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EVALUATION OF THE CHANGE ON WATER VAPOR TRANSMISSION RATE OF DIFFERENT POLYPROPYLENE FILMS IN CONTACT WITH d-LIMONEME AND THE EFFECT SUCH CHANGES HAVE ON THE SHELF LIFE OF CONFECTIONARY PRODUCTS.

By

Anna M. Romero

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ABSTRACT

This paper discusses the changes observed in Water Vapor Transmission Rate (WVTR) of three plastic films while exposed to different concentrations of d-limoneme. The concentration of d-limoneme on the films was determined by means of Headspace Gas Chromatography and Mass Spectrometry. The Water Vapor Transmission rate of all films was determined by means of a MOCON–Water Vapor Permeation Analysis System Permatran-W 3/31. It was observed that d-limoneme affected the films in two ways: at lower concentrations, the WVTR decreased but, after certain concentration was reached, the WVTR increased. These results explain the shortened shelf-life of candies containing d-limoneme which are currently packaged with the studied films. Finally, this paper discusses all the experimental problems encountered on this study as well as possible improvements for future studies.

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INTRODUCTION

Before the packaging industry started the widespread use of plastics, it relied on materials such as glass, metal, or paper. In those times, the interaction between the packaging materials and the foods was well understood: glass was mostly inert and metal could oxidize so coatings were utilized. In any instance those materials did not allow any compounds to exit or enter the package. However, when polymeric films began to be used, the industry encountered a more dynamic and complex material. Polymer films interact with their environment differently than glass or metal containers. Molecules can dissolve and diffuse in a polymer film; thus, free entrance or exit of different compounds will be observed on packages made with those materials. Such interaction between the plastic film and compounds on the vapor phase is called *permeation*.

The permeability of plastic films usually represents a problem when packaging certain food items because it highly reduces the shelf-life of the product. In other instances such permeability is desired. For example, films used to package meat should allow the permeability of oxygen so the meat stays red and looks fresh. The first task on deciding which packaging material to use for certain food application is understanding what kind of shelf-life is required from the product (Paine 1992).

The Shelf-life Concept

Shelf-life is defined as the time in which certain food products can retain their nutrition, quality, and flavor properties when packaged in a certain fashion (Hirsh, 1991). Usually, it is a hard task to predict the point at which the food can be considered spoiled. Many methods have been used to determine such a point depending on the nature of the food and the mode of spoilage. In order to package a food product and predict its shelf-life, it is necessary to understand how this food will loose its freshness, flavor characteristics, or quality, or even at what point a food can become a health hazard.

Food spoilage is a complex issue in the sense that it may occur due to many interactions occurring at once. Most studies agree that one of the most common modes of food degeneration is oxidation resulting from the reaction between oxygen and some food ingredients such as fats, oils used for flavoring, and enzymes. Another mode of food degeneration is the gain or loss of moisture. It is critical that moist foods do not dehydrate and that dry foods do not gain water that can cause changes in appearance, taste, texture and microbiological growth. Flavor degeneration can also occur due to the migration of the flavor and aroma molecules present on the food to the outside environment. In the opposite way, the contamination of the foods with aromas or flavor molecules from the outside environment can also cause off-flavors and result in food degeneration. In general, there are primarily 10 ways in which food deteriorates (Cairns 1974):

1. Lipid Oxidation, which causes off flavors and rancidity
2. Water gains or loss, which can cause changes in texture, flavor, nutritional value and the growth of microorganisms.
3. Non-enzymatic browning
4. Vitamin degradation
5. Absorption of flavoring agents by the package or exit of flavors to the outside environment
6. Absorption of off-odors from the package or the environment
7. Microbiological decay
8. Physical degradation: bruising, crushing, breaking, etc.
9. Pest infestation
10. Temperature induced texture changes

Usually, a package is designed to help minimize the effect of such factors on the food products. It is important to note that many of those mechanisms of degradation have been well studied and their likelihood and rate of reaction can be predicted. Specifically, studies by Labuza on water ingression/absorption, lipid oxidation, and vitamin degradation mechanisms have helped in creating models that can be used to predict the shelf-life of many foods with a certain degree of accuracy.

In fact, many food companies use such models to predict the shelf-life of their products in order to make final decisions on whether to select certain packaging systems for a specific product. It is also common practice to conduct regular or accelerated shelf-life studies to corroborate any theoretical data obtained from the use of such models.

Shelf-life Model

A model for predicting the shelf-life of a product whose mode of failure is due to gain or loss of moisture was derived by Labuza and summarized as follows:

$$m = m_e - \{ (m_e - m_i) / \ln^{-1} [(P/t)(A/W)(P_o/b)\, T] \}$$

Where: m = moisture content of the food at time T
m_e = Equilibrium moisture content with no package
m_i = Initial moisture content
P = Water vapor permeability of the package
T = Thickness of the film
A = Area of transmission
W= Food mass
P_o/b = Water vapor pressure of Pure water at storage temperature, divided by the slope of the moisture sorption isotherm curve between m and m_i.

The moisture sorption isotherm (MSI) curve is a graph of the moisture content of the food as a function of the equilibrium relative humidity of the environment surrounding the food. As can be seen, many of the data needed to calculate shelf-life must be obtained from analytical chemical analysis of the food to be tested. The ways in which those values are obtained can be reviewed in the literature (Castellano 2001, Gnanasekharan 1993)

This model has been used with a high degree of success on products such as bread, crackers, cookies, dried fruits, breakfast cereals, etc. However, this model is simply a good predictor as no one can estimate the exact environmental conditions each package will see during its lifetime cycle: temperature, relative humidity, location in store, handling by consumer, etc. In addition, this model cannot predict all possible interactions between the package, the product, and the outside environment.

There have also been attempts to create accurate models for other mechanisms of degradation such as lipid oxidation, vitamin degradation, flavor permeation, and so on but those models still need more work (Castellano 2001, Gnanasekharan 1993) and are not widely used by the food and packaging industry.

Shelf-Life Studies

It is common practice in the food industry to conduct shelf-life studies for any new food product or foods placed in a new package system. This is done in order to have enough information for coding expiration dates and determining the maximum amount of time such products can be distributed and kept in stores. This is generally done to corroborate any theoretical values obtained by means of the shelf-life model, or whenever there is not an accurate model that can predict all the interactions occurring between the food and the environment. Such studies usually involve placing the packaged goods in a controlled environment for large amounts of time. Product is analyzed over regular intervals to determine any changes. The quantification of any quality or flavor lost is usually done in either one of the following ways: 1) By means of chemical analysis to obtain concentration of water or chemical of interest, presence of chemical byproducts or microorganisms; and/or 2) Organoleptic studies in which a panel of people will analyze the product and record any comments on appreciable food characteristics differences.

Factors analyzed during testing include the following:

- Weight: Loss or gain of weight can indicate the amount of moisture gained or lost during storage
- Seals: Visual inspection and seal strength determination should be conducted to verify any lost over time

- Material Integrity: Visual inspection of opened package, in order to find any defects that occurred over time such as ply separation, discoloration or pin holes
- Product Inspection: Visual inspection of the product and sensory testing when applicable in order to record any change.

