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PERMEABILITY OF ORGANIC VAPORS THROUGH A PACKAGED CONFECTIONERY PRODUCT WITH A COLD SEAL CLOSURE: THEORETICAL AND PRACTICAL CONSIDERATION

presented by

CHAI-HUNG LIN

has been accepted towards fulfillment of the requirements for

MASTER degree in PACKAGING

Major professor

Date JANUARY 19, 1996

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# PERMEABILITY OF ORGANIC VAPORS THROUGH A PACKAGED CONFECTIONERY PRODUCT WITH A COLD SEAL CLOSURE: THEORETICAL AND PRACTICAL CONSIDERATION

by

Chai-Hung Lin

A THESIS

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

MASTER OF SCIENCE

School of Packaging

## ABSTRACT

## PERMEABILITY OF ORGANIC VAPORS THROUGH A PACKAGED CONFECTIONERY PRODUCT WITH A COLD SEAL CLOSURE: THEORETICAL AND PRACTICAL CONSIDERATION

## by Chai-Hung Lin

The permeability of toluene and ethyl acetate were determined for the following commodity films: (i) oriented polypropylene; (ii) polyethylene; (iii) glassine; (iv) saran coated oriented polypropylene; (v) acrylic coated oriented polypropylene; and (vi) metallized polyethylene terephthalate/oriented polypropylene laminate. Parameters evaluated included the permeant vapor activity and temperature. For each temperature, three vapor activity levels were evaluated. The temperature dependency of the transport processes was found to follow well the Arrhenius relationship.

The extent of toluene vapor uptake by a confectionery product packaged in the respective commodity packaging structures and sealed by a cold seal closure was also evaluated and the predicted and experimentally determined levels of toluene uptake compared. The toluene uptake values for the six package/product systems were compared statistically, with the oriented polypropylene package system being assigned as the control. Based on the statistical analysis, there was no statistically significant difference between the performance of the control package system and the comparison package systems, with respect to toluene uptake, except for the glassine package. To my parents

#### ACKNOWLEDGMENTS

I would like to express my deepest thanks and appreciation to my major advisor, Dr. Jack R. Giacin, for his encouragement, advice and thoughtful guidance throughout my graduate program.

I would also like to express my appreciation to Dr. Bruce Harte and Dr. Ian Gray for serving on my guidance committee members. A special appreciation to Dr. D. Gage for helping me to operate the equipment in the Department of Biochemistry - Mass Spectrometry Laboratory, Michigan State University.

Also, I would like to thanks all my friends, Shu-Shin Chou, Shu-Jung Huang, Shaun C. Chen, Kuo-Chung Yin, and all my friends in School of Packaging, for their help and encouragement through my research study.

Finally, a special thanks will give to my dear parents in Taiwan, for their love, encouragement and support throughout my life and education.

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#### INTRODUCTION

Since 1970, the use of flexible packaging materials has continued to grow, and has found wide use in food, snack food, confectionery product and beverage packaging (Minifie, 1970, and Martin, 1987). Selection of the appropriate packaging material for a specific food packaging application is essential in order to prevent the development of off-odor or flavor by the product, as a result of permeability of low molecular mass organic compounds from the storage environment through the package to the product, or the migration of low molecular mass organic compounds regularly contained by the package itself into the product. With respect to migration, package printing with organic solvent based inks can result in the development of off-odor or offtaste in packaged products such as snack foods, confectionery products, and baked foods (Kontominas, 1985; Kontominas and Voudouris, 1982; and Wilks and Gilbert, 1968). Another example of the development of off-odor or flavor by a product is the uptake of diesel odor or soap aromas by a packaged food product, as a result of either improper storage or inappropriate packaging material selection (Franz, 1993 and Hotchkiss, 1995).

The flavor or aroma of a food product is comprised of a particular and often delicate balance of organic compounds. With the extensive use of flexible films for food packaging, consumers have become more aware of the occurrence of product off-flavor and off-odor. Consumer perception of inferior product quality, as a result of the development of off-odor and flavor, has resulted in the food industry becoming more sensitive to off-flavor complaints (Whitfield, 1986).

The basic mechanism of transmission of vapors and gases through polymeric films is either by flow through macrovoids or by permeation through micro-voids. Flow through macro-voids may be due to pinholes, cracks, or a faulty package seal. Permeation is a complex process which includes dissolution of the permeant at the high permeant concentration contact surface, diffusion through the polymer film bulk phase, and desorption or evaporation of the permeant from the downstream surface of the film. In practice, knowledge of the permeability of water vapor, carbon dioxide, oxygen and nitrogen has been utilized to design packaging systems to prevent or retard product deterioration during product transportation and storage.

The rate of permeation is affected by several parameters, such as the nature of the permeant molecule, to include molecular structure and polarity; as well as the nature of the barrier material to include percent

crystallinity, glass transition temperature, level of plasticizer added, and polymer morphology. The barrier properties of polymer films can also be affected by environmental parameters such as the temperature, relative humidity, and the driving force or partial pressure gradient of the permeant (Lebovits, 1966, and Kontominas, 1985).

Recent developments have made available high barrier flexible packaging materials. For example, the present combination of aluminum foil in laminate structures, surface deposition of silicon oxide and aluminum to polymer films, and the incorporation of high barrier polymers like ethylene-vinyl alcohol copolymers (EVAL) in multilayer laminations have resulted in the availability of high barrier flexible structures exhibiting barrier characteristics similar to glass and metal (Schaper, 1989).

In addition to the barrier characteristics of the packaging material, the packaging seal characteristics, as previous indicated, are also very important. Traditionally, a heat sealing technique was used to form and seal the package structure. However, at present there is a trend to use a cold seal closure in fabrication of simple wrappers and bags (Stone, 1976 and Jones, 1985). For a cold seal closure, a self adhesive coating is applied to the polymer films. Advantages of a cold seal closure include an increase in the speed of wrapping and a decrease in the total cost of sealing. Therefore, the development of high barrier polymer

films, together with the application of a pattern cohesive to allow sealing by a cold seal closure is very important to the food industry, for protecting packaged products from the external package environment.

Toluene, methyl ethyl ketone, and ethyl acetate are among the most common organic solvents found as residuals from laminating and printing processes (Kontominas, 1985). Mueller (1990) also showed that printed materials, such as newspapers, are a major source of toluene contamination of food. Based on these findings, the organic permeants evaluated in the present study included toluene and ethyl acetate. For the respective permeant, the temperature and concentration dependency of the permeability process was determined. For seal integrity studies, toluene was selected, based on the fact that it was representative of a residual solvent, could serve as a model compound for diesel fuel volatiles and it had a known sensory threshold level in chocolate.

The specific objectives of the study include:

- Determine the temperature and concentration dependence of the permeability of toluene and ethyl acetate through a series of commodity packaging structures used for packaging confectionery products.
- 2. Utilize data on the temperature and concentration dependence of the permeability of toluene through the

respective test structures to estimate the permeance of the barrier films at permeant concentration levels below which it would be impractical to measure experimentally.

- 3. Develop a continuous flow system to allow determination of the rate of toluene uptake by a packaged confectionery product at conditions of constant temperature and toluene vapor activity.
- 4. Determine the extent of toluene vapor uptake by a confectionery product packaged in a series of commodity packaging structures sealed with a cold seal closure and compare the predicted and experimentally determined levels of toluene uptake.

### LITERATURE REVIEW

## Permeation Mechanism for the Transfer of Organic Vapor Through Polymeric Packaging Materials

The deterioration of food flavor during storage may be due in part to the loss of volatile components from the packaged food product or to the uptake of contaminants permeating from the external environment. Therefore, measurement of the rate of permeation of various organic permeants through polymeric packaging materials is of significant importance.

Permeability is the phenomenon of transmission of a gas or vapor through a polymer. This process is characterized by three basic steps which are summarized below:

- Adsorption the dissolution of a gas or vapor into the polymer matrix at the high penetrant concentration surface.
- 2. Diffusion the movement of a gas or vapor penetrant through the polymer bulk phase, along a concentration gradient.
- 3. Desorption the desorption or evaporation of the penetrant from the low concentration surface of the polymer membrane.

Mass transfer in polymeric packaging materials can be referred to as either permeability, sorption or migration. When small molecules permeate through a polymeric membrane, the rate of permeation is governed by the physical and chemical nature of the penetrant and the polymer membrane, as well as external factors which include: temperature, vapor pressure, and relative humidity.

In general, the permeability of a gas or vapor through polymer films is a function of two fundamental parameters: the diffusion coefficient (D), and the solubility coefficient (S). Functionally, the diffusion coefficient is a kinetic term and describes how rapidly permeant molecules are advancing and the time required to reach steady state and the solubility coefficient is a thermodynamic term, describing how many permeant molecules are sorbed by the barrier structure. The diffusion process is the result of polymer molecules having a random kinetic agitation or heat motion. Above the glass transition temperature  $(T_{a})$ , polymer chain segments have vibration, rotation, and translation properties which continually create temporary - "holes" or voids within the polymer matrix. The "holes" allow penetrant molecules to pass through the matrix under a concentration gradient. For polymer membranes below  $T_a$ , the rate of diffusion will be a function of the size and frequency of preexisting "holes" or the void volume between polymer chains. Whereas, the solubility involves the affinity of the

permeant for the polymer (Baner, 1986 and Imbalzane et al., 1991).

Permeation is a measure of the steady-state transfer rate of the permeant, which is usually described by the permeability coefficient, P. The permeability constant can be expressed in terms of two fundamental parameters: the diffusion coefficient (D) and the solubility coefficient (S). Their relationship is described by Equation 1.

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

Where the diffusion coefficient (D) is a measure of the rate at which penetrant molecules are advancing through the polymer, and the solubility coefficient (S) describes the amount of permeant contained or dissolved in the polymer matrix or slab at equilibrium conditions (Crank, 1968).

The mass transfer of organic volatiles is a major concern associated with polymeric packaging films. First, there is the potential loss of aroma/flavor compounds due to their permeation through the film, or to their sorption by the polymeric packaging material. Further reason for concern involves the possibility of contamination of the food due to the permeation of organic vapor from the external environment through the packaging film (Mohney et al., 1988; Tou et al., 1990; and Franz, 1993) and sorption by the product.

In food product/package systems, understanding the sorption mechanism is necessary to assure quality control and prediction of product quality change. In addition, measurement of the loss of product volatiles by permeation is also associated with product quality change or shelf life. Sorption can be described as a function of sorbate concentration by a sorption equilibrium isotherm, that can be represented by Henry's Law or other mathematical models. Specifically, Henry's Law describes the relationship between the vapor pressure of the organic penetrate and the mole fraction of penetrant sorbed by the polymer membrane at equilibrium.

The partition coefficient K is defined as the ratio of the equilibrium concentration of a component in a fluid phase (e.g. food phase), and the equilibrium concentration of the component in a contracting polymeric material. For a specific value of concentration, the partition coefficient K provides a practical way to calculate the change in a component concentration, either in the food or packaging material, from the time that the food product and packaging material are contracted, up to the moment they reach equilibrium, provided the initial concentrations are known.

Since sorption and migration are essentially the same mass transport phenomenon, migration can also be described by a partition and diffusion coefficient. The diffusion coefficient determines the dynamics of the sorption process.

The larger the value of D, the shorter the time to reach equilibrium. (Giacin, 1995).

None-interaction molecules like oxygen, nitrogen, and carbon dioxide will have little or no effect on polymer morphology when sorbed into the polymer matrix. However, organic vapors are comparable in size or larger than the polymer chain segments associated with chain segmental mobility at temperatures above T<sub>a</sub>. These organic penetrants diffuse by a complicated mechanism which is dependant upon the motions of both the polymer and diffusant molecule. Organic molecules may also have a higher solubility in the polymer, which can result in significant swelling of the polymer matrix by the sorbed organic molecules. Organic molecules sorbed by the polymer can act like a plasticizer, lowering the glass transition temperature  $(T_a)$  and increasing the polymer's segmental motions at any temperature. This will results in further plasticization and swelling (Meares, 1965 and Marner, 1986).

### Permeation theory

The rate of transfer of a diffusing substance can be expressed mathematically by Fick's first and second laws of diffusion, as described in Equations 2 and 3. The solubility can be described by Henry's law (Crank, 1975).

$$F = -D \frac{dc}{dx}$$
(2)

$$\frac{dc}{dt} = \frac{d}{dx} \left( \begin{array}{c} D \\ - \end{array} \right) = \begin{array}{c} D \\ - \end{array} \left( \begin{array}{c} d^2 c \\ - \end{array} \right) = \begin{array}{c} D \\ - \end{array} \left( \begin{array}{c} d^2 c \\ - \end{array} \right)$$
(3)

When the permeant molecules enter into the polymer, a boundary layer is created. The boundary layer phase of the polymer is swollen and the diffusion coefficient of the permeant in this phase is not equivalent to that of the nonswollen phase. The diffusion coefficient in the swollen phase is larger than in the unswollen phase. Also, Fick's laws of diffusion do not apply because the boundary phase is changing with time (Crosby, 1981 and Maekawa, 1994).

