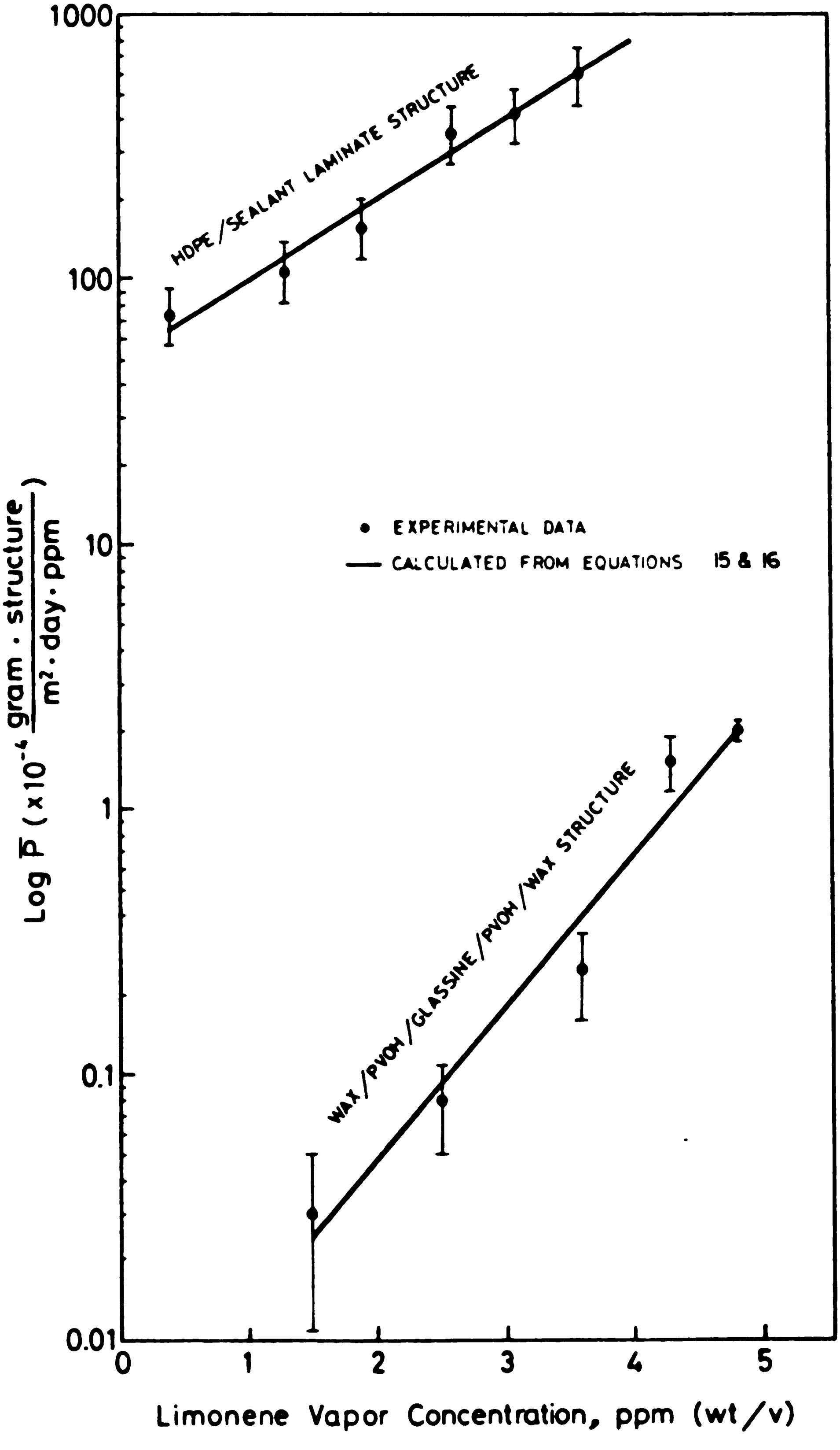


Figure 20. THE EFFECT OF LIMONENE VAPOR CONCENTRATION ON Log $\overline{P}$ FOR HDPE BASE AND GLASSINE BASE STRUCTURES

exponentially with increased limonene vapor concentration over the entire vapor concentration range evaluated. Equations 15 and 16 were derived by using the ordinary (exponential) least square method and applying experimental data.

From the general Exponential expression: $\overline{P} = a * e^{bC}$ (12)

By taking the log on both sides: $\ln\overline{P} = \ln a + bC$ (13)

leads to the linear equation: $y = K + bx$ (14)

where: a, b, and K are constants and C is concentration. Equation (12) was used as a model to determine the correlation between permeability coefficients and penetrant concentration. For the HDPE based structure, the relationship between the permeability coefficient ($\overline{P}$) and limonene vapor concentration (C_v) was found to be:

$$\overline{P}_{HDPE} = 4.865 \times 10^{-3} e^{0.6951\ C_v} \quad (15)$$

For the glassine based structure the relationship between ($\overline{P}$) and (C_v) is found to be:

$$\overline{P}_{GLASSINE} = 3.3146 \times 10^{-7} e^{1.3301\ C_v} \quad (16)$$

The correlation coefficients were 0.99 and 0.98 for the HDPE structure and the glassine structure respectively.

As shown in Figure 20, the permeability coefficient ($\overline{P}$) of limonene is substantially lower for the glassine structure than the HDPE structure at similar concentration levels and temperature. The glassine structure exhibited 3 to 4 orders of magnitude reduction in relative permeability as compared to the polyolefin structure, over the entire limonene concentration range studied. Since the permeability coefficient is reflective of the steady state transmission rate, permeation losses of limonene vapor from a fruit flavored cereal product could be greatly reduced by packaging in the glassine structure.

The physical and chemical properties of a polymeric film structure may influence the mechanism or mechanisms responsible for aroma loss. For the HDPE based structure, the loss of volatile aroma constituents, such as limonene, was found to be the result of both sorptive and diffusion mechanisms, in that the limonene solubility (dissolution) and permeability (diffusivity) were both high. For the glassine based structure, both loss mechanisms were operative, however, the solubility and diffusivity characteristics of this structure were significantly lower than that of the polyolefin structure.

It is important to note that for a polymeric food package, such as the cereal liner systems described in this study, the loss of limonene is the result of both sorptive and permeation losses and both mechanisms must be considered with regards to volatile aroma constituents.

SENSORY ANALYSIS

Sensory evaluation and G.C. Headspace analysis, were used to qualitatively and quantatively measure components related to the products characteristic aroma. The results of the sensory analysis are shown graphically by a histogram (see Figure 21), where the average relative response of the sensory panel is presented as a function of limonene headspace concentration within the package. The relative response was based on a scale of acceptance which ranged from 0 - 10, where a response of 0 represented an undetectable aroma node and a response of 10 was representative of a product of highly acceptable aroma quality.

Freshly packaged product, analyzed within five (5) weeks of commercial packaging, gave a limonene headspace concentration of 0.03 ppm (wt/v) and was rated as highly acceptable. This value represents the average of 18 sample containers. After storage for 3 and 6 months (from the date of production) the limonene headspace concentration showed a decrease to 0.02 ppm (31% loss) and 0.013 ppm (55% loss), for the respective storage periods. The change in headspace concentration reflects a loss of aroma caused by a combination of permeation, sorption and suspected leakage from an ineffective sampling septum. Following nine months of storage, a reduction in the limonene concentration in the headspace of approximately 86% (0.004 ppm) was found.