Such studies are usually costly and time consuming, since the final results cannot be obtained until the product reaches the end of its useful shelf-life. Depending on the product, this can take a few months or several years. The length of such studies can affect the successful launch of new products on the market, so instead many companies rely on accelerated shelf-life studies.

Accelerated Shelf-life Studies

In accelerated shelf-life studies, product is placed in extreme environments where the temperature and/or relative humidity are much higher than the product will see during its lifetime. Many studies by Labuza and others have been done to predict the exact increase in the rate of the degradative reactions due to the controlled increase in temperature. Models have been created to link the equivalent times of the accelerated conditions in the lab vs. the normal distribution environment. This has all been done by means of well-known kinetic theories in many labs around the world. Usually, data obtained in accelerated shelf-life studies for moisture gain or loss, oxidation reaction, and permeability of flavors is accurate enough to replace the most costly shelf-life studies.

Accelerated shelf-life focuses on the changes of moisture over time. Humidity and vapor pressure are used to increase the rate of ingress or egress of moisture from the package. The rate increase is proportional to the change of humidity and water vapor pressure of the outside environment. In this test, product is placed in environmental rooms for a determined length of time. The packages are weighed over time to measure the gain or loss of moisture. At the beginning and end of the study, the humidity and critical moisture of the product are measured. *Critical moisture* refers to the amount of water needed to change the physical properties of the product to a point at which the product becomes unacceptable. When all data is obtained, a mathematical equation is used to calculate the equivalence between the time in the environmental room and the time in the "regular" environment. All the data is then included in the shelf-life model to predict the rate at which the product would spoil in the "regular" environment.

The Relationship between Permeability and Shelf-life

By packaging foods with plastic films, an engineer encounters an immediate problem: The entrance or exit of small molecules such as oxygen, carbon dioxide and water vapor inside the package. As was stated earlier, such molecules are responsible for the spoilage of the foodstuff. Therefore, it is clear that the permeability of the film will greatly affect the final shelf-life of the packaged product. In fact, permeability equations are part of the shelf-life predictor model (Briston 1974):

$$\Delta Mx / \Delta t = P\,A\,\Delta px / L$$

In this case, ΔMx is interpreted as the maximum amount of compound that is allowed to migrate as determined by measurements such as critical moisture minus initial moisture. The parameter Δt can be interpreted as the shelf-life. The environmental factors affecting shelf-life and permeability are described by Δpx or the partial pressure of the migrant in the atmosphere or the inside of the package. The package characteristics can be described by the other factors in the equation: Area (A), Permeability (P), and Thickness (L). Before one can truly understand this relationship, it will be necessary to review basic information on permeability and the most widely recognized permeability theory for plastic films or membranes.

The Permeability Theory

Permeability is the transmission rate of a vapor normalized for both the thickness of the film and the difference in pressure. The rate at which a gas will permeate through a membrane is dictated by many factors dependent on the properties of both the membrane and the gas, as well as the degree of interaction between the two of them.

Permeation occurs in films due to the nature of polymeric materials. Such materials are not a completely continuous arrangement of matter, but consist of a network of molecules containing “pores” of variable sizes. Some polymers can arrange themselves in a very orderly way in crystalline regions or in amorphous regions tightly packed due to orientation or the lack of bulky functional groups attached to the backbones. In those cases, the “pores” are more limited than in bulkier polymers that arrange in a more disorderly way allowing for more free “empty” spaces. In any case, the network of pores will be more or less rigid, depending upon the degree of vibration of the molecules forming it. Highly organized networks generally vibrate less than disorganized more flexible networks. As a consequence, the more rigid networks may allow some selective permeation which only few small molecules could permeate. On the other hand, the more elastic networks allow more space for greater displacement, so more and larger molecules can permeate.

The permeation process occurs in four steps (Stern 1989):

1. Collision of the penetrating molecule with the polymer
2. Sorption of the molecules into the polymer
3. Migration through the polymer
4. Desorption of the permeant from the polymer

In the first step, the penetrant molecules collide with the membrane until they blend with the polymer. This step is obviously dependent on the concentration of permeant and its partial pressure, and also depends on the film surface area. In the second step, the polymer absorbs the penetrants. This step depends primarily on the polarity and chemical affinity between the polymer and the penetrant, as well as on temperature and pressure. In the third step, the penetrant “jumps” through the “pores” or empty spaces available in the film. The nature and arrangement of the polymer in addition to the size of the penetrant determine this step. The last step consists of the desorption of the penetrant molecule. This step depends on the temperature, partial pressure, and chemical nature of both penetrant and polymer.

The step in which the molecules migrate through the polymer could be the most difficult to visualize. It can be more easily understood if one observes that polymers are molecules in constant movement particularly as temperature increases. Above certain temperatures the molecules will vibrate and the holes will constantly disappear and re-form. Diffusion occurs when the molecules of the permeant trapped in the holes jump through such mechanisms from a disappearing pore to a new one. Thus, diffusion only requires that new penetrant molecules occupy any "hole" that becomes vacant. From this it can also be concluded that permeability will increase with temperature due to the higher mobility of the networks.

It has been proven that the process of permeation can reach a steady state: after an initial period of increased permeability from zero until equilibrium, a steady rate of permeation will be reached provided that the pressure difference between the two sides is maintained. During the steady state, the permeability of vapors in polymeric structures usually follows Fick's First Law of Diffusion, which can be written as (Halek 1988):

$$\Delta Mx / \Delta t = P A \Delta px / L$$

Where: $\Delta Mx / \Delta t$ = Transport rate of species x across a film

P = permeability

A = film area

Δpx = pressure drop of species x across the film

L = film thickness

This equation is widely used in the prediction of shelf-life for many food products, but it does not truly explain the chemical nature of the permeation occurring in films.

There is another equation used for the steady state that consists of two parameters: the diffusion coefficient (D) and the solubility coefficient (S). This can be described in the following equation:

$$P = D * S$$

The diffusion coefficient is a kinetic parameter that measures the rate of transport of permeants through the polymeric film. This value relates to the degree of cristallinity or order of the polymer structure and the presence or absence of large amorphous areas inside the structure. The solubility coefficient is a parameter that indicates the concentration of penetrant molecules that will be able to diffuse on the polymeric material. This is a thermodynamic parameter in which the value has been calculated for several series of polymers and permeants at different sets of temperature and vapor pressure (Paine 1992). The solubility coefficient, however, reflects the most general rules of solubility, such as increasing value with temperature and its relationship to the polarity of the compounds and films as well as their chemical affinities.

It makes sense that the solubility coefficient will be related to the energy required to keep the compounds in a vapor phase. The higher the energy, the more likely the compound will stay in the vapor phase. This may explain why it has been observed that in compounds of homologous series, solubility will increase if there is an increase in the number of methylene or other groups attached to the backbone. Such groups usually cause higher boiling points and heat of vaporization. Strandburg has confirmed this in studies conducted in the 1980s. Such results allow us to predict which compounds will be more soluble in a determined film base on its backbone and boiling points, and help to predict its permeability.