Under low vapor concentration levels, the vapor pressure of the penetrant is proportional to its concentration in the polymer. According to Henry's law (Equation 4), the rate of transfer of a diffusing substance can be expressed in terms of the permeant partial pressure between surface x = 0 to x = L by the relationship:

 $C = S \times \Delta p \tag{4}$ 

- S = solubility coefficient
- Ap = partial pressure of the penetrant in the gas
  phase.

At steady state, the diffusion flux (F) (Equation 5) of a permeant in a polymer can be defined as the amount of penetrant which passes through a unit surface area per unit time.

$$F = \frac{Q}{A \times t}$$
(5)

t = time.

Also the diffusion flux (F) (Equation 6) of the permeant can be integrated through the total thickness of the polymer between the two concentrations, assuming that the diffusion coefficient (D) is constant and independent of concentration.

$$F = \frac{D (c_1 - c_2)}{L}$$
(6)

where:  $c_1$ ,  $c_2$  = concentration of gas or vapor on the surface x = 0 and x = L, respectively  $(c_1 > c_2)$ L = film thickness.

ā С Ξ Pe a:: ab Te: the ch<sub>a</sub> inte From Equations 4, 5 and 6 one can then calculate the amount of penetrant:

$$Q = \frac{D (c_1 - c_2) \times A \times t}{L}$$
(7)

$$Q = \frac{D \times S (p_1 - p_2) \times A \times t}{L}$$
(8)

and by using the definition of permeability:

 $P = D \times S$ 

one can then solve for the permeability constant using Equation 9:

$$P = \frac{Q \times L}{A \times t \times (p_1 - p_2)}$$
(9)

### Permeation measurement

Generally, there are three methods for measuring gas and vapor permeability of packaging materials: (i) the absolute pressure method; (ii) the isostatic method; and (iii) the quasi-isostatic method. Basically, each test method is designed to measure the permeability by mounting the film in a hermetic environment between two test cell chambers. A fixed and constant gas or vapor concentration is introduced into the high concentration cell chamber. The permeant then diffuses through the barrier membrane and is desorbed from the low concentration film surface into the low concentration cell chamber, where it is then quantified using some appropriate method of detection.

The absolute pressure method involves use of no gas or vapor other than the permeant/vapor in question. There is a total pressure gradient between the two chambers which provides the driving force for the mass transfer process (ASTM D3985-81).

More recently, the isostatic and quasi-isostatic procedures have become two widely employed methods for measuring permeability. Since organic vapor and aroma permeability measurements are very complicated procedures, there are no standard technique for analysis. Also, there is a very limited number of commercial instruments available for measuring organic vapor permeability. To date, most research in this area has been conducted using a permeation system of the investigator's own design (Blakesley, 1974; Niebergall et al., 1979; Kontominas, 1985; Barner, 1986; Hernandez et al., 1986; Hatzidimitriu et al., 1987; Liu et al., 1991; and Franz, 1993). Most of these have been designed to measure the transmission rate of organic vapor through barrier membranes by maintaining a constant partial pressure differential across the test membrane.

## Isostatic method:

In this procedure, the total pressure in both chambers of the permeation cell is kept constant by maintaining the same atmospheric pressure in both chambers of the test cell. The permeability measurement involves maintaining a constant permeant partial pressure, or a concentration gradient between the two cell chambers. The permeant which has permeated through the film and into the lower concentration chamber is then conveyed by a carrier gas to a detector where is quantified.

Figure 1 presents a typical transmission rate profile curve obtained using the isostatic procedure. The permeability measurement involves determining the change in the ratio of  $[(\Delta M/\Delta t)_{t}/(\Delta M/\Delta t)_{t}]$  as a function of time.

Equation 10, which was derived by Pasternak et al. (1970), describes the transmission rate profile curve (Hernandez et al., 1986):

$$\frac{(\Delta M/\Delta t)_{t}}{(\Delta M/\Delta t)_{\infty}} = \left(\frac{4}{\sqrt{\Pi}}\right) \left(\frac{L^{2}}{4Dt}\right)^{1/2} \exp\left(\frac{-L^{2}}{4Dt}\right)$$
(10)

A value of  $(L^2/4Dt)$  can then be calculated for each value of  $[(\Delta M/\Delta t)_t/(\Delta M/\Delta t)_e]$ . A straight line can be obtained by plotting  $(4Dt/L^2)$  as a function of time. From the slope of the straight line, the diffusion coefficient (D) was obtained from Equation 11.

$$D = \frac{(\text{slope}) \times L^2}{4}$$
(11)

Ziegel et al. (1969) derived Equation 12, from a different expression for  $[(\Delta M/\Delta t)_t/(\Delta M/\Delta t)_o]$  (Hernandez et al., 1986) to solve for D.

$$D = \frac{L^2}{7.199 \times t_{0.5}}$$
(12)

where:  $t_{0.5}$  = the time required to reach a rate of transmission ( $\Delta M/\Delta t$ ), value equal to half the steady state ( $\Delta M/\Delta t$ ), value.

Finally, the permeability coefficient (P) can be calculated from data obtained using the isostatic method by substitution into Equation 13:

$$P = \frac{a \times G \times f \times L}{A \times \Delta p}$$
(13)

- f = flow rate of sweep gas conveying penetrant to
   detector
- A = area of the film exposed to permeant in the permeation cell
- L = film thickness
- △p = partial pressure gradient.

## <u>Ouasi-isostatic</u>

This method involves measurement of accumulated permeated gas or vapor as a function of time. In this method, one of the two chambers between which the film is placed is completely closed. The gas or vapor being tested is allowed to flow through the high concentration cell chamber at atmospheric pressure. At the same time, the gas permeates into the lower concentration cell chamber and aliquots are withdraw from the low concentration cell chamber for analysis at predetermined time intervals.

Using this method, the quantify of permeant accumulated increases as a function of time. When the relationship between quantity accumulated per unit of time is constant, steady-state rate of diffusion has been reached. By extrapolating the linear segment of the curve to the x-axis, the lag time ( $\Theta$ ) can also be calculated. It is the intersection of the projection of the steady state portion of the transmission curve (Hernandez, et al., 1986 and Wangwiwatsilp, 1993). Figure 2 illustrates a typical transmission rate profile curve for the quasi-isostatic test procedure.

The diffusion coefficient is expressed by Equation 14:

$$D = \frac{L^2}{6\Theta}$$
(14)

where: 0 = lag time
L = film thickness

and the permeability coefficient at steady state can be described by Equation 15.

$$P = \frac{\text{slope x L}}{A \times \Delta p}$$
(15)

### Taints and Off-flavors in Foods and Confectionery Products

As a result of increased competition in the market place and stronger consumer demands for high product quality, the food industry has strived to minimize adverse consumer reactions. The unpleasant nature of food contaminants or taints can cause severe problems for retailer, producer, ingredient supplier, farmer, and equipment supplier. According to the International Standardization Organization (ISO, 1992), the standard definition of a taint is a taste or odor foreign to the product. In addition, ISO also defines an off-flavor as a typical flavor usually associated with deterioration. An alternative means of defining taints and off-flavor has been described by Kilcast (1993):

- Taints: unpleasant odors or flavors imparted to food through external sources.
- Off-flavors: unpleasant odors or flavors imparted to food through internal deteriorative change.

Perception of a taint in a food product is dependent on the volatile chemicals, chemical structure, concentration, the type of food, and the sensitivity of the consumer (Kilcast, 1993).

### Confectionery packaging

The packaging requirements for chocolate confectionery products are similar to those of other food products (Martin, 1987):

Protection: The product should be protected by the package from the time of manufacture until consumption is completed. Keep product flavor inside the package, while water vapor, oxygen and undesirable environmental odors need to be excluded.

- Function: The package should be functional and facilitate the manufacture, shipping, storage, display and use of the product.
- Sales Appeal: The package must attract the shopper, appeal to emotions, inform and trigger the sale.

There are several common polymeric films and flexible materials used as confectionery packaging structures. These include cellulose, high density polyethylene (HDPE), polypropylene (PP), polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), aluminum foil, and paper/glassine. In addition, a number of newer materials with very good barrier properties are suitable for confectionery packaging.

## Source of taints

Basically, taints in foodstuff are the result of poor handling, transportation or storage of the product, or exposure of the product to an alien compound.

Air acts as a good carrier for a broad range of compounds which can be deposited on, the surface of a sensitive food product. For example, a cake product or biscuits can absorb volatile compounds from newly-painted walls or new flooring in factories. Food may also pick up
pesticide, diesel or petrol fumes flavor, which can cause tainting (Saxby, 1982).

Packaging can serve as yet another source of taints in food. Packaging materials in direct contact with food may result in the transfer or migration of volatiles into the food product. During polymer manufacture, residual volatiles such as monomer can become incorporated into the resin beads, which when converted into film, can affect food flavor. Other factors that can affect package flavor contribution during film processing include: sealing temperature, sterilization, residual solvent from printing inks (eg., ethyl acetate, hexane, toluene, and heptane), types of adhesives, coatings and coextrusion processes (Wilkes and Gilbert, 1972; Halek and Levinson, 1988; and Thompson et al., 1994). Residual solvent can migrate into a packaged food by either direct contact or via head space inside the package.

# Threshold for volatile compounds

Generally, threshold can be defined as the minimum concentration of a stimulus which can be detected (absolute threshold), discriminated (just-noticeable-difference) or recognized (recognition threshold) by 50% of a specific population (Pangborn, 1981). ISO 5492 (ISO, 1992) has presented a more detailed definition for threshold levels (kilcast, 1993):

Detection threshold: Minimum value of a sensory stimulus needed to give rise to sensation.

Recognition threshold: Minimum value of a sensory stimulus permitting identification of the sensation perceived.

Difference threshold: Value of the smallest perceptible difference in the physical intensity of a stimulus.

Terminal threshold: Minimum value of an intense sensory stimulus, above which no difference in intensity can be perceived.

Several researchers have studied the perception threshold for organic vapors in air and in foods. The American Conference of Governmental Industrial Hygienist (ACGIH) publishes an annual listing of threshold limit values (TLV). Amoore and Hautala (1983) summarized water odor threshold levels and TLV for 214 organic vapors. In their paper, they reported the TLV value for toluene is 100 ppm (v/v) (ACGIH, 1982), the air-dilution threshold for toluene is 0.042 ppm (w/v).

When a consumer is exposed to a complex flavor profile, the threshold value for a specific organic flavor compound will increase. Granzer et al. (1986) reported the threshold of toluene is 1 - 20 ppm (mg/kg) in water, 50 - 500 ppm (mg/kg) in butter cookies, and 100 - 500 ppm (mg/kg) in coconut oil.

The amount that is sorbed by the food depends on the partitioning of the migrant between the packaging material and the contained food product (Gilbert, 1979 and Halek et al., 1988). Several factors have been found to affect the partitioning from the packaging materials into the closed contents. (Koros and Hopfenberg, 1979; Adamson, 1982). In general, direct migration of substances from packaging materials occurs more with fatty foods. Fats and oils can penetrate some packaging surfaces and actually promote residual solvent migration into the food product. Studies conducted by Halek and Hatzidimitriu (1988) have suggested that the partioning of the solvents varies according to the target materials, and the order of affinity for organic solvents is as follows: soybean oil > chocolate liquor > cookie. This order is related to the fat content percentage in the target materials. Ruter (1992) also investigated the partition coefficient  $(K_{\alpha,l})$  of typical printing solvents in food stuffs at 23°C. The results of this study are summarized in Table 1.

The residual solvents from laminate films or printing inks can cause off-odor and off-taste of the packaged product. Ruter (1992) investigated and determined the partition coefficients and the sensory threshold values of commonly used solvents in different foodstuffs. The sensory thresholds in chocolate at 23°C are shown in Table 2.