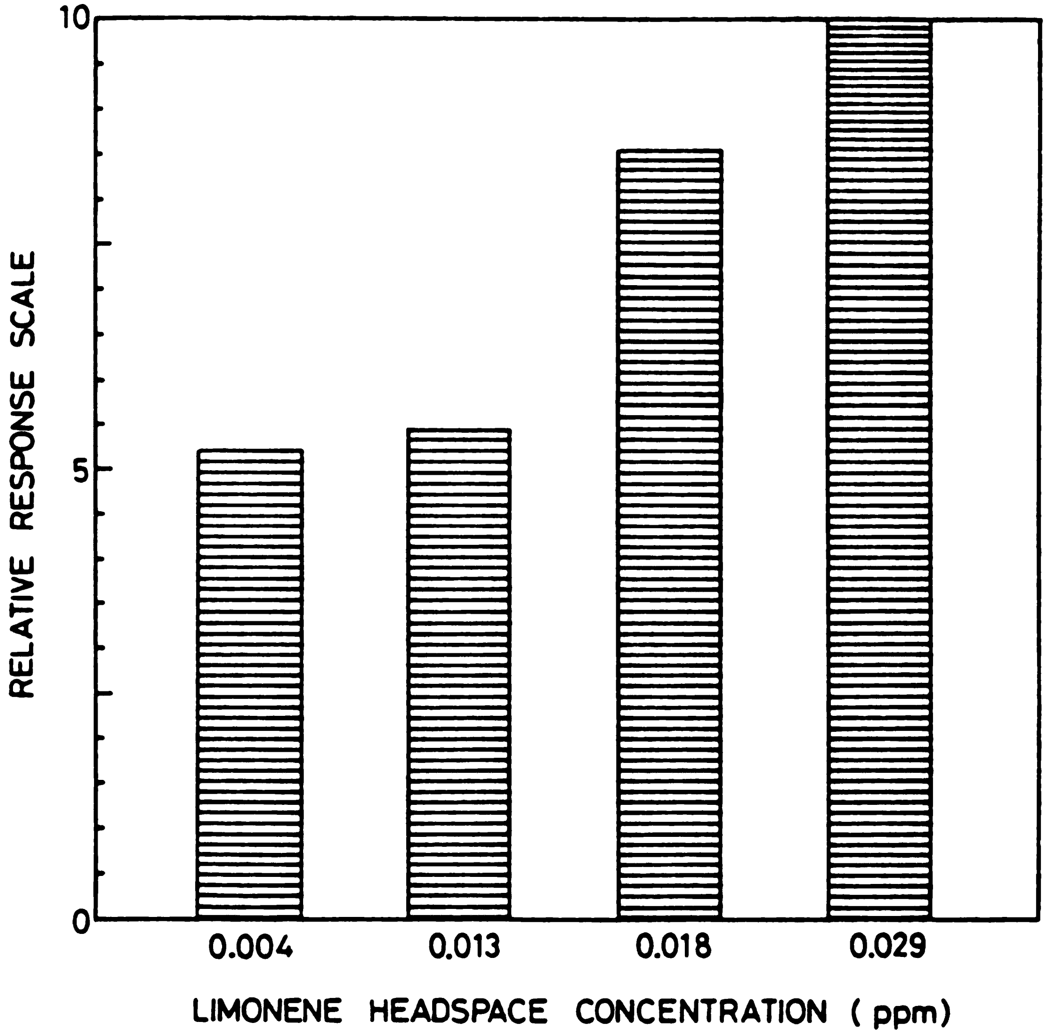


Figure 21. BAR GRAPH DATA RELATING QUANTITATIVE HEADSPACE ANALYSIS WITH QUALITATIVE SENSORY ANALYSIS OF A FRUIT-FLAVORED CEREAL PRODUCT

However, this product was still found acceptable, based on sensory evaluation. A perceived loss in relative product quality was noted, however, as the level of measurable limonene in the headspace diminished.

A qualitative relationship was established between the limonene within the headspace of a commercially packaged fruit-flavored cereal product and the acceptability level based on sensory evaluation.

The results of the sensory studies provide a means of determining a critical aroma node concentration, below which the product is considered unacceptable regardless of the mechanism of aroma loss.

SUMMARY AND RECOMMENDATIONS

Both qualitative (sensory evaluation) and quantitative (permeation and sorption) measurements, relating to the aroma character of a packaged fruit flavored cereal product, were performed. Aroma is a key factor in the acceptability of many products. For cereal products in general, moisture is of primary concern followed closely by aroma in terms of typical barrier requirements (Hamiliton, 1985).

Of practical importance, this study provides information relating to the aroma barrier properties of selected packaging materials to limonene vapor. Assuming the vapor concentration within the package headspace remains constant, potential candidate packages may be evaluated and shelf life estimated.

The results of these studies are summarized below:

(1) The permeability of d-limonene vapor through the respective cereal liner structures is concentration dependent, with the transmission through the HDPE based structure being 3 to 4 orders of magnitude greater than the glassine based structure, at the same vapor concentration.

(2) The solubility of d-limonene in the respective cereal liner structures follows a Henry's Law

relationship at low vapor concentration levels (i.e. below 5 ppm), but showed deviation from linearity at higher penetrant levels. This was attributed to non-Fickian related sorption.

(3) d-Limonene solubility was found to be substantially lower in the glassine based structure than in the HDPE based structure, at the same vapor concentration and temperature. This relationship can be of major importance in avoiding the effect of "flavor scalping" or loss due to a sorptive mechanism.

(4) The loss of volatile aroma moieties such as d-limonene can be the result of sorptive and/or permeation mediated processes and both mechanisms should be considered in understanding the relationship of mass transport to the storage stability of a product, such as the fruit flavored cereal product, where quality is associated with the retention of aroma compounds.

Results show glassine to be a superior barrier to the polyolefin structure in both the permeability and solubility studies. Assuming the primary mechanism for quality loss involves aroma retention for the product package system described, the glassine based structure would appear to be the material of choice.

The results also could be used to develop a simulation model to predict the shelf life of a packaged product, where quality is related to the retention of volatile aroma constituents within the package headspace.

Because of the inherent errors involved in the commonly used accelerated storage test method for estimation of product shelf life, more emphasis is being placed on the development of the simulation modeling approach for product shelf life estimation. Here, the entire package/product system is taken into consideration and a mathematical expression developed that includes a measure of:

(1) Product sensitivity,
(2) Package effectiveness, and
(3) Environmental severity.

For the fruit flavored cereal product where quality is related to the retention of an aroma constituent, the parameters to be considered include:

(1) A sorption isotherm which describes the relationship between the concentration of limonene in the product and the vapor pressure of limonene above the product (i.e. in the package headspace).
(2) The permeability rate and permeability coefficient of limonene through the packaging material.
(3) The solubility and solubility coefficient of limonene in the packaging material.
(4) Sensory characteristics of the product.