When trying to estimate the permeability of the package, another factor should be taken into account: the activity of the permeant in the package wall. Many organic compounds can act as plasticizers at high concentrations in some films (Halek & Luttmann 1991). Plasticizers increase permeability because they allow more flexibility between the network, cause swelling, and in general allow more empty spaces. One factor that is usually ignored when designing packages is the interaction between multiple migrants. When there are several compounds migrating through the film, one component may assist or retard the migration of the other. The permeation can increase because of increased solubility or a plasticizing effect. On the other hand, the permeation could decrease because both migrants are competing for the same sorption sites. In many cases it is hard to predict what the final outcome may be and it is necessary to obtain empirical data.

Permeability Measurements: Determining the WVTR of Films

Transmission rate is the volume or mass of a substance passing through a structure of stated dimensions within a stated time at a fixed pressure difference. Most shelf-life modeling done on food spoilage follows the mechanism of gain/loss of moisture. Therefore, the water vapor transmission rate value is greatly used in the industry to predict shelf-life. The mathematical equation for the water vapor transmission rate is as follows:

$$\mathrm{WVTR} = q\,(t) \,/\, A\,(T)$$

Where: q = mass of water vapor transmitted (g)
t = thickness of barrier (mils)
A = area of transmission (100 sq. in)
T = time (days)

Methods Available for Determining WVTR

There are several methods available for testing the water vapor transmission rate (WVTR) of packaging materials. One method is the standard dish method (TAPPI Standard T448-M49.In this method, a water absorbing material is separated from a controlled humid atmosphere by the material being analyzed, which is sealed over a dish. The moisture gain is determined by weight gained over a determined period of time. Some of the disadvantages of this method are the length of time required to get meaningful data and its unsuitability for high barrier materials with a WVTR of less than 1 g/sq meter a day. Due to these limitations, more rapid methods to determine WVTR were developed.

Another way to measure WVTR is by using special equipment. The Honeywell Model W 825 was the first instrument specifically designed to determine WVTR. In this instrument, a cell is surrounded by a water jacket that maintains the temperature within the range (4°–54° C). The dry section can be raised or lowered by compressed air. When not in use, the relative humidity in the dry side is maintained at 10% RH, which is the lowest test level. After insertion of samples and before starting analysis, the dry cell is purged with dry air until the relative humidity falls below the test values and then the cell is isolated. The relative humidity will start increasing due to the passage of water vapor through the film, and after a short time, the rate will stabilize. At this point, the dry cell relative humidity is set to the value needed and measurements are started. This instrument eliminated the need for the numerous weighings required by the dish method (Paine 1992).

Another commonly used instrument used for water vapor transmission determination is the Mocon Permatran instrument. In this instrument, the packaging material is clamped in between two halves of a cell. One half of the cell consists of a water reservoir (100% relative humidity) at a constant temperature. The other half is dried by purging with nitrogen or dry air. The whole cell is isolated and kept at a constant temperature; the movement of water vapor is then measured and recorded by means of a humidity recorder. The humidity recorder employed is an infrared detector that provides results within a few hours.

Barrier Materials

A barrier material is one that impedes the transfer of a substance into or out of a food. Most plastic films are finite barriers to gases, moisture, and food constituents in the sense that they allow some passage. However, films that allow limited amount of passage are considered barrier materials.

There are a number of barrier materials that are commonly used in food packaging applications. They have been used over time because they have shown appropriate barrier properties and good mechanical properties for well-defined applications. However, little has been done to determine the compatibility of food with those films, and therefore there is a chance that some quality will be lost when they are used for packaging certain foods and ingredients.

Why Are Some Polymers Better Barriers Than Others?

Obviously, when looking for barrier materials, one is trying to find materials with low solubility and diffusion coefficients because those two parameters are responsible for permeability. Polymers vary in crystallinity and polarity. Crystallinity is associated with the diffusion parameter, while polarity is associated with the solubility coefficient. . The polarity is usually determined by the kind of functional group attached to the main polymer. For example, polyethylene and polypropylene are non-polar, but polyvinyl alcohol is polar due to the hydroxyl (OH) group. Non-polar materials are usually a better barrier against water and other polar molecules, but they are poor barriers for non-polar molecules such as organic flavors. On the other hand, polar polymers are not a good barrier against water, but they are better barriers against non-polar organic compounds (Koros 1989).

Another factor affecting polymer barrier properties is the ratio of amorphous to crystalline solid state matter. The more crystalline a material, the less permeable it is due to the rigidity of the structure. In addition, there are other factors that affect performance such as molecular weight, molecular weight distribution, cross-linking, thermal history, and additives such as plasticizers. As a general rule, barrier polymers share the following characteristics: regularity of molecular structure and tight chain to chain packing (Koros 1989).

One way of increasing the barrier properties of a material is orientation. Depending on the mode of deformation, one can increase the barrier because of the increased efficiency in the packing of the molecules to an extent where fewer pores or holes are available for permeation (Smith 1991). Another popular way of increasing barrier properties of a certain film is by means of metallization. The usage of metallized films has increased considerably in the food industry in the last few years. The reason for this is that metallized films are excellent barriers, cost-efficient, attractive, and reasonably easy to run in most packaging equipment. One disadvantage of metallized films is that they cannot be used if a clear package is needed. In that case, there are other options in the market such as PVDC, EVOH, and PVC.

Types of Barrier Films

Polypropylene: Polypropylene is an excellent barrier for both water and oxygen. When oriented, its barrier properties increase 50-100%, making it a preferred choice in the food industry. For food applications where moisture is the main spoilage factor, this clear, coated, or metallized film is widely used. When oxygen is the main spoilage factor, there is a tendency to use polyester films either in clear or metallized form. Polypropylene cannot be used for frozen applications and due to its low polarity, it is not a good barrier against organic compounds such as flavors and oil. This is a film widely used for snacks, cookies, crackers, and confectionery products.

PVDC: Polyvinylidine Chloride is one of the most common flexible materials used in the packaging industry. Generally, PVDC is used as a coating for other more economical materials to increase barrier. One of the advantages of this polymer over other materials is that its molecules are mostly inert due to their high chlorine content. The high barrier property is derived from the structure's high symmetry: tight packing is possible and the molecule presents high density, which imparts the desired qualities. However, this polymer is brittle so it is often plasticized by means of co-polymerization thus decreasing its high barrier. PVDC prevents various gases from permeating, but it is most commonly used to prevent oxygen permeation. It has been determined over time that the rate of oxygen transmission is usually independent of the substrate, but is totally controlled by the

PVDC coating, so any substrate can be selected (Bicerano 1989). Also, the industry uses PVDC coatings as a barrier against water, aroma, and flavors of different products. PVDC can be placed anywhere on the packaging material: on the surface or sandwiched between different layers. Generally speaking, PVDC provides weak seals that are adequate for light products only.

PVC: Polyvinyl Chloride is a thermoplastic film that has fairly good barrier properties against water and oxygen. However, its use is somewhat limited due to concerns caused by possible food contamination by low weight monomer residues. Later developments in newer higher barrier resins of the Saran type have produced new packaging opportunities for the food industry.