Table 1. The partition coefficie	ent (K <sub>g,1</sub> ) of organic sorbates
at 23°C (Rūter, 1992)	

	Partition coefficient $(K_{g,I})$			
Sorbate	Potato chips	Coffee	Yogurt	Chocolate
Acetone	53.0	52.0	8.6	100
Cyclohexane	18.0	33.0	600.0	53
Ethyl acetate	18.0	46.0	36.0	60
MEK <sup>(1)</sup>	22.0	38.0	11.0	66
Toluene	3.6	9.4	57.0	11

. MEK: Methyl ethyl ketone

Table 2. Sorbate sensory threshold in chocolate (Rüter,

1992)

	Smell (odor)		Taste (flavor)	
Sorbate	stimulus threshold	recognition threshold	stimulus threshold	recognition threshold
Acetone	10 - 20	20 - 100	20 - 50	50 - 100
Cyclo- hexane	50 - 100	100 - 500	500 - 1000	1000 - 2000
Ethyl acetate	10 - 50	20 - 100	20 - 50	50 - 100
MEK <sup>(1)</sup>	20 - 50	50 - 100	50 - 100	100 - 500
Toluene	5 - 15	20 - 25	5 - 15	20 - 25

". MEK: Methyl ethyl ketone

Mueller et al. (1990) evaluated the food sold at service stations, which may have been contaminated with petroleum-based constituents. In this study, the investigators found that the confectionery products sold in service stations and placed near newspapers showed the highest concentration of toluene contamination (216 ppb,  $\mu$ g/kg). Products sold in supermarkets which were displayed near printed materials such as newspaper and magazine, showed higher toluene concentration level than the products displayed in the absence of printed materials. Mueller et al. (1990) concluded that the toluene contamination can depend on the presence of printed materials in the vicinity of the tainted food product.

## Techniques of Analysis of Flavors

The aroma profile of a food product is a complex mixture of volatile organic chemicals. Aroma virtually never stands alone, but is combined with other sensory attributes. Difficulty in the isolation and analysis of flavor or aroma compounds is due to the presence of such compounds in very low concentrations. These trace aroma compounds are generally in a complex food system which contains thermally labile constituents (eg. sugar, protein, lipid and vitamins), food emulsifiers, aqueous and fat soluble components and other volatile components. The basic principle used in the isolation of aroma compounds from the

major food components is either by means of the compounds volatility or solubility properties. Most flavor components are soluble in organic solvents, while most food components are soluble in water. The presence of a high level of lipids (which are soluble in organic solvents) in a food product may cause the isolation to be more complicated (Reineccius, 1993).

Normally, there are three methods that are commonly use for flavor isolation: distillation extraction, direct headspace analysis, and a dynamic purge and trap procedure with a porous polymer absorbent (dynamic headspace) (Alberola and Izquierdo, 1978; Reineccius, 1984 and Reineccius, 1993).

## Distillation/Extraction methods

One of the simplest and most efficient approaches for aroma isolation is direct solvent extraction. However, one major limitation of this method is that it is useful only on foods or samples that do not contain any lipids. Also, the biases imposed on the aroma profile by solvent extraction which are related to the relative solubility of various aroma constituents in the organic/aqueous phases (Reineccius, 1993).

One of the most commonly used methods for separating volatile compounds from a food or beverage is steam distillation followed by extraction with an organic solvent. The distillation method can be defined broadly, to include: high vacuum molecular distillation, steam distillation or simple heating of the food product. Each method is based on volatility. It is the technique which allows a larger concentration of solvent to evaporate.

The most commonly used extraction method involves some modification of the Linkens-Nikerson extraction apparatus. This apparatus involves aroma volatiles isolation by distillation and extraction procedures carried out simultaneously under vacuum, which allows for more efficient extraction of the distillate and the use of a minimal volume of solvent. Reduced pressure operation results in minimal thermally induced artifact formation (Alberola and Izquierdo, 1978). However, the loss of low-boiling volatiles and the trapping of solvent impurities may occur during concentration of the sample volatiles. Thus, care must be exercised in the use of this apparatus (Parliment, 1987).

## Headspace technique

Headspace sampling is the simplest, fastest and one of the most precise techniques for analysis of volatile compounds. This technique is based on an equilibrium distribution of the volatiles between the sample and the gas phase in a closed and thermosetted vial (Kolb, 1984). The analysis of headspace vapors above food stuffs by gas chromatography (GC) or gas chromatography/mass spectroscopy

(GC/MS) has been widely applied in flavor chemistry. Wyllie (1978) defined headspace as the gaseous mixture surrounding a sample within a closed system at equilibrium.

This method was recommended by the working group on Methods of Analysis of the International Organization of the Flavor Industry (IOFI), because this direct injection method is very suitable for routine analysis of the quality of orange juice volatile fraction (Alberola and Izquierdo, 1978). Unfortunately, this method can not provide adequate sensitivity for trace compound analysis, and is limited to volatile partial pressure levels in the headspace equal to concentrations above  $10^{-7}$  g/L (Schaefer, 1981). Use of inlet splitless injection when using GC can enhance these detection limits.

Direct headspace sampling has been widely used for rapid analysis and major component analysis. The cryogenic trapping technique offers some advantages and disadvantages. The cryogenic trap collects headspace vapors irrespective of compound polarity and boiling point. However, water is typically the most abundant volatile in food products and further procedures may be required to remove the trapped water vapor (Reineccius, 1984).

## Adsorbent trapping - thermal desorption technique

Many "headspace" determinations involve the flowing of a non-condensible gas over the sample to sweep the volatiles

into a trapping device. This technique is also commonly referred to as a dynamic headspace method or the dynamic purge and trap method. Normally, the dynamic headspace technique can provide a sensitivity 10 times greater than the sensitivity obtained using the static headspace technique. The sample is continuously purged with an inert gas such as nitrogen or helium, which strips volatiles aroma constituents from the sample, and conveys the aroma volatiles to a trapping system where they are sorbed. The aroma constituents can be trapped by Tenax (porous polymer), charcoal, or other suitable trapping adsorbents.

Tenax-GC (poly 2-6 diphenyl-para-phenylene oxide) is widely used for aroma trapping. Tenax-GC has a low affinity for polar compounds (water vapor) and high affinity for nonpolar compounds (volatile and semi-volatile compounds). Investigators initially used Tenax as the trapping medium for isolating and concentrating volatile organics in food, environmental and biochemical samples (Bellar and Lichtenberg, 1974 and Bertsch et al., 1974).

Activated carbon traps have a strong affinity and high capacity for most aroma constituents. Generally, adsorbents begin to efficiently trap most classes of volatile organic flavor compounds when their carbon skeletons are above C-3. The pore diameter and particle size distribution of activated carbon profoundly affects the breakthrough volumes of analities. Smaller particles and pores are more efficient

for trapping highly volatile, low molecular weight hydrocarbons such as C2 - C4 species. Silica gel has been used to trap low molecular weight polar compounds. Often, the ideal adsorbent trap may be a mixed bed design with a number of adsorbents in combination (Supelco, 1990).

Porous polymer and carbon-type adsorbents have a low affinity for water vapor, which will elude the pores of the adsorbent and inhibit the diffusion of volatile organic compounds into the porous polymer resin, thereby decreasing trapping efficiency. This problem can be eliminated by introducing a "bone dry" make-up gas line into the purge gas outlet directly before the adsorbent trap. The dry make-up gas will serve to lower the relative humidity of the purge gas (Hartman et al., 1993).

The volatile organic moieties concentrated in the adsorbent trap are subsequently released by thermal desorption and transferred into a gas chromatograph. This technique was termed the purge and trap/thermal desorption (PT&T-TD) procedure, and has been accepted as a means of isolating flavor chemicals and enriching headspace flavors prior to GC and GC/MS analysis (Boyko et al., 1978 and Wyllie et al., 1978).

Investigators at Supelco, Inc. (Bellefonte, PA) evaluated carbotrap adsorbents and found that they can sorb a more wide range of airbone organic compounds than Tenax-GC or AD-2 resins. In addition, they found that carbotrap

adsorbents have no surface ions or active functional groups. Therefore, the entire surface is available for interaction that depends solely on dispersion (London) forces. In comparison, the other widely used adsorbents, Tenax-GC and Amberlite AD-2 resins, have localized surface charges for specific adsorbent/adsorbate interactions. Furthermore, carbotrap adsorbents are hydrophobic in nature, allowing their performance to be unaffected by humidity (Anonymous, 1986).

# Identification and Quantification of Trace Volatile Compounds by Gas Chromatography/Mass Spectrometry

Gas Chromatography/Mass Spectrometry (GC/MS) combines analytical specificity and sensitivity together for analysis of a diverse range of organic compounds, and can confirm the presence of or identify the structure of a suspected contaminant compound. The gas chromatograph is used to separate the particular species, while the mass spectrometer is used to determine the identity of the compounds. The detector of the Mass Spectrometer can be operated in three modes:

(a) total ion monitoring - used for quantification

- (b) total mass spectrogram used for structure elucidation of an unknown compound

characteristic of the

volatile

There are three major functional parts of the mass spectrometer: (1) the ion source; (2) the mass analyzer; and (3) the output system. Sample molecules are ionized by the ion source, using a variety of techniques. The ions are separated and displayed as a function of their mass and relative abundance. This constitutes a pattern or profile called the mass spectrum, which usually is uniquely diagnostic of a particular molecule (Merritt and Robertson, 1982).

The most commonly used ion source is the electron impact (EI) type, where the sample molecules are bombarded by an energetic electron beam. Normally, the energy of the electron beam is 70eV which is above the ionization potential for organic compounds. After ionization occurs, positive singly charged ions are produced predominantly, with a small co-existing population of double positively charged and single negatively charged ions. (Gilbert, 1984)

For an organic molecule X, the production of a molecular ion X<sup>.+</sup> occurs as follows:

 $X + e \rightarrow (X)^{+} + 2e^{-}$ 

The collection of ions of differing mass to charge

ratio (m/z) produced in the ion source of the mass spectrometer is then accelerated away as a beam by a series of focusing slits operated at different voltages. This beam then passes to the next stage of the mass spectrometer. This involves the separation of these ions and their collection.

Two fundamentally different instrumental methods of separation of ions are used and these form the basis of the two major types of mass spectrometers. One is by deflection through a magnetic field (magnetic sector instruments), the other is by using a collection of four rods at radiofrequency and direct current voltages (quadrupole instruments). The quadrupole type instruments have the capacity of rapid scanning and additionally, a simplicity of operation for obtaining selected ions by rapid switching between various rod voltages.

Normally, the total mass spectrogram is utilized as a confirmation tool. Each specific organic compound has a unique mass spectrum. By comparing the mass spectrogram of an unknown with standard spectra, the structure of the unknown sample can be identified. If other organic compounds are eluting from the column at the same retention time, this will be evident by comparing the mass spectrogram.

By focusing on the relative abundance of a limited number of ions monitored simultaneously, rather than operating the mass spectrometer in the full scanning mode, the sensitivity increase dramatically. This is called the

selected ion monitoring (SIM) mode, which can be defined as "the dedicated use of a mass spectrometer to acquire and record ion currents only at certain selected mass-to-charge (m/z) values" (Gilbert, 1987). In the roles of confirmation and quantification, the selected ion monitoring (SIM) mode is most commonly employed. Quadrupole instruments are typified by good calibration stability, but SIM is normally operated at constant magnetic field with switches in the accelerating voltage to bring the desired ions into focus.

In the selected ion monitoring mode of operation, specificity and quantitative analysis is obtained by monitoring one or more ion fragments in combination with the gas chromatographic retention time. Sometimes, it is necessary to monitor more than one ion fragment in each standard to establish an area ratio, and any charge in the area ratio. By using SIM the particular choice of either one ion or a number of ions in the spectrum is governed by two principles. First, to achieve maximum sensitivity, ions of a high relative abundance are desirable, as the absolute sensitivity attainable by SIM is frequently better than is likely to be necessary for a particular assay. Second, as a general rule specificity tends to improve with increasing m/z value and the ideal choice is of a high m/z, preferably of greater than m/z 200 (Gilbert, 1987).

The migration of residual monomer, such as vinyl chloride, vinylidene chloride, acrylonitrile and styrene

from food packaging to a contained product has been a major concern as a source of food contaminant. By using the GC/MS techniques, identification and quantification of monomers have been accomplished (William and Miles, 1975; and Lierop and Stek, 1976). The SIM mode of the mass spectrometer also provides a useful technique to identify specific contamination compounds from a complex flavor profile (Gilbert and Startin, 1981; and Gilbert and Startin, 1982). This particular application of the mass spectrometer has been used for extensive surveys of a wide range of retail foods for styrene monomer contaminates. Low resolution SIM, in the majority of cases, has proved to be quite adequate in determining the presence of specific volatiles in food products.