The latter three parameters have been investigated in detail in the present study. Determination of the sorption isotherm, coupled with sensory and mass transport data, would provide the necessary elements for development of a simulation model. This would provide an analytical method for shelf life estimation. Such a simulation model would however only be appropriate for a packaged product whose quality is related to retention of volatile aroma moieties. Products undergoing loss by more than one mechanism would require additional information with regard to the nature of the product and the mechanisms of loss.

EXPERIMENTAL ERROR ANALYSIS

Temperature, relative humidity, and maintainance of the penentrant driving force concentration are among the conditions which must be properly and continually monitored throughout each section of this study (Permeation, Sorption, and Sensory Evaluation). To avoid characteristic changes due to fluctuating relative humidity, the film samples were stored in desiccators prior to each test.

Permeation Evaluation

It is often difficult to reproduce data relating to a specific penetrant concentration. As time progresses, a syringe tends to loss its reproducability through loose fittings, plugged tip, seals and/or adsorption. Sampling technique is acquired only through means of practice and may substantially effect the data acquired, leading to the possibility of erroneous conclusions.

Flowmeters were positioned in stream for each permeability cell. These were provided as a means for controlling the rate of flow (penetrant vapor) and for detecting possible leaks within the permeation apparatus assembly.

Difficultly can be encountered in placing a film sample within the permeation cell. The permeation cell system is made up of three chambers; the center ring containing the penetrant vapor and two outer chambers containing the permeated vapor, thus two films are simultaneously evaluated. In the process of mounting these film samples, it's possible for the test material to move out of position causing an unacceptable evaluation (i.e. crease, pinhole, non-effective mount/seal .

Permeation of a polymer film sample may be due in part to the presence of defects such as microscopic or macroscopic pinholes or cracks. One of the two films tested in this study was coated with a layer of wax. Depending on the consistency of this layer, duplication of resultant data can be difficult to achieve.

Sorption Evaluation

Variable results were also found in determining the sorption lag time values concerning the HDPE structure, especially at the low levels of limonene concentration (0.30 ppm). These results were due most likely to the difficulty experienced in mounting a film sample. Limonene is quite soluble in polyolefin (HDPE) structures and a change in weight of the sample due to adsorption is seen instantaneously. Therefore, the time required to mount a film sample becomes a critical factor.

At low limonene concentration levels (0.30 ppm), the glassine film structure showed a loss in weight over a period of time. At somewhat higher concentration values, (1.54 ppm) a slight loss again is observed prior to a gain in weight. The loss in weight was apparently a loss in moisture. Therefore, the glassine based structure was placed in a desiccator and allowed to set for a period of at least one week prior to conducting solubility studies. This eliminated the problem.

Sensory Analysis

Evidence indicates that loss of limonene through the package liner may have been affected by leakage due to sampling. The more headspace samples removed from a particular package system, the more apparent the loss when compared with other packages stored over the same period of time but sampled less frequently.

Data collected through quantitative measure shows that approximately 31% of the headspace area response may have been loss due to pinhole leakage.

APPENDIX

LIST OF APPENDIX: EXPERIMENTAL DATA

LIST OF APPENDIX cont...

APPENDIX: A

APPENDIX A

Table 5: Data for Transmission Rate Profile Curve HDPE based structure:

Limonene Vapor Conc. ppm (w/v)	Time (x-axis) minutes	Quantity (y-axis) $\times 10^{-8}$ grams
0.4	0	0.0
(run #36)	135	18.1
	146	24.9
	153	25.2
	174	42.2
	189	41.8
	209	59.2
	229	77.1
	246	98.0
	268	128.3
	299	180.5
	324	209.9
1.3	0	0.0
(run #5)	15	19.4
	25	17.4
	35	9.5
	45	10.1
	55	9.8
	65	16.3
	75	17.1
	85	14.2
	95	18.2
	105	26.9
	115	38.5
	125	53.3
	135	82.4
	145	118.0
	155	156.9
	167	199.2
	185	341.9
	195	417.6
	215	616.7
	225	711.0
	230	881.0

Table 5: continued

Limonene Vapor Conc. ppm (w/v)	Time (x-axis) minutes	Quantity (y-axis) x 10^{-8} grams
1.9 (run #3)	0	0.0
	15	0.0
	30	0.0
	45	0.0
	63	4.5
	71	12.4
	77	18.0
	85	30.5
	95	48.6
	105	102.8
	115	165.8
	125	265.1
	135	355.7
	145	602.0
2.6 (run #2)	0	0.0
	28	0.0
	45	0.0
	65	14.4
	75	34.5
	85	79.1
	95	185.8
	105	351.9
	115	622.7
	125	972.7
3.6 (run #14)	0	0.0
	25	0.0
	35	0.0
	45	10.1
	55	27.3
	65	83.8
	75	245.4
	85	632.6
	95	1217.2
	105	1913.5
	115	2701.1
	125	3510.2
	135	4356.9
	145	4673.7
	165	6238.2
	175	6648.1
	185	7550.2
	195	7648.7

Table 6: Permeation Data For HDPE Based Structure

RUN #	LIMONENE VAPOR CONCENTRATION	% OF LIMONENE PERMEATED THRU FILM	SLOPE (g/min) x 10^{-9}
36	0.39	0.93 to 10.73	10.05
35		0.00 to 10.14	10.22
avg.			10.14
42	0.38	0.94 to 7.68	7.21
41		1.23 to 16.46	9.69
avg.			8.45
44	0.38	1.10 to 13.92	11.67
43		1.12 to 11.88	8.82
avg.			10.25
average	0.38		9.61
46	0.96	1.59 to 13.90	46.34
45		1.95 to 11.28	62.80
average	0.96		54.57
6	1.22	1.49 to 11.12	52.83
5		1.21 to 10.25	65.83
avg.			59.33
20	1.29	0.91 to 3.35	30.02
19		1.32 to 3.74	34.19
avg.			32.11
average	1.26		45.72
4	1.92	1.21 to 4.25	92.19
3		1.10 to 6.47	118.80
average	1.92		105.50

Table 6: continued

RUN #	LIMONENE VAPOR CONCENTRATION	% OF LIMONENE PERMEATED THRU FILM	SLOPE (g/min) x 10^{-9}
2	2.58	1.58 to 11.54	296.20
1		1.03 to 10.35	201.00
avg.			248.60
8	2.53	3.37 to 11.44	437.50
7		1.50 to 11.21	306.50
avg.			372.00
average	2.56		310.30
18	2.89	0.95 to 11.49	441.60
17		1.54 to 11.96	537.10
avg.			489.40
12	3.16	1.04 to 11.74	419.00
11		1.02 to 11.72	336.60
avg.			377.80
10	3.21	2.01 to 11.06	482.90
9		1.86 to 10.30	447.80
avg.			465.40
average	3.09		441.20
14	3.55	1.29 to 10.10	558.90
13		2.87 to 12.29	892.70
average	3.55		725.80

Table 7: Permeation Data Continued For HDPE Based Structure

RUN	AVERAGED (a) PERMEABILITY COEFFICIENT	CORRELATION COEFFICIENT	STANDARD DEVIATION	COEFFICIENT OF VARIABILITY
36	74.22	0.9751		
35	75.47	0.9860		
avg.	74.84			
42	54.65	0.9626		
41	73.46	0.9942		
avg.	64.05			
44	88.45	0.9917		
43	66.85	0.9707		
avg.	77.65			
average	72.18		11.1075	15.4 %
46	139.02	0.9941		
45	188.40	0.9987		
average	163.71		34.9160	21.3 %
6	124.71	0.9778		
5	155.40	0.9811		
avg.	140.06			
20	67.02	0.9945		
19	76.33	0.9995		
avg.	71.65			
average	105.85		41.6076	39.3 %
4	138.29	0.9835		
3	178.20	0.9625		
average	158.25		28.2242	17.8 %