EVOH: Ethylene vinyl alcohol has excellent barrier properties for gases, but it is moisture sensitive due to hydrogen bonding so it must be protected from moisture. While PVDC can be placed on the surface of the packaging material, EVOH must be sandwiched between polyolefin layers. Data suggests that EVOH is an excellent barrier for aroma/flavors due to its high polarity and hydrogen bonds with areas of high crystallinity. The food industry commonly uses this material as a barrier for flavors. The usage is limited though due to its high price. One advantage of this material over other barrier materials is that EVOH is not made of possible poisonous monomers, so migration is not a concern.

Selecting an Appropriate Barrier Material for a Packaging Application

When selecting a packaging material for a certain application, one has to consider factors such as the total cost, market requirements, availability, barrier needed, ability to use that material in current manufacturing equipment, and the total physical and chemical properties of both the food and the package.

Usually, film manufacturers and converters provide much needed technical information on the different options available in the market. Data sheets for films contain information on structure, gauge, sealability, barrier properties, yield, and so on. However, it is up to the package designer to determine what film to use and where to locate it in the package system. There are a few factors that need careful attention when choosing a barrier.

Location of Barrier: Incorrect position of the barrier in a barrier system can lead to a loss of efficiency, so careful thinking should be involved in determining not only the materials to use in the system, but also the position of each component in the system. A few general considerations are as follows:

- If the problem arises from the components of the food escaping to the outside environment, locate the barrier as close to the food as possible.
- Oxygen and water vapor barriers can be located almost anywhere in the barrier system.
- Determine whether migration from any of the components of the package to the food could be a problem. Locate the barrier between the source of contaminant and the food.
- Moisture sensitive barriers should be protected from both food and the outside environment, so they should be located on intermediate layers.
- If there is interaction between the food and one of the layer materials, separate those two substances with intermediate layers as well (Gerlowski 1989).

Product Package Compatibility: Usually, little thought is given to the possible interaction between the packaging material and the product it is intended to contain. This can prove to be costly, so a key understanding of food-package interaction is necessary. Basically, there are two ways in which food can interact with a polymer material used for packaging: 1) The food can react or form a bond with the packaging material; 2) the food can be absorbed into the packaging material. The interaction will always depend on the nature of both the food and the polymer including factors such as polarity, state of matter, molecular weight, type of bonds and so on.

There are two basic interactions that must be predicted in order to increase shelf-life and/or avoid possible health hazards. Those two interactions are 1) the migration from the packaging material to the product; and 2) the possible absorption of aroma or flavor compounds from the food by the packaging material (Arora 1991). In many cases such interactions will be strong enough to cause package failure in the long or short run. Therefore, it can be understood that it is necessary to have the ability to understand and predict such occurrences in order to make more sensible choices of packaging materials.

The following are a few examples that illustrate how a package can fail because of chemical interactions with the product.

1- Sealants can be sensitive to solvents or other organic compounds present on the product. Thus in constant contact with the solvent, the seals weaken or break, which can cause microbial attack, spillage, or increased ingress of water, oxygen, or light.

2- Organic compounds could attack the adhesive of a lamination causing delaminative failure of the package.

3- The organic compound of the product may be able to migrate through the package without affecting the sealant or the adhesive, but affecting the whole material in some other way; for example, plasticizing the flexible material to a point in which its barrier properties are greatly decreased, as well as altering some key mechanical properties.

4- Organic compounds can react with the flexible materials causing change in color, cristallinity, or other optic properties.
5- Flexible film can absorb flavors or aroma added to the food affecting the quality of the product.

6- The migration of potentially toxic compounds found on plastic materials into the food causes a potential health hazard. This one mode of failure is strongly controlled by the FDA

One important interaction relevant to this study is the one occurring between d-limoneme and several commonly used packaging materials. Several studies have been conducted on the permeability and solubility of d-limoneme on several plastic materials including LDPE, HDPE, and polypropylene (Brant 1991). The reason this flavor compound is studied and cited in the literature so extensively are many; this compound is a natural flavor for many fruits and juices and is added as a flavor to a variety of drinks, desserts and confectionery products. Also, and most importantly, this compound is non-polar (highly soluble inn polyolefins) and its behavior follows many chemical models used for permeability, making it the perfect example for this type of study. One particular study conducted at Michigan State University (Hirose 1988) quantified the changes in properties of sealant polymers saturated with this organic compound. The study concluded that at the saturation point, absorption of d-limoneme affected the following film properties: modulus of elasticity, tensile strength, ultimate elongation, seal strength, impact resistance and oxygen permeability. The researchers reasoned that such changes occurred due to the plasticizing effect d-limoneme has on polyolefins.

Other studies have been conducted trying to determine the solubility of d-limoneme on certain films commonly used for packaging applications (Kobayashi 1991). Such studies were conducted because when packaging orange juice in tetra-pack packages, it was observed that the films used were absorbing high quantities of this natural flavor. The review of such studies is of some relevance for other people interested in knowing the solubility of d-limoneme in different materials. This solubility value is of great importance when predicting the permeability of that organic compound in the film. Also, those studies suggest that after films such as LDPE or Polypropylene absorbed d-limoneme, the solubility of other compounds such as caretonoid pigments, other natural flavors found in juices, and oxygen in those films increased considerably (Letinski 1992). Thus, from those studies, it can be concluded that d-limoneme plasticized those films and changed the natural barrier properties of the films considerably. Even more dramatic changes were noted in this study: metallized films exposed to d-limoneme developed pinholes, and in the most severe cases, “windows” or loss of metallized areas. Such strong interactions are an indicator that many packaging materials should not be used for foods containing this flavor, or that the shelf-life predictions should be reviewed to include those discoveries. There are many reasons to believe that not only d-limoneme affects the barrier and mechanical properties of plastic films; other flavoring compounds of similar chemical nature will have the same effect as well.

STATEMENT OF THE PROBLEM

A company manufacturing hard candy noticed that while their shelf-life model estimated the shelf-life of their lemon flavored candy to be 50 weeks, the actual shelf-life for that products was only 35 weeks. The same model, however, has predicted correctly the shelf-life of other flavored candies packaged with the same materials and undergoing the same distribution system. The objective is to determine the reasons why the shelf-life model is not providing accurate predictions and to find a way to predict the shelf-life of the lemon candies in a quick and economic way.

HYPOTHESIS

The hypothesis is that the flavoring compound used for confectionery products (d-limoneme) interacts with the packaging films, decreasing their barrier properties and thus affecting the shelf-life of the candies.

TEST DESIGN AND METHODOLOGY:

Experiment Design

Purpose

This experiment was designed in order to determine the effect that d-limoneme absorption by several plastic films would have on their WVTR. It was assumed that there would be a direct relationship between the amount of d-limoneme absorbed by any given film and its water vapor transmission rate. The experiment intended to measure films WVTR at increasing d-limoneme concentrations in order to establish a mathematical relationship between amount of d-limoneme absorbed and WVTR. This relationship would be then expressed as an equation that could be used to predict the WVTR of the studied films at any given d-limoneme concentration from zero ppm until the saturation point. Three films would be study to establish any trends.