## Characteristics of Packaging Seal

In selecting an adhesive system used to provide a package seal, two major factors should be considered. One is the chemical nature of the adhesive components which acts as the binder. Second is to consider the manner in which the bond is formed. In practice, adhesives are widely used in forming multilayer structures involving the combination of polymeric films or other non-polymeric polymers, as well as to seal fabricated package systems (Lazarus, 1990).

In general, the primary bonding associated with adhesives include three types: (1) covalent bonds; (2) ionic

bonds; and (3) metallic bonding. Three general methods can be described for adhesive bond formation (Lazarus, 1990) and are summarized below:

(1) Loss of carrier - This bond is formed when the carrier (water or solvent) is lost through adsorption into the substrate or by evaporation. Water-based adhesives are preferred from an environmental point of view, but its removal requires more energy. For most cases, solvent based adhesive systems are more common. However, if solvent based adhesives are employed, there is a need to consider residual solvent remaining in the packaging material or sealing area following package fabrication.

(2) Loss of heat - The application of a molten adhesive, such as a hot melt, which solidifies on cooling. Such an adhesive type has application with both porous and impermeable substrates. However, this molten adhesive can not be applied to an heat-sensitive substrate.

(3) Chemical reaction - A solution of the adhesive system is applied to the substrate and then reacts chemically to yield a solid coating on the substrate surface. This method is commonly used for structural adhesives, where high bond strengths are needed.

# Heat seal

By their very nature, hot melt adhesives are thermoplastic and largely amorphous, softening gradually over a wide temperature range. This can give rise to potential problems, unless the thermal properties of the adhesive system are known and fully understood by the user. Adhesive performance can be best understood by discussing the solid to liquid change in relation to adhesive application, and the liquid to solid change in relation to the formation of a good bond (Kettleborough, 1990).

The speed of bond formation on modern high-speed machinery depends on several factors such as the specific adhesive system, temperature, porosity and surface characteristics of substrates, as well as application conditions, and the time and extent of compression of the surfaces. If all factors are carefully considered, the relative high price of 100% solids hot melts may be offset by various economic factors, including operational costs and performance (Skeist and Miron, 1990)

Booth (1990) defined the process of a heat seal as "to

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reactivate a layer of thermoplastic material or adhesive on an adhered substrate by heat, enabling it to form a bond with another adhered substrate, usually assisted by pressure".

Heat seal adhesives are based on several different chemical compositions. Those based on ethylene - vinyl acetate (EVA) copolymers represent the majority of the market. The EVA resin emulsions have a high degree of versatility and potential to tailor the formulation of the adhesive system for specific end use applications. The EVA polymer systems offer excellent machine operation, setting and adhesion characteristics, coupled with good low temperature flexibility, as well as very good compatibility with other formulating constituents used in the manufacture of hot melts or heat seal adhesives. Other types of polymers employed as hot melt adhesives include polyethylene, polyamides, polyurethanes, amorphous polypropylene, and thermoplastic copolymers (Coggin, 1990).

Hot melts are well known for their versatility and functionality. There are also certain limitations in their application which include: (i) a limited heat resistance due to the thermoplastic nature of the adhesive system. It should be noted that most hot melts used for packaging have little mechanical strength at 60°C; (ii) susceptibility to solvent and plasticizer attack; (iii) bond failure under high stress or load; and (iv) a clean substrate surface is a

requirement for effective bonding.

Hot melts based upon ethylene-vinyl acetate (EVA) copolymers are dominant in this field, with 50-55% of the market volume. Polyolefins, such as LDPE and amorphous PP account for 30-40% of the market volume, with the remaining 5-15% balance made of "specialty" hot melts (Kuzma, 1990).

## Cold seal

Cold seal adhesives were first introduced in the 1960's for confectionery packaging. Since then, their usage has increased significantly, and a wide range of substrates have been evaluated (Stone, 1976 and Anonymous, 1980).

The term "Cold seal" is used to describe the creation of an effective seal without the use of heat. This technique requires two surfaces of cold seal adhesives being bonded together under pressure alone. Booth (1990) defined cold seal as "the ability of a non-tacky adhesive film to bond to itself under pressure at room temperature".

In the field of packaging, cold seal closures have been widely use for food products as well as for other heat sensitive products. Early applications of this sealing technique were hindered. However, by the need to use organic solvents, which were not suitable for food contact, in applying the cold seal adhesive pattern. Now, with the development of new cold seal materials, which are waterbased, rubber latex stabilized with alkali (Jones, 1985),

the use of cold seal adhesives has found considerable utility in the packaging of confectionery products.

Cold seal adhesives are normally used on flexible film webs to replace a laminated or extruded polyethylene layer as the sealing medium. This improves the output and economy in the flexible packaging industry.

Cold seal adhesives are based on a mixture of natural and synthetic rubber latexes, combined with a number of lesser ingredients, such as antifoams, antifungicides, and filling agents. The natural latex confers the characteristics of self adhesion. Synthetic latexes are used to control the variable cohesive properties, to improve stability, to increase resistance to oxidation, or to improve adhesion to difficult substrates, and may also be used to reduce costs (Anonymous, 1980).

The application of cold seal adhesives in the confectionery industry is recognized as revolutionary with respect to optimization of machine efficiency and reduction of running costs (Layfield, 1990). According to Levine (1976) and Jones (1985), the most important factors contributing to the dramatic growth in the use of cold seal coated materials were:

 Elimination of heat damage to heat sensitive products, such as chocolate. There is no heat required in the bonding process, only contact pressure required.

- (2) Less distortion and shrinkage of polypropylene packaging films.
- (3) Water based adhesive formulation eliminate solvent related concerns.
- (4) Elimination of costly temperature control equipment on the packaging line and lower power consumption.
- (5) Easier machine maintenance, ease of clean-up and nonsticking of the coating to the product.
- (6) A faster process than heat sealing, packaging equipment can run at a faster line speed.

Compared to heat sealing techniques, machine speeds can be doubled with the use of a cold seal. Heat sealing is a more difficult procedure due to the short heater dwell time and the excessively high jaw temperature needed to compensate for this.

Cold seals are normally based on the type of natural rubber latex and are widely categorized into two types which can be described by the nature of the dried film (Layfield, 1990):

"Hard" cold seals are essentially non pressuresensitive and usually exhibit low bond strength. The nature of the dried film is less prone to blocking and stringing. These would be more likely to give good flow properties on a packing line, as a result of the low coefficient of surface friction. "Soft" cold seals show a greater degree of pressure sensitivity and will seal more readily. This characteristics lead to much higher seal strengths and in some cases to cause film tear. It has a higher probability of blocking and stringing. The softer varieties of cold seals are usually more tolerant to surface contamination. However, they exhibit a slight reduction in seal strength.

In recent years, the trend with respect to cold seals has been towards maximizing bond strength and obtaining 100% fiber tear on single web films, especially low density pearlized polypropylene. Some fragile products need an easyopen, peelable bond, this requirement necessitates a seal strength in the region of 100g/25mm (Layfield, 1990).

In addition, to the well-established confectionery and biscuit markets, cold seal adhesives may find use in other applications, such as medical packaging, tea packaging or frozen food packaging. Also development of adhesive technology to maintain performance with new films and inks/lacquers will be critical to the industry (Stone, 1976 and Layfield, 1990).

### MATERIALS AND METHODS

# Part I: Permeability of Organic Volatiles Through Packaging Film Roll Stock

## Packaging materials:

Six commercial barrier film structures were evaluated in the present studies. All six packaging films were coated with a 1/2" wide pattern cold seal (PCS) on the side of film. The six polymer structures evaluated included:

- Printed Oriented Polypropylene (OPP) 1.7 mil
- High Density Polyethylene (HDPE) 1.7 mil
- White Opaque Glassine (Glassine) 1.7 mil
- Saran Coated Oriented Polypropylene (Saran OPP) 1.5 mil
- Acrylic Coated Oriented Polypropylene (Acrylic OPP)
  - 1.7 mil
- Metallized Polyester/Polypropylene (Met PET/OPP)
  - 1.5 mil

All film samples were approximately 1.5 to 1.7 mil in thickness. Ethyl acetate and toluene were evaluated as the organic penetrants. Acetonitrile and methanol were used as solvents to prepare standard solution used for developing the respective calibration curves for quantification.

Ethyl Acetate (CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>): J. T. Baker Chemical Co. (Phillipsburg, NJ) Analytical Reagent grade Molecular weight Molecular weight 88.11 Density at 25°C, g/ml 0.894 88.11 Boiling range 77.2 ± 0.5°C Purity 99.98 Toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>): J. T. Baker Chemical Co. (Phillipsburg, NJ) Analytical Reagent grade Molecular weight 92.14 Density at 25°C, g/ml 0.893 Boiling range  $110.4 \pm 0.2$ °C Purity 99.98 Acetonitrile (CH<sub>z</sub>CN): EM Industries, Inc. (Gibbstown, NJ) HPLC grade Molecular weight 41.05 Density at 25°C, q/ml 0.78 Boiling range 82.0 ± 0.1°C 99.88 Purity Methanol (CH<sub>z</sub>OH): Sigma Chemical Co. (St. Louis, MO) HPLC grade Molecular weight 32.04 Density at  $25^{\circ}C$ , g/ml 0.791 Boiling range  $64.7 \pm 0.1^{\circ}C$ 99.98 Purity

# **Permeation test:**

Permeability studies were carried out by an isostatic procedure utilizing the MAS 2000<sup>TM</sup> Permeability Test System (MAS Technologies, Inc., Zumbrota, MN). The system allows for the continuous collection and measurement of the permeation rate of an organic vapor or gas through a polymer membrane, from the initial time zero to steady state conditions. The system incorporates a flame ionization detector (FID), precise temperature and flow rate control and is interfaced to an IBM 486SX computer system. The computer controls many of the parameters that are established during set-up. It will activate and deactivate the gas flow direction, cell opening/closing, as well as display data on the screen, while recording all pertinent instrument parameters. Finally, all permeation data can be stored in the computer hard drive or on a floppy disc, and LOTUS 1-2-3 used to recall the permeation data to calculate and print out the respective mass transfer parameters and the transmission rate profile curve.

For each test film, a sample approximately 6" x 6%" was cut, mounted on a paperboard film holder with tape, and the mounted film sample placed in the permeability cell. The film was mounted with the pattern cold seal facing away from the high permeant concentration stream. The permeability studies were carried out at three temperatures, and for each temperature, three vapor activity levels were evaluated.

A constant concentration of permeant vapor for the "high concentration" cell chamber was produced by bubbling nitrogen through the liquid permeant. The liquid permeant is contained in a vapor generator consisting of a Kontes Fritted Midget Bubbler, \$24/40, 25 ml (Fisher Scientific,

Pittsburgh, PA). The organic vapor stream was then mixed with another source of pure nitrogen. Rotameters were used to provide an indication of settings required for the desired vapor activities. The gas flows to the rotameters were regulated by Nupro "M" series needle valves. The vapor generator system was maintained at a constant temperature of  $23 \pm 1^{\circ}$ C.

Before actual testing was conducted, flowmeter settings were determined to provide vapor activity (a) values of approximately 0.067, 0.21, and 0.41, respectively. Because of the wide variation in the saturation vapor pressure of toluene and ethyl acetate at the respective temperatures of test, the partial pressure gradient for the permeability experiments was expressed as vapor activity. This allowed for barrier performance to be compared at a standard driving force for the two permeants evaluated. Vapor activity values were calculated by dividing the experimentally determined vapor pressure by the saturated vapor pressure for the respective permeants (Equation 16).

Vapor activity (a) = 
$$\frac{P}{P_o}$$
 (16)  
where: P = partial vapor pressure  
 $P_o$  = saturated vapor pressure

All vapor pressure values were determined at 23  $\pm$  1°C. A sampling port was installed between the dispensing

manifold and the test cell to provide an accurate measure of the permeant vapor concentration or activity. To determine the specific vapor concentration, a 100  $\mu$ l sample was removed from the sampling port with a Hamilton 500  $\mu$ L, 1750SN gas tight syringe (Hamilton Co., Reno, Nevada), and the sample injected directly into the gas chromatograph. Analysis of permeant concentration was carried out by a gas chromatograph (Model 5890A, Hewlett Packard, Avondale, PA) equipped with flame ionization detector and interfaced to a Hewlett-Packard integrator (Model 3395, Avondale, PA). A setting of 1 minute purge "ON" was utilized for all analyses. The gas chromatography conditions are presented as following:

GC condition (Model 5890):

Column: Supelcowax 10 (Supelco Inc., Bellefonte, PA) Fused silica capillary column Polar bounded stationary phase 60 m length x 0.32 mm I.D.