(a) $\frac{\text{grams} * \text{structure}}{m^2 * \text{day} * \text{ppm}} \times 10^{-4}$

Table 7: continued

RUN	AVERAGED [(a)] PERMEABILITY COEFFICIENT	CORRELATION COEFFICIENT	STANDARD DEVIATION	COEFFICIENT OF VARIABILITY
2	330.64	0.9891		
1	224.37	0.9351		
avg.	227.51			
8	498.02	0.9994		
7	348.90	0.9966		
avg.	423.46			
average	350.48		112.6475	32.1 %
18	440.07	0.9743		
17	535.24	0.9835		
avg.	487.66			
12	381.87	0.9795		
11	306.77	0.9809		
avg.	344.32			
10	433.26	0.9878		
9	401.76	0.9855		
avg.	417.51			
average	416.50		75.3548	18.1 %
14	453.42	0.9923		
13	724.22	0.99999		
average	588.82		191.4853	32.5 %
OVERALL COEFFICIENT OF VARIABILITY				25.2 %

(a) $\frac{\text{grams} * \text{structure}}{m^2 * \text{day} * \text{ppm}} \quad x \ 10^{-4}$

Table 8: Permeation Data Continued For HDPE Based Structure

RUN #	LAG TIME UNSTEADY STATE (min)	(hrs)	TIME DURING STEADY STATE (min)	(hrs)	APPARENT DIFFUSION COEFFICIENT (cm^2/sec) x 10^{-10}
36	132	2.2	192	3.2	4.9365
35	130	2.2	186	3.1	4.9745
avg.	131	2.2	189	3.2	4.9555
42	113	1.9	166	2.8	5.7229
41	175	2.9	295	4.9	3.6953
avg.	144	2.4	231	3.8	4.7091
44	138	2.3	220	3.7	4.6861
43	123	2.1	230	3.8	5.2576
avg.	131	2.2	225	3.8	4.8788
average	134	2.2	215	3.6	4.8788
46	98	1.6	137	2.3	6.5988
45	88	1.5	84	1.4	7.3487
average	93	1.6	111	1.9	6.9737
6	126	2.1	84	1.4	5.1324
5	130	2.2	86	1.4	4.9745
avg.	128	2.2	85	1.4	5.0534
20	126	2.1	72	1.2	5.1324
19	120	2.0	70	1.2	5.3890
avg.	123	2.1	71	1.2	5.2607
average	126	2.1	78	1.3	5.1571
4	110	1.8	40	0.7	5.8789
3	100	1.7	45	0.8	6.4668
average	105	1.8	43	0.7	6.1729

Table 8: continued

RUN #	LAG TIME UNSTEADY STATE (min)	(hrs)	TIME DURING STEADY STATE (min)	(hrs)	APPARENT DIFFUSION COEFFICIENT $(cm^2/sec) \times 10^{-10}$
2	92	1.5	43	0.7	7.0292
1	100	1.7	49	0.8	6.4668
avg.	96	1.6	46	0.8	6.7480
8	85	1.4	34	0.6	7.6080
7	88	1.5	46	0.8	7.3487
avg.	87	1.5	40	0.7	7.4783
average	91	1.5	43	0.7	7.1132
18	65	1.1	35	0.6	9.9490
17	66	1.1	29	0.5	9.7980
avg.	66	1.1	32	0.6	9.8736
12	86	1.4	41	0.7	7.5196
11	90	1.5	50	0.8	7.1854
avg.	88	1.5	46	0.8	7.3525
10	70	1.2	45	0.8	9.2383
9	75	1.3	35	0.6	8.6225
avg.	73	1.2	40	0.7	8.9304
average	76	1.3	39	0.7	8.7188
14	72	1.2	33	0.6	8.9817
13	74	1.2	26	0.4	8.7390
average	73	1.2	30	0.5	8.8603

Table 9: Permeation Studies For HDPE Based Structure Continued

Driving Force Vapor Concentration

RUN No.s	d-LIMONENE VAPOR CONC.	AVERAGED AREA RESPONSE	STANDARD DEVIATION	COEFFICIENT OF VARIABILITY
35/36	0.39	*** 1398600	123616	8.8 %
41/42	0.38	*** 1362995	204577	15.0 %
43/44	0.38	*** 1374113	152218	11.0 %
average	0.38	1378569		
45/46	0.96	*** 3460500	127468	3.7 %
5/6	1.22	* 339256	40263	11.9 %
19/20	1.29	* 361440	9337	2.6 %
average	1.26	350348		
3/4	1.92	* 536960	20023	3.7 %
1/2	2.58	* 720200	50796	7.1 %
7/8	2.53	* 707800	16880	2.4 %
average	2.56	714000		
17/18	2.89	** 359565	13333	3.7 %
11/12	3.16	* 883886	65476	7.4 %
9/10	3.21	* 896640	62489	7.0 %
average	3.09			
13/14	3.55	* 992900	45200	4.6 %

* Samples # 1 through 24 (except #'s 17 & 18) were analyized using G.C. Model 5830 and the limonene standard calibration of 1.79 x 10^{-12} grams/area unit.

** Samples # 17 & 18 were analyzed using G.C. Model 5890 and a standard calibration of 4.016 x 10^{-12} was employed.

*** Samples # 25 through 46 were analyzed using G.C. Model 5890 and the Calibration standard of 13.8 x 10^{-14} g/a.u.

Table 10: Data for Transmission Rate Profile Curve
GLASSINE based structure:

Limonene Vapor Conc. ppm (w/v)	Time (x-axis) minutes	Quantity (y-axis) x 10^{-8} grams
1.5	0	0.0
(run #20)	75	0.0
	96	7.8
	128	10.5
	218	13.4
	367	16.7
	794	27.8
	941	34.6
	1081	37.9
	1224	41.3
	1372	39.3
	1804	49.2
	1955	52.0
	2127	55.7
2.5	0	0.0
(run #13)	73	0.0
	115	10.1
	133	13.4
	140	7.8
	258	13.7
	401	19.0
	419	18.7
	587	30.1
	704	34.2
	840	36.1
	984	47.6
	1126	53.8
	1270	58.9
	1410	80.0

Table 10: continued

Limonene Vapor Conc. ppm (w/v)	Time (x-axis) minutes	Quantity (y-axis) x 10^{-8} grams
3.6 (run #18)	0	0.0
	134	13.1
	171	12.9
	282	21.8
	456	44.4
	615	81.6
	712	106.2
	743	107.2
	855	144.9
	999	166.3
	1144	192.2
	1292	234.1
	1447	257.2
	1722	283.7
4.3 (run #10)	0	0.0
	113	16.6
	119	23.4
	128	23.3
	143	33.5
	158	42.6
	164	48.2
	261	170.4
	267	180.3
	282	218.0
	288	230.4
	306	284.8
	544	775.1
	550	969.3
4.8 (run #12)	0	0.0
	10	6.4
	17	6.0
	138	187.8
	140	200.5
	149	232.0
	177	320.4
	200	407.9
	281	699.7
	294	731.0