Design

This experiment was designed to be performed in three steps:

Step 1: Exposure of the films to d-Limoneme

In this step, samples of the films were exposed to d-limoneme. The rate of absorption of d-limoneme by the films was unknown. This made the task of selecting d-limoneme concentrations at which to measure the WVTR impossible. Instead, the experiment was designed in such a way that both the concentration of d-limoneme and the WVTR were unknown. Two assumptions were made: 1) That film exposed to d-limoneme will slowly absorb this organic compound until equilibrium with the environment was reached (at the saturation point); 2) The rate of absorption was small enough to allow for weekly measurements. If the second assumption were wrong, measurements would be performed in shorter periods of time (daily or hourly as needed)

On this step a constant amount of film and d-limoneme were placed on a closed environment. The only variable before measurement was time of exposure to d-limoneme. It was expected that the longer the time the films were exposed to d-limoneme, the higher the concentration until saturation occurred. At the saturation point, no further changes on d-limoneme concentration would occur. If needed, a rate of absorption of d-limoneme by the films could be estimated by plotting time vs. concentration. However, it was expected that the rate of absorption would be non-linear, with a fast absorption occurring during initial exposure and then a gradually decreasing rate until concentration reached the saturation point. Finally, it was expected that the different films would have different d-limoneme absorption rates so even though the WVTR measurements will be done at the same time, the concentration of d-limoneme on each film would be different.

Sample Preparation

After one roll of each film was supplied by the film company, testing samples were prepared. Testing samples consisted of ten (10) grams of packaging film placed in one two-quart Mason jar. A 22 cc glass vial containing one gram of organic compound was introduced as well into each jar. The vial containing the organic compound was left open to allow films to absorb the organic compound. Glass jars were tightly sealed and placed in a "controlled environment" room (72° F, 50% RH) Six Samples of each film were prepared. All those samples were prepared with film from the same roll manufactured on the dates specified below. Samples were taken for analysis weekly for a period of 4-5 weeks when saturation was observed for all films. The rationale was that the concentration would increase with time until the film was saturated; after saturation, concentration stayed constant.

In addition, two more sets of samples were tested. The first set consisted of films prior to any conditioning with the organic compounds (zero ppm). This set was the control samples. The second set consisted of film used to package product. It is important to notice that this film was not printed so it was a good sample to study. Packages were taken from the line and aged for one month at a temperature of 120° F. This was done to quantify the amount of organic compounds on the films in the worst possible storage conditions. It was observed that in all cases the amount of organic materials in the actual packages corresponded to the saturation value.

Step 2: Measurement of the amount of d-limoneme absorbed by the film

The method selected to determine the amount of d-limoneme on the films was Head Space Gas Chromatography to separate the d-limoneme from the film followed by Mass Spectrometry to determine the concentration of d-limoneme. These methods were selected because they were the standard tests followed in the company manufacturing the hard candies. The procedure described below is the company's standard procedure for determining the amount of solvents on plastic films.

a) Determining the Concentration of Reagent on Films: GC-MS Method

The concentration of the reagents in the films was determined by headspace gas chromatography and mass spectroscopy as described below. Note that measurements for all samples were taken twice.

Sample Preparation

Samples were crumbled to fit into a 22mL headspace vial. A drop of 50ppm solution of xylene in olive oil, the internal standard in this method, was added to the samples. The final step was to crimp-cap vials to ensure that no organic material would escape.

Headspace Sampling

A Perkin-Elmer HS-40 Static Headspace Sampler was used. The following were the parameters used for all sets of samples. Experimentally, these parameters were proven to give the most reliable results:

- Thermostat Time = 10 minutes
- Thermostat Temp = 100 deg C
- Pressurization Time = 1.0 minute
- Injection Time = 2.0 minutes
- Withdrawal Time = 0.2 minutes
- Needle Temp = 120 deg C
- Transfer Line Temp = 120 deg C

The HS-40 thermostated the sample vial for the specified time, then withdrew a sample from the vial and injected it into the GC column, which was held at -40 deg C with liquid nitrogen.

Gas Chromatography:

The following were the equipment and parameters used:

- Column = J&W 60 meter DB-5 MS, 0.25 mm ID, 0.25 um film thickness
- Initial Temp = -40 deg C
- Initial Hold = 4.0 minutes
- Temp Ramp = 5 deg C/minute to 200 deg C
- Final Hold = 5.0 minutes

The samples from the HS-40 were cryofocused on the column at -40 deg C, which trapped all the volatiles in a narrow band at the head of the column. The column was then ramped to 200 deg C as specified above, which caused compounds to begin to move down the column as they neared their boiling point. The interactions of the compounds with the column stationary phase (a 0.25 um layer of 5%-phenyl-methyl polysiloxane) caused them to partition into and out of the stationary phase according to their affinity for the phase. The differences in affinity for the phase among different compounds caused them to separate. Each of the compounds thus exited the column at a different time, and entered the mass spectrometer.

Mass Spectrometry

The equipment used was the Finnigan Magnum Ion-Trap GC-MS. The parameters used were:

- MS Transfer Line Temperature = 220 deg C
- Mass Range Scanned = 29 to 650 AMU
- Ionization Mode = Electron Ionization (EI)

As the peaks corresponding to each compound exited the GC column, they passed into the mass spectrometer, where the compounds were bombarded with electrons, causing them to ionize and fragment. The pattern of fragmentation (ion mass and abundance) was the fingerprint for the compound and was therefore used for identification purposes. The intensity of the total ions produced (the area under the chromatographic peak) is proportional to the concentration of the compound, and was thus used for quantitation purposes.

Quantitation

The amount (ppm) of each compound was determined by the following formula:

ppm= (Area of contaminant peak/Area of standard peak)(standard solution added(g)/(sample weight(g) + standard Weight(g)))*(50)

Step 3: Measurement of the WVTR of the films exposed to d-limoneme

It was important to determine the WVTR at the same time that the concentration of d-limoneme was being measured. Immediately after a small amount of film was taken from the sample to measure d-limoneme concentration, a larger portion of the same sample was divided into three pieces and placed in three different MOCON w 3/31 to analyze WVTR.

WVTR Determination

The Water Vapor Transmission rate of all films was determined by means of a MOCON – Water Vapor Permeation Analysis System Permatran - W 3/31. All measurements were taken three times. The following parameters were used:

Parameters for All Films

- **Temp:** 37.8 C
- **Cell RH**: 100 %
- **Nitrogen Flow:** 100.0 sccm
- **Conditioning Time:** 3.0 Hours
- **Number of Cycles:** 15
- **Cycle Time:** 45 minutes

Those parameters were used because that was the standard testing procedure of that company. In this particular instrument neither the temperature, nor the cell relative humidity could be changed. The conditioning time of three hours was done in order to give the film time to stabilize at that temperature and relative humidity so the values will be more accurate. This issue will be discussed on more detail on the discussion section.

Materials

Reagents

The reagent used for this experiment was: d-limoneme. This organic compound was supplied by Aldrich Chemical Company.