Carrier gas: Helium at 1.5 ml/min

Range: 2

Attenuation: 0

Zero: dependant on the GC signal after ignition

Temperature cycle for ethyl acetate:

Injection temperature		220 °C
Initial temperature		40 °C
Initial time		1 min
Temperature rate	5	°C/min
Final temperature		200 °C
Final time		10 min
Detector temperature		250 °C

Temperature cycle for toluene:

Injection temperature 220 °C Initial temperature 60 °C Initial time 1 min Temperature rate 5 °C/min Final temperature 200 °C Final time 10 min Detector temperature 250 °C	
Integrator setting (Model 3395):	
Zero: 0, 0.021	
Attenuation: 6	
Chart speed: 0.5 cm/min	
Peak width: 0.04	
Threshold: 0	
Area reject: 0	
Retention time for ethyl acetate: 5.4 minutes	
Retention time for toluene: 7.85 minutes	

In both cases, a standard curve of response vs permeant quantity was constructed from standard solution of known concentration. Calibration standard solutions were prepared by dissolution of known quantities of ethyl acetate in acetonitrile and toluene in methanol. A 1  $\mu$ l sample was removed from standard solution and injected into HP 5890 Gas Chromatograph. The standard calibration curves for ethyl acetate and toluene are shown in Appendix I.

Once the operational parameters of gas flow rates, temperature and signal base line have attained steady state, the MAS 2000 Permeability test system was calibrated as follows: A 100  $\mu$ L sample of permeant vapor of known concentration was removed from the sampling port interfaced to the dispensing manifold of the vapor generator system and the gaseous sample conveyed directly to the flame ionization detector of the MAS 2000 test system via the injection port incorporated on the instrument chassis. The detector response (picoamps) is then related to the quantity of permeant injected to determine a calibration factor. All instrument operational parameters were as recommended by the manufacture in the operating manual. After calibration for the permeant, by striking the "Test" key, the internal valve will activate and the organic vapor will enter the test cell and start the permeation test of the film.

The specific temperatures selected for the permeability studies were based on the structures of the respective barrier films. The temperatures selected for the respective test films are presented below:

	<u>Ethyl acetate</u>	<u>Toluene</u>
OPP :	30°C, 40°C, 50°C	30°C, 40°C, 50°C
HDPE:	30°C, 40°C, 50°C	30°C, 40°C, 50°C
Glassine:	23°C, 30°C, 40°C	30°C, 40°C, 50°C
Saran OPP:	40°C, 50°C, 60°C	40°C, 50°C, 60°C
Acrylic OPP:	50°C, 60°C, 70°C	50°C, 60°C, 70°C
Met PET/OPP:	50°C, 60°C, 70°C	50°C, 60°C, 70°C

P

Sà te:

# Part II: Permeability of Toluene Through a Packaged Confectionery Product with A Cold Seal Closure

Samples of a chocolate type confectionery product packaged in the respective test package structures were provided by a commercial supplier. For this study, toluene was selected as the organic permeant and only one vapor activity was evaluated for the packaged product permeation studies. The organic vapor activity selected was based on the lower bound activity level which could be adjusted with the vapor generator system designed.

The toluene level in the four test chambers was determined every third day to monitor the consistency of the vapor generator system. To determine the specific toluene vapor concentration, a 100  $\mu$ l sample was removed from the sampling port with a Hamilton 500  $\mu$ L, 1750SN gas tight syringe (Hamilton Co., Reno, Nevada), and injected into the gas chromatograph. The analytical procedure for toluene analysis was identical to that previously described (see page 48).

All confectionery products (coated with milk chocolate) were wrapped individually with the six barrier membranes which were evaluated in Part I of the study. Sealing of the respective barrier structures was carried out with the same pattern cold seal adhesive and sealing conditions.

The confectionery products were manufactured in the same dimension of 11 cm x 3 cm x 2 cm (length x width x height). As an initial postulate, it was assumed that the

package system was hermetically sealed, and the permeated toluene vapor was sorbed totally by the chocolate layer.

## Permeation chamber design:

A multi-chamber test system was designed and fabricated to allow exposure of the packaged product to a fixed and constant toluene vapor concentration at constant temperature. The test chambers consisted of four (4) stainless steel desiccant chambers of dimension, 30.5 cm x 28 cm x 31 cm (length x width x height). Each chamber was equipped with four open metal shelfs to allow multiple sample exposure under identical conditions. Each test chamber was also equipped with a gas inlet and outlet port, and a gas sampling port to allow continuous monitoring of the toluene vapor concentration over the course of the study. A schematic diagram of the test system utilized is presented in Figure 1. As shown, the test system was designed to evaluate multiple product/package samples concurrently. All studies were carried out at 23 ± 1°C.

A constant concentration of toluene vapor to be flowed continually through the respective exposure test chambers was produced by bubbling nitrogen through the liquid permeant. This is carried out by assembling a vapor generator consisting of a gas washing bottle, with a fitted dispersion tube, containing the organic liquid. To obtain a lower vapor concentration, the permeant vapor stream is



mixed with another stream of pure carrier gas (nitrogen). Flow meter settings were determined to provide the desired vapor activity value of approximately a = 0.003.

As shown in Figure 1, flow meters were used to provide a continuous indication that a constant rate of flow of permeant vapor was maintained to the individual test chambers. Gas flow was regulated with NU PRO needle valves, Type B-25G. The vapor generator system was kept at a constant temperature of 23  $\pm$  1°C. The penetrant vapor concentrations are expressed throughout in ppm (mass/volume) vapor in nitrogen, where 1 ppm equals 1  $\mu$ g toluene per cm<sup>3</sup> of gas mixture at 1 atm (23°C). A photograph of the vapor

## Storage condition:

All studies were carried out at  $23 \pm 1^{\circ}$ C. As a function of time, a series of individual packaged confectionery products were removed from the test chambers and the product analyzed for the quantity of volatile organic permeant (toluene) sorbed by the chocolate.

The sampling frequency varied according to the barrier properties of the packaging structures. The six barrier membranes can be separated into two groups. Samples from group I, which included HDPE, Glassine, and OPP based structure, were evaluated weekly for the first month, then evaluated every two weeks for a two month period. Samples


Figure 2. Photograph of vapor generator system and permeability test chambers for packaged product.

from group II, which included Saran OPP, acrylic OPP, and the Metallized PET/OPP based structures, were evaluated after 11 and 19 days, then evaluated every third week for a period of three months.

## Toluene quantification apparatus for trapping of volatiles:

A dynamic gas purge and trap system was designed for dynamic headspace sampling of the dry product. Six 250 ml Erlenmeyer flasks were modified to 29/42 standard taper male joints to which the dispersion tube assembly of a gas washing bottle could be fitted (Stopper assemblies for Corning 31770 gas washing bottles, Fisher Scientific, Pittsburgh, PA). Modification of the dispersion tube assembly of the gas washing bottles and the erlenmeyer flasks were performed by the Chemistry Department Glass Blowing Shop at MSU. A schematic diagram of the dynamic purge and trap system is shown in Figure 3. As shown, a cylinder of compressed nitrogen was interfaced to a dispersing manifold which consisted of three flow meters and needle valves, all connections were through 1/8" O.D. copper tubing and swagelok fitting. Flow meters were used to provide a continuous indication that a constant rate of flow of nitrogen was maintained to the individual purge and trap cells. Gas flow was regulated with NU PRO needle valve, type B-25G.

The trapping system was designed to ensure that the





sample was continuously flushed with nitrogen gas and the desorbed volatiles conveyed to the trapping tube attached. The sorption trap was connected to the exit port of the dispersion head via swagelok adopters. The dispersion head exit port of 8 mm O.D. glass tubing was connected by a 5/16" swagelok nut and a series of reducing adopters to a 1/4" male swagelok fitting. The sorption trap was mounted to the dispersion head with a 1/4" thumb wheel swagelok fitting (Supelco Inc., Bellefonte, PA) for easy removal and can figuring to both glass and metal desorption traps. By changing the ferrule materials to teflon or graphite, the thumb-wheel swagelok fitting can be employed to fit both metal (Scientific Instrument Services, NJ) or glass (Supelco Inc, Bellefonte, PA) thermal desorption traps. Figures 4 and 5 show the trapping cell and the whole purge and trap system.

The glass lined stainless steel GLT thermal desorption tubes (4 mm I.D. x 100 mm, threaded on both ends) used in the present study were prepacked by Scientific Instrument Services, Inc. (Ringoes, NJ). The trapping tubes were packed with three layers of adsorbent resins (Supelco, PA) - 20/40 Carbon C, 20/40 Carbon B, and 60-80 Carbosieve S-III. Before each trapping procedure, the sorption traps were conditioned overnight at 330°C with a nitrogen flow rate of 20 ml/min.



Figure 4. The apparatus of trapping cell.



Figure 5. Photograph of dynamic purge and trap system.

## Flavor Analysis Procedure:

## Dynamic purge and trap procedure

To establish optimum procedure conditions for the analysis of sorbed toluene in the product samples, several temperature/time combinations were evaluated in a series of preliminary runs. A water bath temperature of 40°C and a purge time of 20 hours provided chromatograms which showed good peak resolution. These conditions were therefore selected for analysis of the sorbed toluene.

To determine if a water bath temperature of 40°C and a purge time of 20 hours would provide quantitative desorption of sorbed toluene from the confectionery product samples, the procedure was run twice on the same sample, which was known to contain sorbed toluene.

A comparison of the chromatograms obtained from the first and second runs showed no detectable levels of toluene present when the purge and trap procedure was repeated. It was therefore assumed that with an water bath temperature of 40°C and a purge time of 20 hours, more than 90% of any sorbed toluene would be desorbed from the sample during the initial heating period.

Individual packaged confectionery products were removed from the permeation test chambers as a function of storage time. The package was opened, the product removed and a sample (11 cm) cut from the end of the chocolate layer. Approximate 0.3 grams of the chocolate layer weighed

accurately were placed in the trapping flask. The desorption cells were assembled and the traps connected. The desorption cells were then placed in a water bath maintained at 40°C. Nitrogen gas was continually flowed through the desorption cells at a flow rate of approximately 25 cubic centimeters per minute for 20 hours. The water bath temperature was maintained at 40°C throughout the purge period.

## Gas chromatography - mass spectrometric analysis

The trapped volatile compounds were directly desorbed and injected into a gas chromatograph - mass spectrometer (GC/MS) system using a Short Path Thermal Desorption unit (Scientific Instrument Services, Ringoes, NJ). Before carrying out the desorption procedure, the sorption trap was screwed on a 30 mm long side hole syringe needle (Scientific Instrument Services, Ringoes, NJ), and attached to the thermal desorption unit. The complete injection and desorption mechanism is shown in Figure 6. The trapped volatile compounds were heated and desorbed from the carbon adsorbent by the desorption heater block into the injection port of the gas chromatograph (GC) (Figure 7). The sorption trap was heated at 290°C with helium gas flushing (10 ml/min) for 6 minutes.

The GC/MS analysis was simultaneously started with the beginning of the desorption process. The volatile compounds were separated and identified using a HP 5890 gas





Figure 7. Short Path Thermal Desorption Unit operation with the gas chromatograph.

chromatograph (Hewlett Packard, Avondale, PA) interfaced to a HP 5970 mass selective detector (MSD) mass spectrometer. This GC/MS system was equipped with a HP 59970 Chemstation Data System. The GC/MS analysis was performed at the Mass Spectrometry Laboratory in the Department of Biochemistry at Michigan State University. A SPB-5 non-polar fused silica capillary column (60 m x 0.32 mm I.D., 1  $\mu$ m film thickness, Supelco Inc., Bellefonte, PA) was used to separate the desorbed compounds. The GC temperature program was set as following: the initial temperature was 35°C for 6 minutes, and the temperature was increased at 5°C/min to 80°C then increased at 15°C/min to a final temperature of 250°C maintained for 10 minutes. Helium was the carrier gas with a flow rate of 10 ml/min. The injection port temperature of the GC and the transfer line temperature between the GC and the MS were set at 250°C.

The mass spectrometer was operated in the electron impact mode with an electron energy of 70eV and an ion source temperature of 250°C. The separated volatile compounds were then introduced into the mass spectrometer directly from the capillary column. A selective ion mode (SIM) with 4.7 cycles per second, and three ion masses (m/z) 65, 91, and 92 were selected.

The total ion chromatograph was used for quantification. However, by using the SIM mode of operation, the total ion spectrum screened out or eliminates all

eluting compounds except for volatile compounds containing the three selected ion masses (m/z = 65, 91 and 92). For identification of the toluene, elution time is compared with the elution time of a toluene standard solution (8.8 minutes), or by comparison of the sample mass spectrum with the standard toluene mass spectrum (the ratio of ion mass 91/92 is about 1.75/1). Toluene quantification was carried out by integrating the peak area under the total ion chromatogram (i.e. area of m/z = 65, 91 and 92 ion peaks).