Table 11: Permeation Data For Glassine Based Structure

RUN #	LIMONENE VAPOR CONCENTRATION	% OF LIMONENE PERMEATED THRU FILM	SLOPE (g/min) x 10^{-11}
20	1.54	0.14 to 0.72	2.23
19	"	0.13 to 0.36	0.96
average	1.54		1.60
14	2.51	0.28 to 0.97	8.43
13	2.39	0.00 to 0.66	4.86
average	2.45		6.65
6	3.50	0.19 to 1.67	44.62
5	"	0.22 to 1.53	39.03
avg.	3.50		41.83
18	3.63	0.25 to 1.46	21.56
16	"	0.28 to 1.69	27.93
15	3.59	0.32 to 1.57	19.73
avg.	3.60		23.07
average	3.55		34.52
8	4.27	0.58 to 2.93	301.40
7	4.26	0.24 to 2.57	271.50
avg.	4.27		286.45
10	4.45	0.19 to 3.52	191.90
9	4.40	0.26 to 4.35	223.10
avg.	4.43		207.50
4	4.34	0.19 to 3.59	193.70
3	4.35	0.26 to 2.79	170.50
avg.	4.35		182.10
average	4.35		225.35
12	4.82	0.79 to 3.08	351.10
11	"	0.46 to 2.43	309.20
average	4.82		330.15

Table 12: Permeation Data Continued For Glassine Base Structure

RUN	AVERAGED (a) PERMEABILITY COEFFICIENT	CORRELATION COEFFICIENT	STANDARD DEVIATION	COEFFICIENT OF VARIABILITY
20	4.2	0.9872		
19	1.8	0.9709		
average	3.0		1.7	56.1 %
14	9.7	0.9947		
13	5.9			
average	7.8		2.8	35.6 %
6	37	0.9895		
5	32	0.9808		
avg.	34.5			
18	17.1	0.9973		
16	22.4	0.9756		
15	15.8	0.9808		
avg.	18.4			
average	24.8		9.2	37.2 %
8	203	0.9994		
7	184	0.9992		
avg.	194			
10	124	0.9911		
9	141	0.9972		
avg.	133			
4	129	0.9785		
3	113	0.9898		
avg.	121			
average	149.7		36.0	24.0 %
12	210	0.9997		
11	185	0.9989		
average	197.3		17.7	9.0 %
OVERALL COEFFICIENT OF VARIABILITY				32.4 %

(a) $\frac{\text{grams} * \text{structure}}{\text{m}^2 * \text{day} * \text{ppm}} \times 10^{-6}$

Table 13: Permeation Data Continued For Glassine Based Structure

RUN #	LAG TIME UNSTEADY STATE (min)	(days)	TIME DURING STEADY STATE (min)	(days)
20	750	0.5	20520	14.3
19	966	0.7	20306	14.1
average	858	0.6	20413	14.2
14	4014	2.8	10086	7.0
13	----	---	---	---
6	2643	1.8	5719	4.0
5	2641	1.8	5719	4.0
avg.	2642	1.8	5719	4.0
18	4559	3.2	12662	8.8
16	2805	2.0	8611	6.0
15	4552	3.2	9905	6.9
avg.	3972	2.8	10393	7.2
average	3440	2.4	8523	5.9
8	1153	0.8	1682	1.2
7	1037	0.7	1682	1.2
avg.	1095	0.8	1682	1.2
10	1580	1.1	3864	2.7
9	1425	1.0	4017	2.8
avg.	1503	1.0	3941	2.7
4	1577	1.1	3690	2.6
3	2196	1.5	3242	2.3
avg.	1887	1.3	3466	2.4
average	1495	1.0	3030	2.1
12	1379	1.0	1558	1.1
11	1377	1.0	1558	1.1
average	1378	1.0	1558	1.1

Table 14: Permeation Studies For Glassine Based Structure Continued

Driving Force Vapor Concentration

RUN No.s	d-LIMONENE VAPOR CONC.	AVERAGED AREA RESPONSE	STANDARD DEVIATION	COEFFICIENT OF VARIABILITY
19	1.54	428807	51729	12.0 %
20	1.54	428807	51729	12.0 %
average	1.54	428807		
13	2.39	666293	70547	10.6 %
14	2.51	700863	52317	7.5 %
average	2.45	683578		
5	3.50	976600	61898	6.3 %
6	3.50	976600	61898	6.3 %
avg.	3.50	976600		
15	3.59	1002225	57707	5.8 %
16	3.59	1003904	63891	6.4 %
18	3.63	1014019	46387	4.6 %
avg.	3.60	1006716		
average	3.55	994670		
7	4.26	1189889	38388	3.0 %
8	4.27	1191750	40602	3.4 %
avg.	4.27	1190820		
9	4.40	1229000	62492	5.1 %
10	4.45	1241625	53139	4.3 %
avg.	4.43	1235313		
3	4.35	1215333	98584	8.1 %
4	4.34	1213222	98144	8.1 %
avg.	4.35	1214278		
average	4.35	1213470		
11	4.82	1347571	68274	5.0 %
12	4.82	1347571	68274	5.0 %
average	4.82	1347571		

All samples (# 1 through 20) were analyized using G.C. Model 5830 and the limonene standard calibration of 1.79 x 10^{-12} grams/area unit.

APPENDIX: B

APPENDIX B

Table 15: Solubility Data For HDPE Based Structure

RUN #	(1) LIMONENE VAPOR CONCEN	(2) ROOM TEMP (^{o}F)	(3) EQUILIBRIUM SOLUBILITY (mg/mg)	(4) SOLUBILITY COEFFICIENT (mg/mg ppm)	(5) DIFFUSION COEFFICIENT (cm^{2}/sec)
39	0.00	71.4	0.00	0.00	---
40	"		"	"	---
10	0.29	71.4	0.26	8.84	---
11	0.30	71.7	----	----	---
12	0.29	70.2	0.21	7.34	---
13	0.29	69.9	0.23	7.87	---
15	0.30	69.1	0.23	7.64	---
avg.	0.29	70.2	0.22	7.62	---
16	1.52	68.5	1.03	6.76	3.63
19	--	68.8	1.02	8.97	4.59
30	1.48	69.1	1.05	7.07	4.65
avg.	1.50	69.0	1.03	7.60	4.29
37	2.50	68.7	1.78	7.11	4.71
38	2.63	67.9	1.95	7.43	5.01
avg.	2.57	67.9	1.87	7.27	4.86
20	4.35	68.4	2.74	6.30	---
21	3.92	68.2	3.05	7.79	5.61
24	4.60	69.2	3.55	7.71	---
25	4.09	67.6	3.50	8.56	6.14
avg.	4.24	68.4	3.21	7.59	5.88
33	6.58	69.6	6.44	9.79	---
34	6.28	68.5	6.04	9.62	8.35
avg.	6.43	68.7	6.24	9.71	8.35

Table 15: continued

RUN #	(1) LIMONENE VAPOR CONCEN	(2) ROOM TEMP ($^{\circ}$F)	(3) EQUILIBRIUM SOLUBILITY (mg/mg)	(4) SOLUBILITY COEFFICIENT (mg/mg ppm)	(5) DIFFUSION COEFFICIENT (cm^2/sec)
5	6.80	71.5	10.38	15.26	12.38
7	7.15	70.9	12.86	17.98	13.07
avg.	6.98	71.2	11.62	16.62	12.73

(1) Concentration express as ppm, vapor in nitrogen on a weight per volume basis.