1. **d-Limonene, 97%**

- **Molecular Formula**: C10H16
- **Molecular Weight**: 136.24
- **Assay:** 97%
- **Density:** 0.840
- **Comments:** Boiling Point (°C): 175.5 to 176 / 760
- **Limoneme's Chemical Structure:**

- **Uses:** Orange and Lime flavors

Polymeric Films

Three (3) films were selected for this study: Bicor 100 LTSC Acrylic Wound Out, Bicor 90 SPW High Energy Surface Wound, and 100 LMB LTSC Sealant Wound In. One of the films was selected for this study because it was the packaging material used for the lemon hard candy. The other two materials were being considered for future applications if they could increase the shelf-life of the product. All information regarding the films was taken from technical data sheets provided by the films' suppliers:

Bicor 100 LTSC Acrylic Wound Out:

Supplier: Mobil Chemical Company

Structure: Acrylic Coating/Adhesion Promoting Layer/ Polypropylene Core/ adhesion layer/ LTSC

Manufacturing date: January 11, 2001

Gauge: 1.0 mil Gauge

WVTR: 5.0 g/m2/24 H/ 38 C/ 90 % RH

Usage: Inner wrapping for Cherry Tablets

Width: 3 1/16"

Cut Off length: 2 1/8"

Bicor 90 SPW High Energy Surface Wound.

Supplier: Mobil Chemical Company

Structure: Treated Surface (High Energy Layer)/ Core Polypropylene/ Sealant

Manufacturing Date: January 17, 2001

Gauge: 0.90 mil Gauge

WVTR: 5.4 g/m2/ 24 h/ 38 C/ 90 % RH

Usage: Inner Wrapping for Mint Tablets

Width: 3 1/16"

Cut-Off Length: 2 1/8"

100 LMB LTSC Sealant Wound In

Supplier: Mobil Chemical Company

Structure: PVdC Coating/Adhesion Promoting Layers/Polypropylene/ Adhesion Promoting Layer/ Low temperature Seal Coating

Gauge: 1.0 mil

WVTR: 3.9 g/m2/24H/38 C/ 90 % RH

Manufacturing Date: January 09 2001

Usage: Proposed Packaging Material

Width: 3 1/16"

Cut-Off Length: 2 1/8"

It is important to note that all the film samples that were tested came from the same rolls manufactured on the dates specified above. Also, none of the films were printed.

RESULTS AND DISCUSSION

A Comparison Between the Results obtained with the Theoretical Shelf-Life Model and The Observed Shelf-life

The theoretical shelf lives of the candies were calculated using the Labuza model for moisture gain and lost. This method proved to be effective, as this is the observed mode of spoilage for the product. It had been noted repeatedly that the loss of all flavoring was not observed prior to the candy's physical changes as caused by water absorption. Due to that observation, the loss of flavor was not included in the model. The shelf-life calculations were made by taking into account the WVTR information provided by the suppliers, as well as critical moisture information previously determined experimentally by the Company and Published on an internal Report. The storage temperature and relative humidity were estimated to be 22°C and 75% respectively. Using this information and the Shelf –Life computer model used by the company, the shelf-life was estimated to be 50 weeks. (See Appendix A for a copy of the report obtained) That value does not agree with the observed shelf-life values obtained from the field. The observed shelf-life for the candies was 35 weeks. It seemed obvious that the theoretical model was overestimating the shelf-life of both products and it could not account for the differences in shelf lives observed for both flavors.

Effect of Absorption of d-Limoneme on the Packaging Films

1- Revising the experiment:

Before discussing the effect that d-limoneme had on the films, it is important to discuss the experiment to more details. After the study was conducted, several flaws were observed on the experiment. Many of those flaws can seriously compromise the validity of the results. Unfortunately, due to the author inability to re-run the experiment, this discussion will be based on the reason why this experiment was not completely successful and ways to improve it for other studies.

a) The samples on this experiment were not randomized: All samples on this study came from the same roll. This means that we can only infer the effects of d-limonme on that particular roll of film. Samples should have been taken from different rolls manufactured on different days to account for manufacturing variability.
b) The number of samples on this study was too small compromising the significance of the results
c) Although the WVTR measurements were done three times for each sample, they were done on pieces of films coming from the same roll. While we can have a more accurate value for the WVTR of that sample, we really can't tell if pieces of films taken from other areas of the roll or from different rolls will behave exactly the same.
d) WVTR measurements were performed after a three-hour conditioning time. After this period one can assume that some of the d-limoneme has evaporated from the film. Therefore the WVTR values obtained from these measurements don't trully correspond with the measured concentrations but with lower unknown concentrations of d-limoneme
e) WVTR was always done on the outside face of the film as stated on the company's standard. However, the WVTR could have been different if the inside face was measured.

2- The results of the experiment

100 LTSC

As shown in Table 1, the changes in WVTR for 100 LTSC film due to absorption of d-limoneme are non-linear. From this data it seems like when absorbing smaller amounts, this film decreased its water vapor transmission rate becoming a better barrier. After certain concentration of d-limoneme was achieved, the WVTR started increasing until the saturation point. At the saturation point, the WVTR achieved a maximum value. It is impossible to clearly state the transition points because there are very few data points. Another reason why it was impossible to derive an equation that could describe this film behavior while absorbing d-limoneme is that some data points showed no significant difference. Example of this is the WVTR obtained on week 1 and 2. At the saturation point, the WVTR was 6.83 g/m2/24/38 C/ 100 RH. This value is 1.45 times higher than the WVTR obtained at zero concentration (4.74 g/m2/24/38 C/ 100 RH). This means that the shelf-life of the product could be only 70% of the expected shelf-life of the same product if no interaction between the flavor and the package were to occur.

Previous studies conducted on the change of properties of polypropylene after absorption of d-limoneme have always been conducted only at the saturation point (Hirose, Paick, Halek). In all studies it has been shown that at the saturation point, d-limoneme increased the WVTR or the OTR. It is agreed that this is due to the plasticizing effect this organic compound has on the polymer network. However, the initial decrease in WVTR at low limoneme concentrations has not yet been explained in the literature to the author's knowledge. One possible explanation is that at low concentrations, both the limoneme and water vapor are competing for the same sorption sites. In this case d-limoneme will be absorbed in higher quantities due to its non-polar nature, thus decreasing the amount of water that the film can absorb and permeate. Evidence for this theory could perhaps being obtained by means of Scanning Electron Microscopy.

Table 1: Water Vapor Transmission Rate (WVTR) of 100 LTSC film tested at 38 C and 100% RH over a 4 week period[1]

Week #	**Amount of Limoneme (ppm)^2**	**WVTR (g/m2/24 H/ 38 C/ 100% RH)^2**
0	0	4.74 ± .56
1	6730 ± 52	3.0 ± .14^{ns}
2	9522 ± 11	2.28 ± .79^{ns}
3	14000 ± 120	4.99 ± .9
4	14790 ± 5	6.83 ± .10

1- All measurements were made on Saturday at 2 pm. WVTR and concentrations were measured at the same time. Weekly measurements showed different d-limoneme concentrations (in ppm). Concentration at week four was determined as the saturation point.

2- Mean Value ± standard error; mean values in columns and rows sharing the same superscript letters are not significantly different ($p > 0.05$; $n = 3$)

90 SPW

Table 2 shows that d-limoneme had the same effect on 90 SPW film as it did on LTSC . Again, samples from week 1 and 2 exhibiting lower concentrations of d-limoneme showed not significant difference on their WVTR. A possible explanation for this trend could be that some of the d-limoneme evaporated during the sample conditioning before WVTR measurements. Samples from week 3 and 4 (10129 ppm and 11360 ppm respectively) didn't also showed a significant difference in WVTR. Once again this data can't help to understand the exact relationship between d-limoneme ppm and WVTR. However, this data shows that there is a significant difference between the WVTR of the film before absorption of d-limoneme and after saturation. At the saturation point, the WVTR was 7.27 g/m2/24/38 C/ 100 RH. This value is 1.43 times higher than the WVTR obtained at zero concentration (5.1 g/m2/24/38 C/ 100 RH).