The standard calibration curve for toluene was constructed using thermal desorption - GC/MS system, operated under the same conditions as previously described. Toluene standard solutions of 4, 10, 20, and 40 ppm (wt/v) were prepared by using methanol as the solvent. A 1.2  $\mu$ l sample of the respective standard solutions was injected into the sorption trap, then the trap was heated and the toluene vapor directly injected into the GC/MS. The calibration curve of toluene vapor by the thermal desorption - GC/MS procedure is presented on Appendix II. The standard toluene mass spectrum is showing on Appendix III. The total ion chromatograms obtained by GC/MS analysis were recorded, stored and analyzed by using a HP Chemstation data system.

## Part III: Leak Testing

The package leak testing was performed by a Nikka Packaging Leak Tester (Model PLT - 3501) (Nikka Densok U.S.A., Inc., Lakewood, CO). The leak tester was connected to a test sample cell of 14.5 x 4.4 x 2.5 cm<sup>3</sup>. This test cell was designed to handle the packaged product system evaluated in the present study. This leak tester is based on measuring the different vacuum pressure change between the test cell and the packaged product itself. The operational parameters were set up as the instrument manufacture recommended. The parameters set up to be used in this study are listed below:

> BAT 1 = 99.9 STAB = 1.5 seconds Measure = 2 seconds A Comp = 2000 mm-H<sub>2</sub>O HI = 999 mm-H<sub>2</sub>O LO = 0 mm-H<sub>2</sub>O

where: STAB = stabilized time after the test cell was
 pulled out air

Measure = actual measuring time for observing the vacuum pressure change

- A Comp = actual vacuum pressure to apply on the packaged product
  - HI = the highest measuring pressure to be
     set up as reject during packaging line
    LO = the lowest measuring pressure

Before initiating the package system permeability studies, 20 package/product samples for each packaging material were randomly selected and their leak test values measured. Leak test values for packaged samples removed from the permeation test chambers were determined directly upon their removal and prior to opening.

#### **RESULTS AND DISCUSSION**

## Part I: Permeation Study of Packaging Films

# The Effect of Vapor Activity and Temperature on Ethyl Acetate Permeability

Permeance values determined at ethyl acetate vapor activity levels of a = 0.095, 0.21 and 0.41 for the respective barrier structures are summarized in Tables 3 - 7. For the metallized polyethylene terephthalate/OPP laminate, no measurable rate of diffusion was detected, following continuous testing for 44 hours at 70°C and a vapor activity of a = 0.41.

To better illustrate the effect of vapor activity on the transmission rates for the respective test films, the results are presented graphically in Figures 8 - 11, where log permeance (P) is plotted as a function of vapor activity, at constant temperature. From Figures 8 - 11, it becomes evident that at the vapor activity levels evaluated, that the effect of penetrant concentration on the permeance values is minimized.

From a least squares fit, the following expressions were derived to describe the correlation between the permeance constant and penetrant concentration.

For the oriented polypropylene structure, the

Table 3. Permeance constant of ethyl acetate through printed oriented polypropylene (OPP) as a function of vapor activity and temperature<sup>(1)</sup>.

Vapor Activity <sup>(2)</sup>	Temperature (°C)	$P\left(\frac{Kg}{m^2.sec.Pa}\right) \times 10^{-12}$	log(P)
	30	0.62	-12.2134
0.095	40	1.72	-11.7696
	50	4.37	-11.3610
	30	0.72	-12.1442
0.21	40	1.94	-11.7134
	50	4.42	-11.3546
	30	0.91	-12.0409
0.41	40	2.08	-11.6831
	50	4.77	-11.3214

(2). Vapor activity values were determined at ambient temperature (24°C).

Table 4. Permeance constant of ethyl acetate through high density polyethylene (HDPE) as a function of vapor activity and temperature<sup>(1)</sup>.

Vapor Activity <sup>(2)</sup>	Temperature (°C)	$P(\frac{Kg}{m^2.sec.Pa}) \times 10^{-11}$	log(P)
0 095	30	1.02	-10.9918
0.095	40	1.72	-10.7668
	50	2.66	-10.5760
	30	2.36	-10.6268
0.21	40	2.80	-10.5531
	50	3.37	-10.4720
	30	2.89	-10.5386
0.41	40	3.76	-10.4256
	50	4.81	-10.3185

analyses.
 <sup>(2)</sup>. Vapor activity values were determined at ambient temperature (24°C).

Table 5. Permeance constant of ethyl acetate through Glassine as a function of vapor activity and temperature<sup>(1)</sup>.

Vapor Activity <sup>(2)</sup>	Temperature (°C)	$P\left(\frac{Kg}{m^2.sec.Pa}\right) \times 10^{-12}$	log(P)
0 095	23	1.17	-11.9370
0.093	30	1.96	-11.7114
	40	4.23	-11.3748
	23	2.28	-11.6557
0.21	30	2.95	-11.5316
	40	5.20	-11.2861

(2). Vapor activity values were determined at ambient temperature (24°C).

Table 6. Permeance constant of ethyl acetate through Saran coated oriented polypropylene as a function of vapor activity and temperature<sup>(1)</sup>.

Vapor Activity <sup>(2)</sup>	Temperature (°C)	$P\left(\frac{Kg}{m^2.sec.Pa}\right) \times 10^{-13}$	log(P)
0 095	40	0.99	-13.0033
0.095	50	5.01	-12.3006
	60	15.07	-11.8220
	40	1.61	-12.7950
0.21	50	5.23	-12.2846
	60	14.90	-11.8271
	40	2.83	-12.5481
0.41	50	7.74	-12.1121
	60	26.48	-11.5772

analyses.
 <sup>(2)</sup>. Vapor activity values were determined at ambient temperature (24°C).

Table 7. Permeance constant of ethyl acetate through Acrylic coated oriented polypropylene as a function of vapor activity and temperature<sup>(1)</sup>.

Vapor Activity <sup>(2)</sup>	Temperature (°C)	$P\left(\frac{Kg}{m^2.sec.Pa}\right) \times 10^{-12}$	log(P)
0 095	50	0.25	-12.6033
0.095	60	1.03	-11.9856
	70	2.65	-11.5769
	50	0.27	-12.5628
0.21	60	1.16	-11.9354
	70	3.60	-11.4434
	50	0.34	-12.4728
0.41	60	1.20	-11.9226
	70	3.29	-11.4824

(2). Vapor activity values were determined at ambient temperature (24°C).

















relationship between the permeance value (P) and ethyl acetate vapor activity (a) was found to be:  $log(P)_{(30^{\circ}C)} = -12.263 + 0.5442(a)$  (R<sup>2</sup> = 1.00)  $log(P)_{(40^{\circ}C)} = -11.784 + 0.2609(a)$  (R<sup>2</sup> = 0.90)  $log(P)_{(50^{\circ}C)} = -11.377 + 0.1302(a)$  (R<sup>2</sup> = 0.95)

For the high density polyethylene structure, the relationship between the permeance value (P) and ethyl acetate vapor activity (a) was found to be:  $log(P)_{(30^{\circ}C)} = -11.035 + 1.3275(a)$  (R<sup>2</sup> = 0.78)  $log(P)_{(40^{\circ}C)} = -10.828 + 1.0333(a)$  (R<sup>2</sup> = 0.91)  $log(P)_{(50^{\circ}C)} = -10.649 + 0.8118(a)$  (R<sup>2</sup> = 1.00)

For the Saran coated oriented polypropylene structure, the relationship between the permeance value (P) and ethyl acetate vapor activity (a) was found to be:  $log(P)_{(40^{\circ}C)} = -13.1209 + 1.4214(a)$  (R<sup>2</sup> = 0.99)  $log(P)_{(50^{\circ}C)} = -12.3821 + 0.6279(a)$  (R<sup>2</sup> = 0.92)  $log(P)_{(60^{\circ}C)} = -11.9399 + 0.8300(a)$  (R<sup>2</sup> = 0.86)

For the Acrylic coated oriented polypropylene structure, the relationship between the permeance value (P) and ethyl acetate vapor activity (a) was found to be:  $log(P)_{(50^{\circ}C)} = -12.6460 + 0.4182(a)$  (R<sup>2</sup> = 1.00)  $log(P)_{(60^{\circ}C)} = -11.9919 + 0.1847(a)$  (R<sup>2</sup> = 0.86)

From the permeance values summarized in Tables 3 to 7, it becomes evident that the permeance (P) is highly dependent on the temperature, at a constant permeant concentration level. This is illustrated in Figures 12 - 16, where permeance is plotted as a function of temperature  $[T^{-1} (^{o}K)]$  for studies carried out on oriented polypropylene, high density polyethylene, glassine, Saran coated oriented polypropylene, and Acrylic coated polypropylene, respectively.

As can be seen, the temperature dependency of the transport process associated with the respective barrier membranes, over the temperature range studied, follows well the Arrhenius relationship. From the slopes of the Arrhenius plots, the activation energy for the permeation process  $(E_p)$  was determined for the respective film samples, as a function of vapor activity. The determined activation energy values are summarized in Table 8.

From the general Arrhenius equation,

$$P = P_{o} \exp\left(\frac{E_{p}}{RT}\right)$$
(17)

$$\log(P) = \left(-\frac{E_{p}}{2.3 R}\right) * \left(\frac{1}{T}\right) + \log(P_{o})$$
(18)

$$Slope = \frac{E_{p}}{2.3 R}$$
(19)

the following expressions were derived by using a least squares fit and applying experimental data.



Figure 12. Temperature dependence of the permeance of ethyl acetate in oriented polypropylene



Figure 13. Temperature dependence of the permeance of ethyl acetate in high density polyethylene



Figure 14. Temperature dependence of the permeance of ethyl acetate in glassine



Figure 15. Temperature dependence of the permeance of ethyl acetate in Saran coated OPP



Figure 16. Temperature dependence of the permeance of ethyl acetate in Acrylic coated OPP

		E(kcal/mole)	
Polymer Membranes	a = 0.095	a = 0.21	a = 0.41
ОРР	17.7	14.6	14.5
HDPE	9.3	4.4	4.9
Glassine	14.6	9.6	N/A <sup>(1)</sup>
Saran OPP	24.9	23.0	24.5
Acrylic OPP	25.9	27.9	25.0
Metallized PET/OP	P N/A <sup>(1)</sup>	N/A <sup>(1)</sup>	N/A <sup>(1)</sup>

Table 8. Activation energy values for the permeation of ethyl acetate through polymer membranes.

<sup>(1)</sup>. N/A denotes not available

# Oriented Polypropylene:

log(P) <sub>(a=0.095)</sub>	=	1.8571	-	4262.0	x	(1/T)	(R <sup>2</sup> =	1.00)
log(P) <sub>(a=0.21)</sub>	=	0.8967	-	3948.2	x	(1/T)	(R <sup>2</sup> =	1.00)
log(P) <sub>(a=0.41)</sub>	= -	0.1696	-	3597.6	x	(1/T)	(R <sup>2</sup> =	1.00)
High Density	Pol	yethyle	ne	.:				
log(P) <sub>(a=0.095)</sub>	= -	4.1255	-	2079.0	x	(1/T)	(R <sup>2</sup> =	1.00)
log(P) <sub>(a=0.21)</sub>	= -	8.0745	-	7739.0	x	(1/T)	(R <sup>2</sup> =	1.00)
log(P) <sub>(a=0.41)</sub>	= -	6.9068	-	1100.2	x	(1/T)	(R <sup>2</sup> =	1.00)
<u>Glassine</u> :								
log(P) <sub>(a=0.095)</sub>	= -	1.2647	-	3161.4	x	(1/T)	(R <sup>2</sup> =	1.00)
log(P) <sub>(a=0.21)</sub>	= -	4.6129	-	2088.9	x	(1/T)	(R <sup>2</sup> =	0.99)
Saran coated	ori	ented P	<u>01</u>	<u>ypropyl</u>	en	<u>e</u> :		
log(P) <sub>(a=0.095)</sub>	=	5.9344	-	5906.3	x	(1/T)	(R <sup>2</sup> =	0.99)
log(P) <sub>(a=0.21)</sub>	=	2.7010	-	4839.8	x	(1/T)	(R <sup>2</sup> =	1.00)
$\log(P)_{(a=0,41)}$	=	2.9711	-	4854.9	x	(1/T)	$(R^2 =$	1.00)

Acrylic coated oriented Polypropylene:

log(P) <sub>(a=0.095)</sub>	=	3.3406	-	5132.0	x	(1/T)	( R <sup>2</sup>	=	0.99)
log(P) <sub>(a=0.21)</sub>	=	4.8100	-	5596.9	x	(1/T)	( R <sup>2</sup>	=	0.99)
log(P) <sub>(a=0.41)</sub>	=	2.8966	-	4952.0	x	(1/T)	( R <sup>2</sup>	=	1.00)

# The Effect of Vapor Activity and Temperature on Toluene Permeability

Determined permeance values for toluene activity levels of a = 0.067, 0.22 and 0.44 for the respective barrier structures are summarized in Tables 9 - 13. There was no

Table	9.	Permeance	constant	of	toluene	e th	rou	lgh prin	ted	
		oriented	polypropy?	lene	e (OPP)	as	a d	Eunction	of	vapor
		activity	and temper	ratu	ire <sup>(1)</sup> .					