(2) Room Temperature +/- 2 degrees

(3) Units expressed as: $\frac{\text{mg limonene}}{\text{mg HDPE}} \times 10^{-2}$

(4) Units expressed as: $\frac{\text{mg limonene}}{\text{mg HDPE * ppm}} \times 10^{-3}$

(5) Units expressed as: $\text{cm}^2/\text{sec} \times 10^{-10}$

Table 16: Solubility Data For Glassine Based Structure

RUN #	(1) LIMONENE VAPOR CONCEN	(2) ROOM TEMP (^oF)	(3) EQUILIBRIUM SOLUBILITY (mg/mg)	(4) SOLUBILITY COEFFICIENT (mg/mg ppm)	(5) DIFFUSION COEFFICIENT (cm^2/sec)
41	0.00	68.6	0.00	0.00	----
42	"		"	"	----
14	0.30	69.2	----	----	----
27	1.44	69.1	1.76	12.20	2.19
28	1.47	68.7	1.32	9.00	3.09
29	1.51	68.3	1.32	8.73	4.32
avg.	1.47	68.9	1.47	9.98	3.20
35	2.50	67.8	4.65	18.58	2.39
36	2.49	68.4	4.63	18.59	1.64
avg.	2.50	68.3	4.64	18.59	2.02
23	4.59	69.3	6.56	14.28	2.40
26	4.61	68.8	6.30	13.66	3.51
avg.	4.60	68.7	6.43	13.97	2.96
31	6.69	68.3	15.37	22.98	4.76
32	6.06	68.1	13.46	22.21	3.79
avg.	6.38	68.1	14.42	22.60	4.28
8	7.40	71.4	58.10	78.51	64.20
9	7.28	70.7	63.11	86.69	72.30
avg.	7.34	71.4	60.61	82.60	68.25

(1) Concentration express as ppm, vapor in nitrogen on a weight per volume basis.

Table 16: continued

(2) Room Temperature +/- 2 degrees

(3) Units expressed as: $\frac{\text{mg limonene}}{\text{mg glassine}} \times 10^{-3}$

(4) Units expressed as: $\frac{\text{mg limonene}}{\text{mg glassine * ppm}} \times 10^{-4}$

(5) Units expressed as: $cm^2/sec \times 10^{-10}$

APPENDIX: C

APPENDIX C

STANDARD CALIBRATION

Basically three standard calibration factors were employed throughout this study, depending on the gas chromatograph (G.C.) model used, as well as test conditions utilized (i.e. oven temp., time factors, cooling time, etc...)

Table 17: This standard was used primarily for Permeation run numbers 1 through 24 concerning the HDPE based structure and Permeation run numbers 1 through 20 concerning the Glassine based structure, utilizing the G.C. Model #5830:

d-limonene standard calibration factor = 1.79×10^{-12} g/a.u.

Table 18: This standard was used only for Permeation run numbers 17 and 18 in regard to the HDPE based film structure, utilizing the G.C. Model #5890:

d-limonene standard calibration factor = 4.02×10^{-12} g/a.u.

Table 19: The standard listed here was applied to a series of studies which include:

(A) Permeation studies: run numbers 25 through 46 concerning the HDPE based structure,
(B) All solubility studies for both polymeric films, &
(C) All sensory evaluation studies involving quantification of headspace samples in cereal packages fabricated from the glassine based structure.

The G.C. Model #5890 was used in obtaining:

d-limonene standard calibration factor = 13.8×10^{-14} g/a.u.

Table 17: Limonene Standard Calibration Curve Data
G.C. Model #5830

INITIAL CALIBRATION: 11/27/84

AREA RESPONSE (x - axis)	ABSOLUTE QUANTITY {x 10^{-9} grams} (y - axis)
0	0.0
30060	60.0
63605	120.0
99705	181.6
132625	242.2
1352500	2421.5

RECALIBRATION: 1/23/86

AREA RESPONSE (x - axis)	ABSOLUTE QUANTITY {x 10^{-9} grams} (y - axis)
0	0.0
2150	4.4
4584	8.8
6905	13.2
10153	17.6
102533	176.0
997650	1760.0