Table 2: Water Vapor Transmission Rate (WVTR) of the 90 SPW film tested at 38 C and 100% RH over a 4 week period[1]

Week #	**Amount of Limoneme (ppm)[2]**	**WVTR (g/m2/24 H/ 38 C/ 100% RH)[2]**
0	0	5.1 ± .10
1	8350 ± 22	3.02 ± .59^{ns}
2	8700 ± 5	2.72 ± .45^{ns}
3	10129 ± 100	6.94 ± .78^{xy}
4	11360 ± 37	7.27 ± .34^{xy}

1- All measurements were made on Saturday at 2 pm. WVTR and concentrations were measured at the same time. Weekly measurements showed different d-limoneme concentrations (in ppm). Concentration at week four was determined as the saturation point.

2- Mean Value ± standard error; mean values in columns and rows sharing the same superscript letters are not significantly different ($p > 0.05$; $n = 3$)

100 LMB:

At first impression, Table 3 shows the same trends observed in the previous films: a decrease on WVTR at low concentrations followed by a rapid increase after certain concentration is reached. However, statistically this data set is showing no significant difference on WVTR at Zero ppm and 9,460 ppm. While the author truly believes such trend exists for all polypropylene films studied, the data on this particular film can't support such observation at a 95% Confidence Level.

At the saturation point, the WVTR of this film was 6.75 g/m2/24/38 C/ 100 RH. This value is 2.1 times higher than the WVTR obtained at zero concentration (3.24 g/m2/24/38 C/ 100 RH). This material is affected to a greater degree by d-limoneme due to its initial high barrier properties derived from the PVDC coating.

Table 3: Water Vapor Transmission Rate of the 100 LMB film tested at 38 C and 100% RH over a 3 week period[1]

Week #	**Amount of Limoneme (ppm)[2]**	**WVTR (g/m2/24 H/ 38 C/ 100% RH)[2]**
0	0	3.24 ± .22^{ns}
1	9460 ± 162	2.356 ± .67^{ns}
2	11630 ± 0	6.27 ± .10
3	13040 ± 29	6.75 ± .36

1- All measurements were made on Saturday at 2 pm. WVTR and concentrations were measured at the same time. Weekly measurements showed different d-limoneme concentrations (in ppm). Concentration at week 3 was determined as the saturation point.

2- Mean Value ± standard error; mean values in columns and rows sharing the same superscript letters are not significantly different ($p > 0.05$; $n = 3$)

Including the lost of barrier properties on the Shelf-life Model

Experimentally, it was observed that the WVTR of the different films varied with the concentration of d-limoneme in the film. However, this experiment could not accomplish some of the original objectives:

1) Describe by means of a mathematical equation the relationship between d-limoneme concentration and WVTR.
2) Estimate the rate of absorption of d-limoneme by the films studied
3) Predict the exact shelf life of the lemon flavored candied on any of the films studied.

The First objective could not be achieved because of several reasons:

1- The WVTR does not correspond to the measured concentrations
2- The relationship was non-linear so a larger amount of data points were needed
3- Some data points did not show significant differences due to the small number of samples measured (n=3)
4- Samples were not randomly selected from a big population. All samples came from the same roll of film

Although, it is impossible to describe the exact relationship between d-limoneme concentration and WVTR, it is clear that :

a) At the saturation point, all samples showed an increase on WVTR making clear that d-limoneme has a plasticizing effect on all the films
b) At low concentrations of d-limoneme , both the 100 LTSC and 90 SPW showed a small decrease on WVTR. This observation needs to be further studied as it has not yet been discussed in the literature.

The second and third objectives are connected. Obtaining a rate of absorption of d-limoneme was necessary in order to predict shelf life accurately. In order to estimate the shelf-life by means of a theoretical model, it is necessary to know what the WVTR of the film would be at all times. From this study it seems like saturation occurs very slowly (taking up to 4 weeks for some films) During that period of time, the film will be varying WVTR. Also, once most of the flavor vapors escape from the inside of the package, one can assume that the film will not be saturated but it will slowly release all d-limoneme.

The task of estimating the WVTR of the films due to the interaction with the flavors can be extremely complicated. A good assumption could be to believe that the film would be saturated at all points. Based on this assumption, it would make sense to believe that the increase in WVTR observed at saturation will be followed by a direct proportional decrease in shelf-life. For example, if at the saturation point, the film exhibited a WVTR twice as high, the shelf-life would be reduced by half.

Such an assumption, however, is too simplistic. In fact, experimentally, such a direct relationship was not observed. The predicted shelf-life for the candy using Labuza model and the saturated point WVTR was 25 weeks while in reality, the shelf-life was 35 weeks (See Appendix B). Due to the complex interactions between the films and flavors, an accurate prediction could be impossible to calculate. However, a basic understanding of the level of decrease in barrier properties that a film can undergo due to interactions with the food ingredients can help the packaging engineer to select a more appropriate package material for a specific application.

CONCLUSION

The purpose of this study was to determine the effect that d-limoneme has on different flexible packaging materials permeability to water vapor. Previous study (Hirose 1988) noted that d-limoneme has a significant effect on Water Vapor Transmission Rates, but such study failed to establish a relationship between limoneme concentration and WVTR. In this study, all of the films that were studied showed changes in WVTR when exposed to different concentrations of d-limoneme. However, due to some flaws on the experiment design, a clear relationship between d-limoneme concentration and WVTR could not be established.

Suggestions for Further Studies:

During the discussion of the experiment design, few suggestions were already made in order to improve the significance of the data:

1- For future design, film samples should be taken from different manufacturing dates and/or locations in order to have random samples.
2- Increase the number of samples (for both concentration and WVTR measurements) in order to increase statistical significance.
3- Increase the number of data points. For example, measurements for concentration and WVTR can be taken daily instead of weekly. This will help to establish a mathematical function to predict WVTR at any d-limoneme concentration.
4- Decrease conditioning time during WVTR measurements to a minimum to avoid the escape of d-limoneme to the environment and thus samples with lower concentration than measured.
5- Measure the d-limoneme concentration of the samples after WVTR has been measured (to exactly know in what degree the concentration of d-limoneme was reduced during the time that the WVTR was being measured)
6- To measure WVTR in both sides of the film (inside and outside face) to establish any significant difference.

7- To use Scanning Electron Microscopy to observe film behavior at the microscopic level.

In addition to the previous recommendations, this study could further investigate the following scenarios:

1- After the film is saturated, what happens when the d-limoneme is released from the film? Would the WVTR of the films undergoing opposite process (de-absorption) follow the same function of concentration vs. time observed in this experiment? Would the films have increased water permeability even after the d-limoneme is released from it? Such questions are important because at this point one can not tell if the changes d-limoneme caused on the films are temporal (based on the presence of d-limoneme) or if the changes d-limoneme made on the films (at a microscopic and macroscopic level) are irreparable thus lowering the WVTR forever.