Vapor Activity <sup>(2)</sup>	Temperature (°C)	$P\left(\frac{Kg}{m^2.sec.Pa}\right) \times 10^{-11}$	log(P)
	30	0.49	-11.3078
0.067	40	1.14	-10.9445
	50	1.77	-10.7512
	30	0.75	-11.1242
0.22	40	1.44	-10.8408
	50	2.67	-10.5739
	30	1.37	-10.8648
0.44	40	2.04	-10.6905
	50	3.05	-10.5157

(1). The results reported are the average of duplicate analyses.
(2). Vapor activity values were determined at ambient temperature (24°C).

Table 10. Permeance constant of toluene through High Density Polyethylene (HDPE) as a function of vapor activity and temperature<sup>(1)</sup>.

Vapor Activity <sup>(2)</sup>	Temperature (°C)	$P\left(\frac{Kg}{m^2.sec.Pa}\right) \times 10^{-11}$	log(P)
	30	2.14	-10.6704
0.067	40	3.36	-10.4742
	50	5.65	-10.2479
	30	3.99	-10.3989
0.22	40	5.49	-10.2603
	50	8.00	-10.0970
	30	7.69	-10.1144
0.44	40	8.56	-10.0675
	50	9.20	-10.0362

analyses.
 <sup>(2)</sup>. Vapor activity values were determined at ambient temperature (24°C).

Vapor Activity <sup>(2)</sup>	Temperature (°C)	$P\left(\frac{Kg}{m^2.sec.Pa}\right) \times 10^{-12}$	log(P)
	30	2.83	-11.5488
0.067	40	3.86	-11.4134
	50	5.08	-11.2943
	30	3.50	-11.4557
0.22	40	5.27	-11.2785
	50	6.60	-11.1802
	30	4.09	-11.3882
0.44	40	5.52	-11.2581
	50	6.80	-11.1677

Table 11. Permeance constant of toluene through Glassine as a function of vapor activity and temperature<sup>(1)</sup>.

(2). Vapor activity values were determined at ambient temperature (24°C).
Table 12. Permeance constant of toluene through Saran coated oriented polypropylene (Saran OPP) as a function of vapor activity and temperature<sup>(1)</sup>.

Vapor Activity <sup>(2)</sup>	Temperature (°C)	$P\left(\frac{Kg}{m^2.sec.Pa}\right) \times 10^{-13}$	log(P)
	40	0.97	-13.0121
0.067	50	5.85	-12.2329
	60	21.90	-11.6601
	40	2.55	-12.5928
0.22	50	9.73	-12.0121
	60	25.00	-11.6026
	40	3.12	-12.5053
0.44	50	12.80	-11.8943
	60	28.90	-11.5393

<sup>(1)</sup>. The results reported are the average of duplicate

(2). Vapor activity values were determined at ambient temperature (24°C).

Table 13.	Permeance constant of toluene through Acrylic
	coated polypropylene as a function of vapor
	activity and temperature .

Vapor Activity <sup>(2)</sup>	Temperature (°C)	$P\left(\frac{Kg}{m^2.sec.Pa}\right) \times 10^{-13}$	log(P)
	50	_ (3)	-
0.067	60	_ (3)	-
	70	_ (3)	-
	50	_ (3)	-
0.22	60	_ (3)	-
	70	_ (3)	-
	50	1.37	-10.8648
0.44	60	2.04	-10.6905
	70	3.05	-10.5157

(1). The results reported are the average of duplicate analyses.
(2). Vapor activity values were determined at ambient temperature (24°C)
(3). Without detectable response after 44 hours test.

measurable rate of diffusion for the polyethylene terephthalate/OPP laminate structure following continuous testing for 44 hours at 70°C and a vapor activity of 0.44.

Figures 17 - 20 illustrate the effect of toluene vapor activity on the transmission rates for the respective test films, where log permeance (P) is plotted as a function of vapor activity, at constant temperature. The following expressions were derived to describe the correlation between the permeance constant and penetrant concentration, using a least squares fit equation.

For the oriented polypropylene (OPP) structure, the relationship between the permeance value (P) and toluene vapor activity (a) was found to be:

 $log(P)_{(30^{\circ}C)} = -11.3866 + 1.1871(a) \qquad (R^{2} = 1.00)$  $log(P)_{(40^{\circ}C)} = -10.9903 + 0.6811(a) \qquad (R^{2} = 1.00)$  $log(P)_{(50^{\circ}C)} = -10.7604 + 0.6057(a) \qquad (R^{2} = 0.86)$ 

For the high density polyethylene (HDPE) structure, the relationship between the permeance value (P) and toluene vapor activity (a) was found to be:  $log(P)_{(30^{\circ}C)} = -10.7524 + 1.4768(a)$  (R<sup>2</sup> = 0.99)  $log(P)_{(40^{\circ}C)} = -10.5279 + 1.0754(a)$  (R<sup>2</sup> = 0.98)  $log(P)_{(50^{\circ}C)} = -10.2596 + 0.5472(a)$  (R<sup>2</sup> = 0.89)

For the Glassine structure, the relationship between the permeance value (P) and toluene vapor activity (a) was found to be:



Figure 17. The effect of toluene vapor activity on the permeance of printed oriented polypropylene



Figure 18. The effect of toluene vapor activity on the permeance of high density polyethylene (HDPE)









 $log(P)_{(30^{\circ}C)} = -11.5665 + 0.4219(a) \qquad (R^{2} = 0.96)$  $log(P)_{(40^{\circ}C)} = -11.4121 + 0.3937(a) \qquad (R^{2} = 0.77)$  $log(P)_{(50^{\circ}C)} = -11.2915 + 0.3197(a) \qquad (R^{2} = 0.74)$ 

For the Saran coated oriented polypropylene structure (Saran OPP), the relationship between the permeance value (P) and toluene vapor activity (a) was found to be:

 $log(P)_{(40^{\circ}C)} = -13.0164 + 1.2914(a) \qquad (R^{2} = 0.80)$  $log(P)_{(50^{\circ}C)} = -12.2601 + 0.8819(a) \qquad (R^{2} = 0.93)$  $log(P)_{(60^{\circ}C)} = -11.6785 + 0.3214(a) \qquad (R^{2} = 0.99)$ 

From Tables 9 to 13 it can be seen that the permeance (P) is highly dependent on the temperature, at a constant permeant concentration level. Figures 21 to 25 illustrate this graphically, where log permeance is plotted as a function of temperature  $[T^{-1} ({}^{0}K)]$ .

The following expressions were derived using a least squares fit and applying experimental data.

## Oriented polypropylene:

log(P) <sub>(a=0.067)</sub>	= -	2.0956	-	2783.0	x	(1/T)	(R <sup>2</sup> =	= 0.97)
log(P) <sub>(a=0.22)</sub>	= -	2.0415	-	2751.5	x	(1/T)	(R <sup>2</sup> =	= 1.00)
log(P) <sub>(a=0.44)</sub>	= -	5.1047	-	1745.5	x	(1/T)	(R <sup>2</sup> =	= 1.00)
<u>High density</u>	pol	yethyle	ne	:				

log(P) <sub>(a=0.067)</sub>	=	-	3.7042	-	2112.5	x	(1/T)	(R²	=	1.00)
log(P) <sub>(a=0.22)</sub>	=	-	5.4217	-	1509.5	x	(1/T)	(R <sup>2</sup>	=	1.00)
$log(P)_{(a=0.44)}$	=	-	8.8215	-	391.0	x	(1/T)	(R <sup>2</sup>	=	0.99)



Figure 21. Temperature dependence of the permeance of toluene in oriented polypropylene



Figure 22. Temperature dependence of the permeance of toluene in high density polyethylene











Figure 25. Temperature dependence of the permeance of toluene in Acrylic coated oriented polypropylene

<u>Glassine</u>:

log(P) <sub>(a=0.067)</sub>	= -	7.3468	-	1272.5	x	(1/T)	(R <sup>2</sup>	=	1.00)
log(P) <sub>(a=0.22)</sub>	= -	6.8968	-	1377.5	x	(1/T)	(R <sup>2</sup>	=	0.97)
log(P) <sub>(a=0.44)</sub>	= -	7.7433	-	1102.5	x	(1/T)	(R <sup>2</sup>	=	0.99)
<u>Saran coated</u>	ori	ented p	<u>01</u>	ypropyl	en	<u>e</u> :			
log(P) <sub>(a=0.067)</sub>	=	8.6543	-	6760.0	x	(1/T)	(R <sup>2</sup>	=	0.99)
log(P) <sub>(a=0.22)</sub>	=	3.2789	-	4951.0	x	(1/T)	(R <sup>2</sup>	=	0.99)
log(P) <sub>(a=0.44)</sub>	=	2.9934	-	4830.0	x	(1/T)	( R <sup>2</sup>	=	0.99)
Acrylic coat	<u>ed o</u>	riented	g	olyprop	yl(	<u>ene</u> :			
log(P) <sub>(a=0,44)</sub>	=	8.1508	-	6884.0	x	(1/T)	(R <sup>2</sup>	=	0.99)

These results are similar to the results of the ethyl acetate permeation studies, as the temperature dependency of the transport process associated with the respective barrier membranes, over the temperature range studied, follows well the Arrhenius relationship. The activation energy values for the permeation process  $(E_p)$ , determined from the slopes of the Arrhenius plots for the respective film samples, are summarized in Table 14.

The Arrhenius expression used to describe the permeance for both ethyl acetate and toluene as a function of temperature is typically applied over a temperature range above or below the glass transition temperature  $(T_g)$  of the polymer, but not within a temperature range which includes  $T_g$ . A straight line extrapolation typically cannot be made through  $T_g$  and a graphical analysis is expected to show a

Polymer		E(kcal/mole)	
Membranes	a = 0.067	a = 0.22	a = 0.44
ОРР	12.63	12.53	7.79
HDPE	9.45	6.90	1.90
Glassine	5.78	6.21	5.02
Saran OPP	34.00	34.10	35.41
Acrylic OPP	N/A <sup>(1)</sup>	N/A <sup>(1)</sup>	30.25
Metallized PET/OP	P N/A <sup>(1)</sup>	N/A <sup>(1)</sup>	N/A <sup>(1)</sup>

Table 14. Activation energy values for the permeation of toluene through polymer membranes.

(1). N/A denotes not available.

change in slope at the  $T_g$  (DeLassus, et al., 1988). This was assumed not to be a concern for the respective polymer structures evaluated in the present study, since the temperatures evaluated in this steady were well above the glass transition temperatures of polyethylene ( $T_g = -120^{\circ}C$ ), polypropylene ( $T_g = -19^{\circ}C$ ) and Saran ( $T_g = -19^{\circ}C$ ), while the  $T_g$  value of PET ( $T_g = 81^{\circ}C$ ) is above the maximum temperature evaluated in the present study.

Results involving studies designed to evaluate the activation energies of the respective test structures for the permeability of ethyl acetate and toluene (see Tables 8 and 14) showed that for both oriented polypropylene and polyethylene activation energy values decreased with an increase in vapor activity, while the activation energy values for the Saran and Acrylic coated polypropylene structures were not affected by permeant concentration levels.

While not fully understand, the concentration dependency of the activation energy for the polyolefins may be due in part to penetrant-induced relaxation effects occurring within the polymer matrix. Such relaxation effects would be most favorable above the glass transition temperature  $(T_g)$  of the polymer membrane, which is the case for PE and OPP. The absorption of organic vapors can result in polymer swelling and thus change the conformation of the polymer chains. These conformational changes are not instantaneous, but are controlled by the retardation times of polymer chains. If these times are long, stresses may be set up which relax slowly. Thus, the absorption and diffusion of organic vapors can be accompanied by concentration as well as time-dependent processes within the polymer bulk phase, which are slower than the micro-Brownian motion of polymer chain segments which promote diffusion (Mears, 1965).