Figure 22. d–LIMONENE STANDARD CALIBRATION CURVE: G.C. MODEL #5830

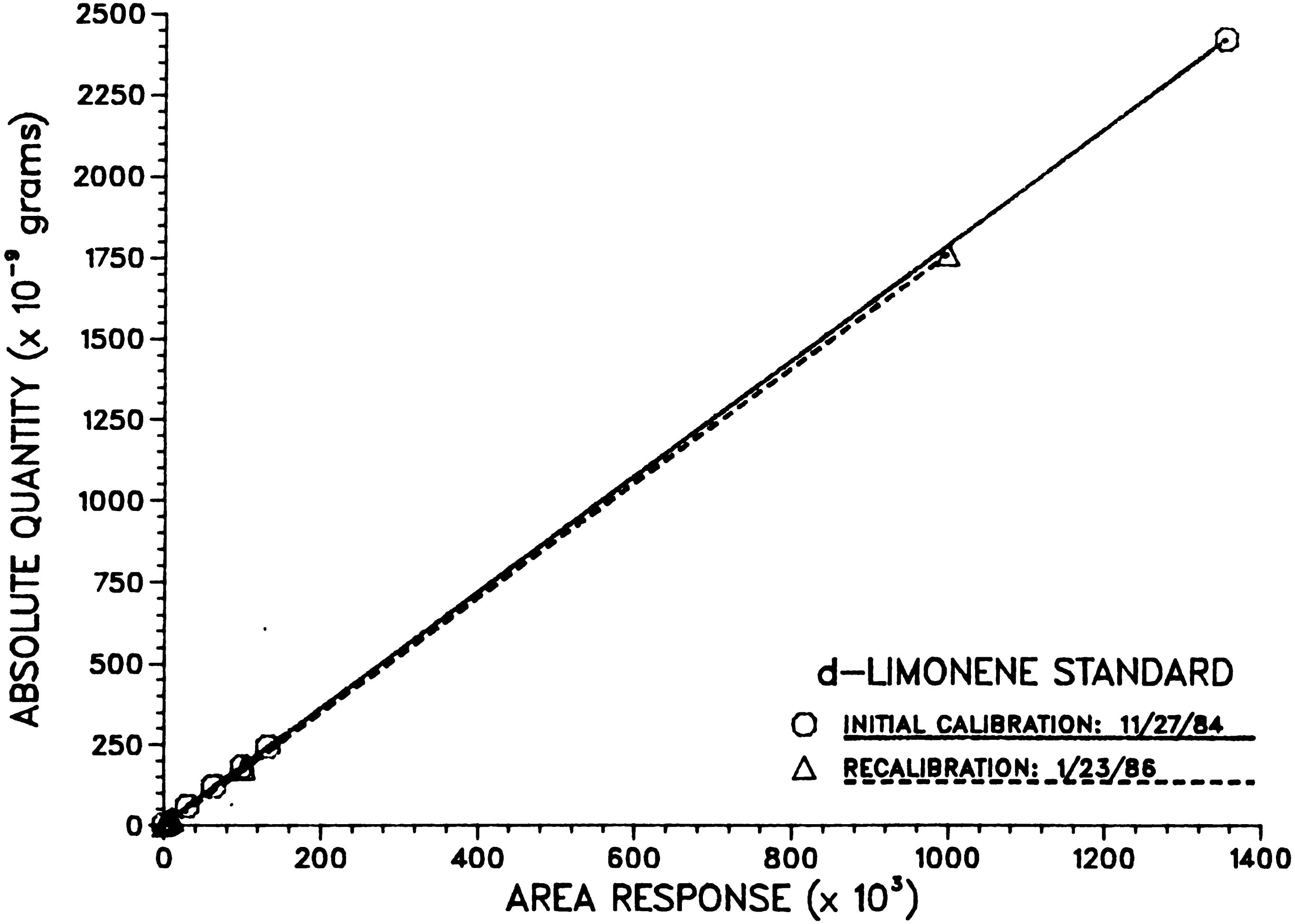


Table 18: INITIAL CALIBRATION 4/9/85

AREA RESPONSE (x - axis)	ABSOLUTE QUANTITY {x 10^{-9} grams} (y - axis)
0	0.0
18438	71.8
28617	125.3
47195	180.4
63168	250.5
623680	2505.0