2- The effect of d-limoneme on different films or perhaps the same films used for this study after undergoing some common packaging processes: coating, metallization, and /or printing. Does d-limoneme have a bigger or smaller impact on printed or metallized films? Can metallization prevent the changes on barrier properties caused by this organic compound?

3- The effect of other organic compounds on these films. Can one predict which compounds will affect films permeability based on chemical structure?

The Importance of this Study:

This study proves that a previous understanding of the interactions that may occur between food products and their packaging materials is necessary before designing a package system for food items. Studies can be conducted prior to selecting materials to determine whether different films will interact with the food to lower barrier properties. If this is done, a packaging engineer will not be surprised by packages providing shorter shelf lives after production has been started. There is no doubt that such research can save money in the long run.

If after preliminary testing, none of the available materials can provide adequate shelf-life in a cost-effective way, at least the packaging engineer on charge will have a better estimate of the shelf-life so that he or she can make changes such as:

- Increasing the ratio of food to packaging material to increase shelf-life (i.e, larger packages as opposed to single serving packages)
- Shortening storage and distribution times.
- Distributing and storing products in a less humid or warm environment
- Planning production based on a shorter shelf-life.

Obviously, such decisions may not be feasible in many cases, but the information obtained from interaction studies would greatly help a food company to think about packaging alternatives or to look for other solutions.

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APPENDICES

APPENDIX A- Calculations for the Shelf-life of the Cherry and Wintergreen Mint Candies using Labuza Model and WVTR of films at zero organic compound concentration

APPENDIX B- Calculations for the Shelf-life of the Cherry and Wintergreen Mint Candies using Labuza Model and WVTR of films at the saturation point

APPENDIX A- Calculations for the Shelf-life of the Candies using Labuza Model and WVTR of films at zero organic compound concentration

Shelf Life Report

Date: 14/10/02

Type of Package 100 LMB

Product Name: nfectionary

Product parameters:

Product Weight	450
Product Initial Moisture (%)	0.01
Initial Relative Humidity (%)	30
Critical Moisture of The Product (%)	0.1
Critical Relative Humidity (%)	38

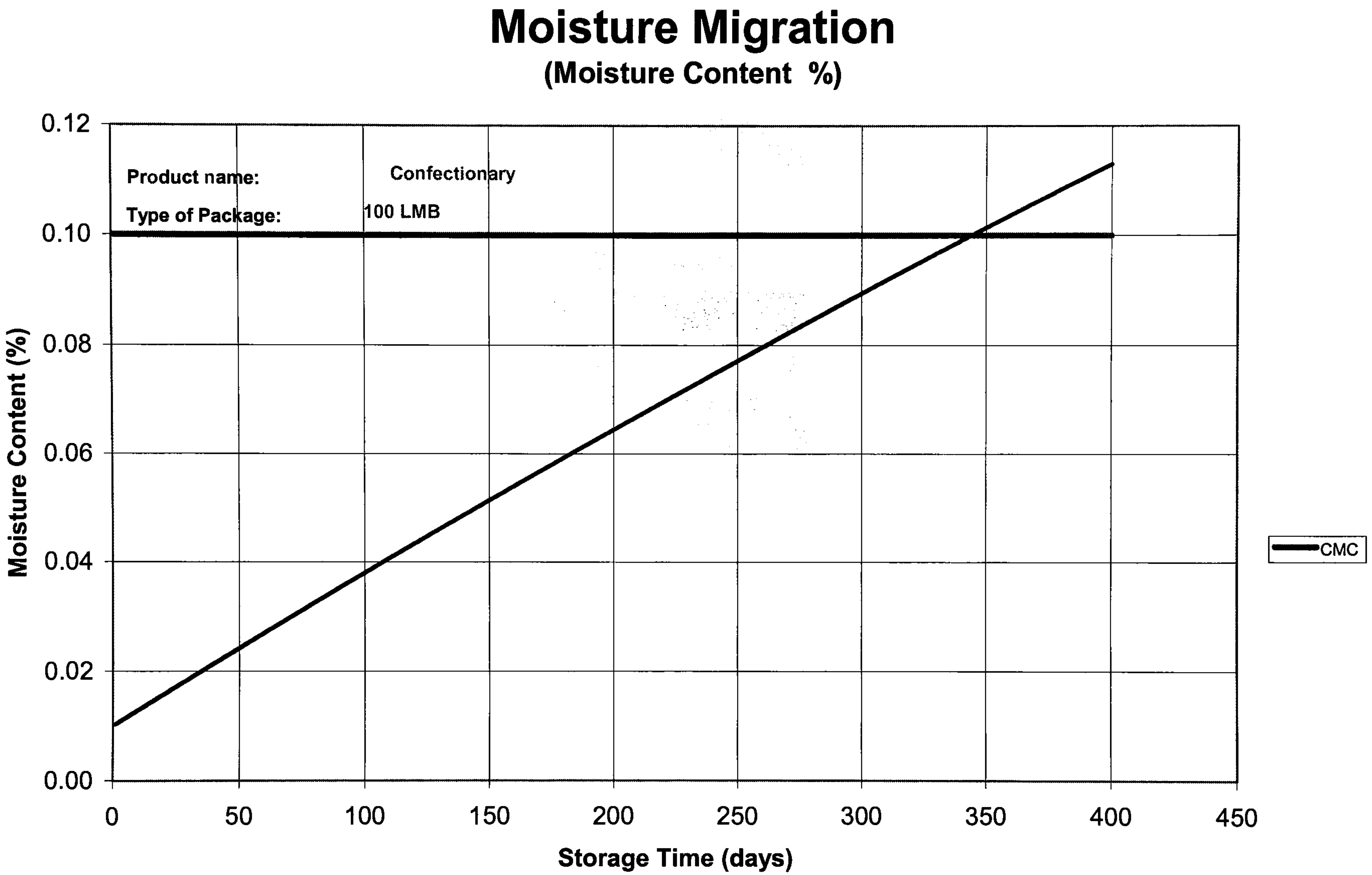
Package Parameter:

WVTR:	3.24
Film Area (sq meters)	0.002

Environmental Parameters:

Storage HR (%)	75
Temperature of Storage (22)	22
Length of Study (days)	400

Estimated Shelf Life= 345 dias

Moisture Migration
(Moisture Content %)
Product name: Confectionary
Type of Package: 100 LMB
Moisture Content (%)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
50
100
150
200
250
300
350
400
450
Storage Time (days)
CMC

APPENDIX B- Calculations for the Shelf-life of the Candies using Labuza Model and WVTR of films at the saturation point

Shelf Life Report

Date: 14/10/02

Type of Package 100 LMB

Product Name: nfectionary

Product parameters:

Product Weight	450
Product Initial Moisture (%)	0.01
Initial Relative Humidity (%)	30
Critical Moisture of The Product (%)	0.1
Critical Relative Humidity (%)	38

Package Parameter:

WVTR:	6.75
Film Area (sq meters)	0.002

Environmental Parameters:

Storage HR (%)	75
Temperature of Storage (22)	22
Length of Study (days)	400

Estimated Shelf Life= 166 dias

Moisture Migration

(Moisture Content %)