Figure 23. LIMONENE STANDARD CALIBRATION CURVE: G.C. MODEL #5830

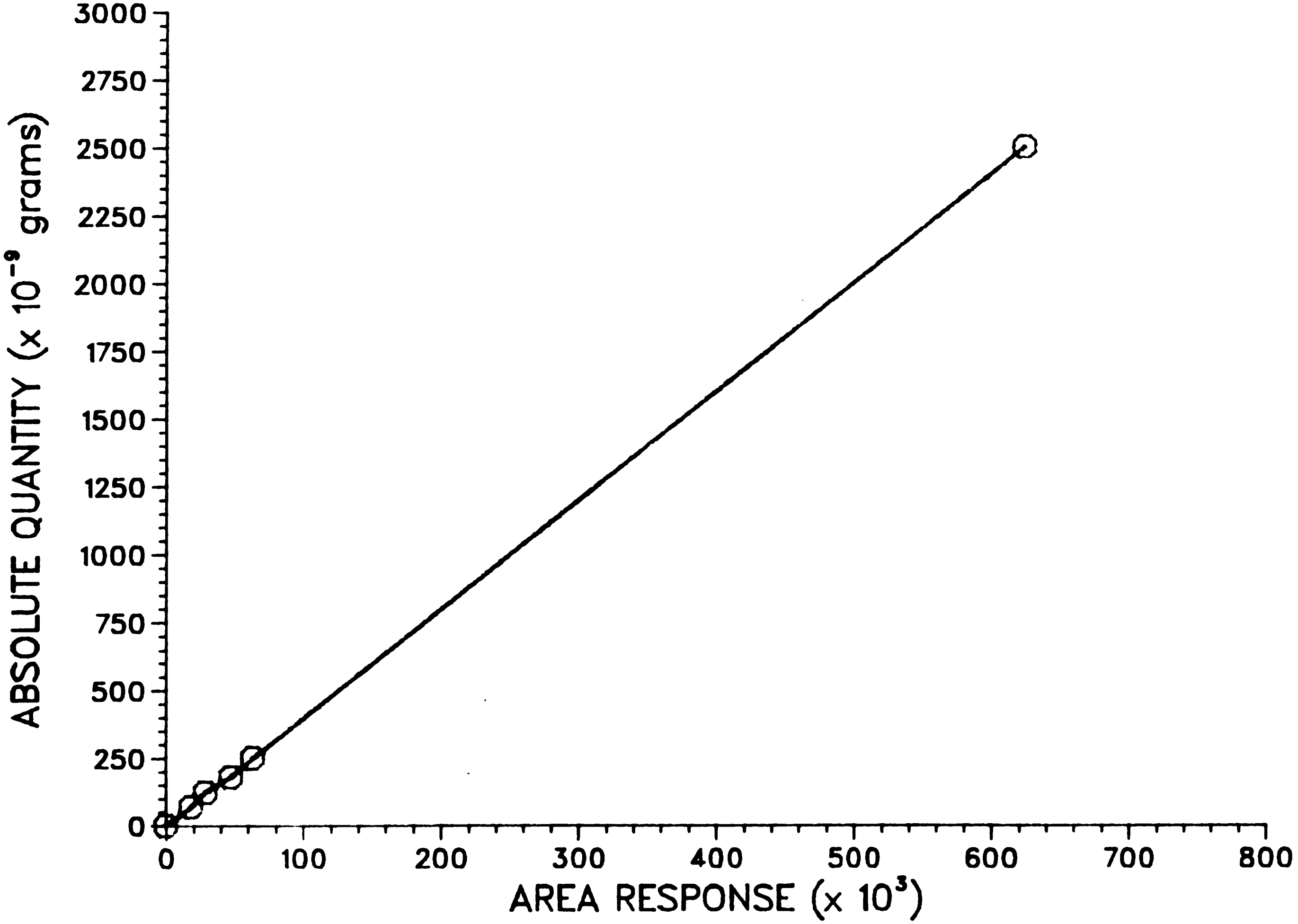


Table 19: Limonene Standard Calibration Curve Data
G.C. Model #5890

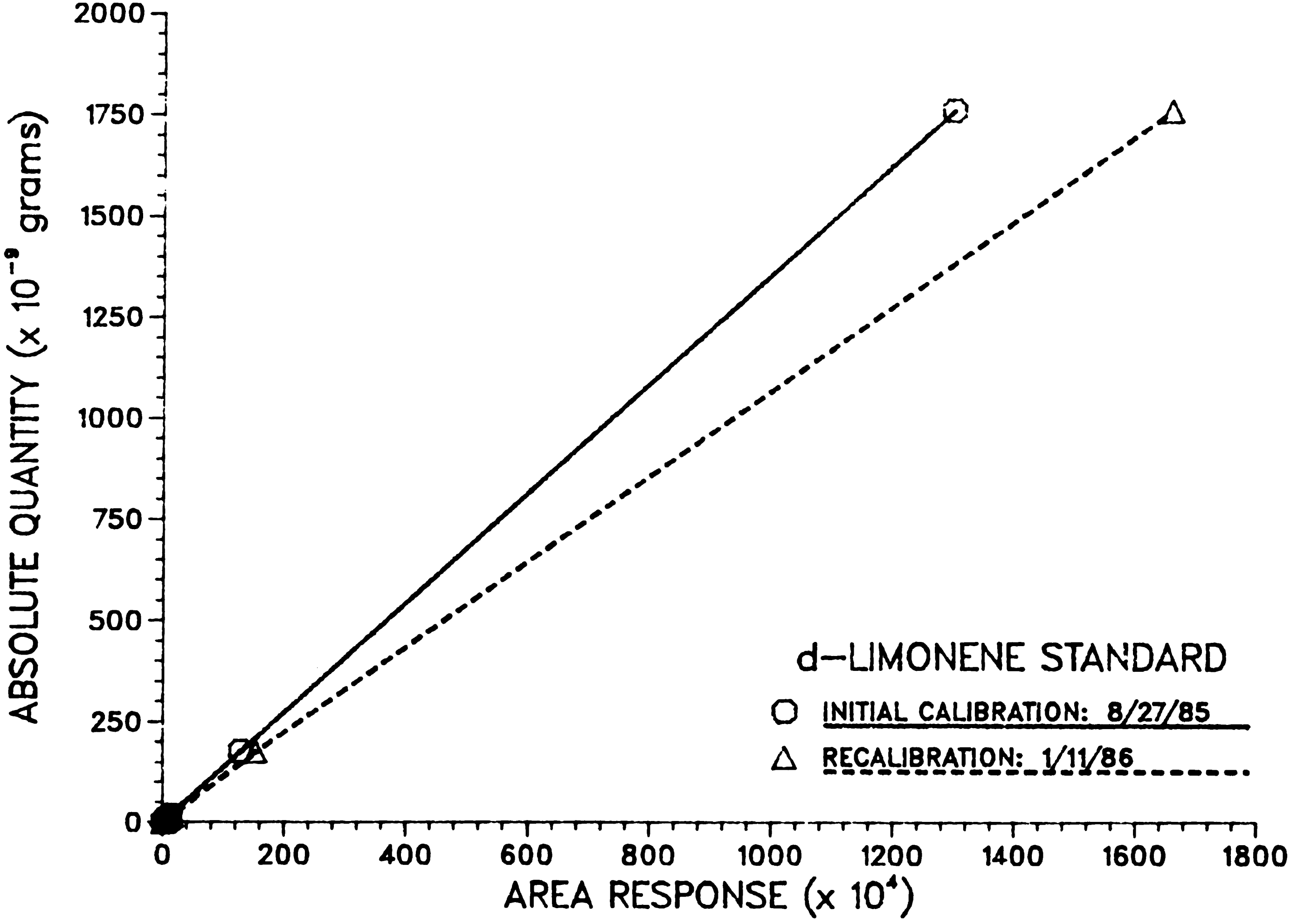
INITIAL CALIBRATION: 8/27/85

AREA RESPONSE (x - axis)	ABSOLUTE QUANTITY {x 10^{-9} grams} (y - axis)
0	0.0
20920	4.4
53717	8.8
81261	13.2
117803	17.6
1269767	176.0

RECALIBRATION: 1/11/86

AREA RESPONSE (x - axis)	ABSOLUTE QUANTITY {x 10^{-9} grams} (y - axis)
0	0.0
23757	4.4
62671	8.8
93310	13.2
142003	17.6
1524900	176.0

Figure 24. d–LIMONENE STANDARD CALIBRATION CURVE: G.C. MODEL #5890



APPENDIX: D

APPENDIX D

Table 20: Sensory Bar Graph Data
Glassine Base Structure Only

APPROXIMATE STORAGE TIME (months)	LIMONENE HEADSPACE CONCENTRATION (ppm) x-axis	RELATIVE RESPONSE SCALE (quality) y-axis
9	0.004	5.2
6	0.013	5.4
3	0.018	8.5
initial	0.029	10.0

Figure 25. AROMA EVALUATION OF FRUIT FLAVORED CEREAL

Name:

Please evaluate the cereal samples in regards to the perceived aroma detected. Then determine, on the given lines, the degree of aroma for each cereal sample. Be sure your mark follows the example as shown. Use only one line per cereal sample. Please feel free to comment on the aroma quality of each sample (i.e. stronger cereal grain aroma than the fruit aroma) in the space provided. Thank you for your participation.

Example: ____________________/__________
N M S

Indicate your response on the following lines:

Sample No.__________

____

No Fruit Aroma	Moderate Fruit Aroma	Strong Fruit Aroma

Sample No.__________

____

No Fruit Aroma	Moderate Fruit Aroma	Strong Fruit Aroma

Sample No.__________

____

No Fruit Aroma	Moderate Fruit Aroma	Strong Fruit Aroma

Sample No. Comments

Table 21: Sensory Analysis Data; Quantitative Study Followed Immediately By A Qualitative Evaluation (Glassine Based Structure Only)

3 MONTHS STORAGE PERIOD: 6/21/85 thru 9/25/85

SAMPLE NUMBER	INITIAL LIMONENE (a.u.)	FINAL LIMONENE (a.u.)	LIMONENE CONCEN (ppm)	LOSS OF LIMONENE (%)	SENSORY EVALUATION (scale=10)
103_1	108020	61353			
103_2	111950	68823			
avg.	109985	65088	0.018	41	7.7
104_1	101770	63640			
104_2	102230	64614			
avg.	102000	64127	0.018	37	8.7
105_1	108190	71225			
105_2	108200	68907			
avg.	108195	70066	0.019	35	8.9
108_1	99432	62590			
108_2	99605	64143			
avg.	99519	63367	0.017	36	9.5
112_1	102890	65709			
112_2	107320	64358			
avg.	105105	65034	0.018	38	7.9
OVERALL AVERAGE	104961	65536	0.018	38	8.5

Table 22: Sensory Analysis Data; Quantitative Study Followed Immediately By A Qualitative Evaluation (Glassine Based Structure Only)

6 MONTHS STORAGE PERIOD: 6/21/85 thru 12/20/86

SAMPLE NUMBER	INITIAL LIMONENE (a.u.)	FINAL LIMONENE (a.u.)	LIMONENE CONCEN (ppm)	LOSS OF LIMONENE (%)	SENSORY EVALUATION (scale=10)
109_1	105890	34816			
109_2	101780	41937			
avg.	103835	38377	0.011	63	5.6
110_1	103690	39989			
110_2	99441	41911			
avg.	101566	40950	0.011	60	4.2
111_1	101630	45020			
111_2	100640	44439			
avg.	101135	44730	0.012	56	5.0
90_1	107200	62874			
90_2	110550	65884			
avg.	108875	64379	0.018	41	5.7
89_1	99643	45690			
89_2	99735	46490			
avg.	99689	46090	0.013	54	6.0
88_1	100260	57011			
88_2	104870	56494			
avg.	102565	56753	0.016	45	5.8
OVERALL AVERAGE	102944	48546	0.013	53	5.4

Table 23: Sensory Analysis Data; Quantitative Study Followed Immediately By A Qualitative Evaluation (Glassine Based Structure Only)

9 MONTHS STORAGE PERIOD: 7/25/85 thru 4/25/86

SAMPLE NUMBER	INITIAL LIMONENE (a.u.)	FINAL LIMONENE (a.u.)	LIMONENE CONCEN (ppm)	LOSS OF LIMONENE (%)	SENSORY EVALUATION (scale=10)
C_1	119460	22201			
C_2	125890	20312			
avg.	122675	21257	0.006	83	5.0
D_1	110980	14727			
D_2	116030	13209			
avg.	113505	13968	0.004	88	5.0
E_1	121380	14903			
E_2	126720	14261			
avg.	124050	14582	0.004	88	4.1
F_1	113180	8577			
F_2	113900	8295			
avg.	113540	8436	0.002	93	8.8
OVERALL AVERAGE	118443	14561	0.004	88	5.7

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BIBLIOGRAPHY

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