There is precedence in the literature in support of such long time period relaxation effects occurring in polymer films above their glass transition temperature (Berens, 1977, and Blackadder and Keniry, 1973). Thus, there may be concentration dependent relaxation effects occurring during the diffusion of ethyl acetate and toluene through the polyolefin films investigated. Such relaxation processes which occur over a longer time-scale than diffusion may be related to a structural reordering of the free volume elements in the polymer. Thus, providing additional sites of appropriate size and frequency of formation, which promote diffusion and may account for the observed decrease in activation energy levels with increased vapor activity.

From this study, the metallized PET/OPP based structure was found to have the best organic vapor barrier properties among the six polymer membranes evaluated, when tested in film form. The order of barrier properties for the six polymer membranes evaluated, in order of decreasing barrier performance is as follows: Metallized PET/OPP, Acrylic OPP, Saran OPP, OPP, Glassine, and HDPE.

## Estimation of Permeance Values at Vapor Activity Levels Impractical to Measure Experimentally

Knowledge of the temperature and concentration dependence of the mass transfer process provided a means of estimating the permeance of the barrier membranes, at toluene concentration levels below which it would be impractical to measure experimentally. As discussed above, by application of the Arrhenius Equation, expressions describing the relationship between permeance and temperature were derived for the respective toluene vapor activity levels evaluated.

Based on the linear expressions derived, permeance values at ambient temperature (24°C) were estimated for each individual vapor activity. Table 15 summarizes the calculated permeance values at 24°C, for the respective packaging structures evaluated, at three vapor activity levels. Permeance values varied as a function of the vapor activity levels. The concentration dependency of the permeance values for the respective test structures at 24°C, is presented graphically in Figure 26, where the permeance values are plotted as a function of vapor activity. The relationship between the permeance constants and vapor activity for the respective films evaluated at 24°C can be

Table 15. Estimated permeance values of test packaging structures for toluene at 24°C (based on Arrehenius Equation).

Vapor activit	У				
	OPP	HDPE G	lassine s	Saran OPP	Acrylic OPP
0.067	3.42x10 <sup>-12</sup>	1.52 <b>x</b> 10 <sup>-11</sup>	2.35 <b>x</b> 10 <sup>-</sup>	<sup>12</sup> 7.71x10	<sup>-15</sup> N/A <sup>(1)</sup>
0.22	4.96x10 <sup>-12</sup>	3.12x10 <sup>-11</sup>	2.93x10 <sup>-</sup>	<sup>12</sup> 3.99x10	<sup>-14</sup> N/A <sup>(1)</sup>
0.44	1.05x10 <sup>-11</sup>	7.27x10 <sup>-11</sup>	3.52 <b>x</b> 10 <sup>-</sup>	<sup>12</sup> 5.66 <b>x</b> 10	<sup>-14</sup> 5.40x10 <sup>-16</sup>

<sup>(1)</sup>. N/A denotes not available.





described by the following expressions derived from a least squares fit.

OPP $P = 1.5885 \times 10^{-12} + 1.9415 \times 10^{-11}$  (a) $R^2 = 0.96$ HDPE $P = 1.7591 \times 10^{-12} + 1.5656 \times 10^{-10}$  (a) $R^2 = 0.98$ Glassine $P = 2.1809 \times 10^{-12} + 3.1049 \times 10^{-12}$  (a) $R^2 = 0.99$ Saran OPP $P = 3.9076 \times 10^{-15} + 1.2722 \times 10^{-13}$  (a) $R^2 = 0.92$ Acrylic OPPN/AMetallizedN/A

Assuming these expressions are valid over a broad range of vapor activity levels, permeance values at toluene vapor concentration, not measurable experimentally can be readily estimated by substitution into the appropriate equations. Permeance values estimated for vapor activity levels of a = 0.0015, 0.003, 0.005 and 0.01 at 24°C are summarized in Table 16.

Because of the broad range of temperature variation, statistical analysis for toluene permeability was based on two temperature levels, namely: 40°C and 50°C, and vapor activity levels of 0.067, 0.22 and 0.44 respectively, for the polymer structures: (i)OPP; (ii)HDPE; (iii)Glassine; and (iv)Saran OPP. The toluene permeance values for the respective polymer structures were analyzed by using a three-way factorial analysis. The analysis of variance (ANOVA) showed that the interaction between polymer

	Permeance (kg/m <sup>2</sup> .sec.Pa)								
Vapor activity	OPP	HDPE	Glassine	Saran OPP					
0.0015	$1.62 \times 10^{-12}$	$1.99 \times 10^{-12}$	2.19 x $10^{-12}$	4.10 x $10^{-15}$					
0.003	$1.65 \times 10^{-12}$	$2.23 \times 10^{-12}$	2.19 x $10^{-12}$	$4.29 \times 10^{-15}$					
0.005	$1.69 \times 10^{-12}$	$2.54 \times 10^{-12}$	$2.20 \times 10^{-12}$	4.54 x 10 <sup>-15</sup>					
0.010	1.78 x 10 <sup>-12</sup>	$3.32 \times 10^{-12}$	2.21 x $10^{-12}$	5.18 x 10 <sup>-15</sup>					

Table 16. Vapor activity dependence of the permeance for toluene at 24°C

membranes and temperature or vapor activity had significant differences. A detailed description of the statistical analysis performed is presented in Appendix IV. Based on the results of the analysis of variance, a comparison of the estimated permeance values at ambient temperature (24°C) was carried out. Estimated permeance values for the four polymer membranes were compared, with the oriented polypropylene (OPP) being assigned as the control group. The Dunnett's tvalue was calculated for the respective polymer membranes and the t-values compared with two-sided Dunnett's ttabulated values (Gill, 1987). A summary of the statistical comparison is presented in Table 17. The results showed highly significant differences between the control structure (OPP) and the other polymer structures at a 99% confidence level, except for the comparison group of OPP - Glassine at a vapor activity of 0.22.

Based on the statistical analysis, there are statistically significantly differences between the toluene barrier properties of the respective polymer structures, in flat sheet form. The four polymer structures considered for statistical comparison included:

- Control: Oriented polypropylene (OPP)
  - 1: High density polyethylene (HDPE)
    - 2: Glassine
    - 3: Saran coated OPP
- Table 17. Statistics comparison of toluene permeance for polymer structures

Comparison	Dunnett	Dunnett's t-value <sup>(1)</sup> (calculate)					
group	a = 0.067	a = 0.22	a = 0.44				
1 vs Control	6.93**	38.81**	17.42**				
2 vs Control	1.78	4.65**	6.45**				
3 vs Control	20.71**	162.73**	19.33**				

<sup>(1)</sup>. Difference between the tabulated Dunnett's t-value (twosided) and the calculated t-value. \* = significant at P  $\leq$  0.05; \*\* = significant at P  $\leq$  0.01.

 $t_{D(\alpha=0.05,m=3,\nu=24)} = 2.51$  $t_{D(\alpha=0.05,m=3,\nu=24)} = 3.22$ 

### Part II: Permeability of Packaged Confectionery Product Systems with a Cold Seal Closure

In this aspect of the study, six package/product systems and one organic vapor, at one vapor activity level were evaluated for packaged product permeation. Toluene was selected as the organic permeant. The average toluene vapor activity levels in the respective permeation chambers varied from 0.0013 to 0.0018, with an average of 0.0015 (0.15 ppm, g/mL). The average vapor activity levels and the specific product/package samples in each individual test chamber are as follows:

		Vapor ac	ti	<u>lvity</u>	Stored pro	oduct/pac	<u>ckage</u>	system
Chamber	1:	0.0018	±	0.0005	Saran OPP, Metallized	Acrylic PET/OPP	OPP,	and
Chamber :	2:	0.0017	±	0.0006	HDPE			
Chamber	3:	0.0014	±	0.0004	OPP			
Chamber ·	4:	0.0013	±	0.0004	Glassine			

The consistency of the vapor activity levels in the four test chambers, over the total storage time of 83 days, is shown graphically in Figures 27 and 28, where vapor activity is plotted as a function of run time. At predetermined time intervals, a series of individual packaged confectionery products were removed from the test chambers and the quantity of organic permeant sorbed by the chocolate determined.

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## Predicted Uptake Levels of Toluene Vapor by the Packaged Confectionery Product as a Function of Time (24°C)

Based on estimated permeance values for the respective barrier structures, at a vapor activity level of a = 0.0015, and the following assumptions:

• Hermetic seal integrity

- Total sorption of permeated toluene by the chocolate layer
- Vapor sorption is a function of permeation of toluene through the barrier structure

Sensory threshold levels of toluene in chocolate taken from Rüter (1992)

The time required for the packaged product to exceed the sensory threshold level, at the conditions of test (i.e.  $24^{\circ}C$ , a = 0.0015), for the respective package structures was estimated. A detailed example of the calculation is illustrated in Appendix V. This estimation is based on the assumption that mass transfer only results from permeability and not flow through microvoids within the seal area. The time required to reach or exceed the reported toluene threshold level in chocolate (20 ppm, wt/wt) (Rüter, 1992) for a chocolate product packaged in the respective test structures, was estimated as follows:

(i) Determine the quantity (Q) of permeant (i.e. toluene)
 to be absorbed by the product, equivalent to the
 literature threshold concentration level. This is based
 on the assumed threshold level of 20 ppm (wt/wt) and

the mass of the product. The product mass was taken to be only the chocolate coating, which was approximately 28 gram.

(ii) Based on the mathematical expressions describing the relationship between permeance and vapor activity, permeance values corresponding to a vapor activity of a = 0.0015 were derived. Substitute the maximum allowed permeant quantity (Q), the vapor activity level expressed as a partial pressure, and the corresponding permeance values into the following expression and solve for time (t):

$$t = \frac{Q}{A \times \Delta P} \times \frac{1}{P}$$
(20)

- where: t = time to sorb allowed permeant quantity (Q)
  A = package surface area (0.0122 m<sup>2</sup>)
  AP = vapor pressure or vapor concentration
  P = Permeance constant
- (iii) Based on the assumptions described above, the time required to reach or exceed the purported sensory threshold level of toluene in chocolate was estimated for the respective package structures at a toluene vapor activity of a = 0.0015. The predicted shelf life values are summarized in Table 18. For comparison, predicted shelf life values for toluene vapor activity levels of 0.003, 0.005 and 0.01 are also summarized in Table 18.

	Time (days)							
Toluene - vapor activity	OPP	HDPE	Glassine	Saran OPP				
0.0015 (P = 4.9 Pa)	67.3	54.6	49.8	26568.4				
0.003 (P = 9.8 Pa)	32.7	23.2	24.7	12381.7				
0.005 (p = 16.3 Pa)	19.4	12.9	14.9	7190.9				
0.01 (P = 32.5 Pa)	9.1	4.9	7.4	3153.0				

Table 18. Estimated uptake time to exceed toluene sensory threshold levels in a packaged chocolate product<sup>(1)</sup>

(1). Assumed toluene threshold level in chocolate is 20 ppm (wt/wt) from Ruter (1992).

# Experimental uptake levels of toluene vapor by the packaged confectionery product as a function of time (24°C)

The calculated toluene uptake levels, based on the estimated permeance constant, and the experimentally determined levels of sorbed toluene, quantified by the dynamic purge/trap - thermal desorption GC-MS procedure, are summarized in Tables 19 and 20. To better illustrate the relative uptake of toluene vapor by the respective product/package systems, the results are presented graphically in Figure 29, where total toluene uptake is plotted as a function of storage time for the individual package systems. As shown, all six package/product systems had detectable levels of toluene in the chocolate product.

The statistical analysis for toluene uptake by chocolate was based on a completely randomized design (CRD). The toluene uptake values for the respective package/product systems were analyzed using a two-way analysis of variance (ANOVA) (Table 21). The MSTAT (ver 4.0, 1987) microcomputer statistical program was used for calculation. Significant differences between mean squares were evaluated at the 95% confidence level ( $P \le 0.05$ ).

The toluene uptake values for the six package/product systems were compared, with the oriented polypropylene (OPP) package/product system being assigned as the control group. The Dunnett's t-value was calculated for the respective package/product systems and the t-values compared with two-

Table 19. Total toluene uptake by chocolate for OPP, HDPE and Glassine based package structures as a function of time (Experimental and calculated data)

		Total Quantity (g) x 10						
Time	(days)	OPP		HDPE		Glassine		
	_	Exp <sup>(1)</sup>	Cal <sup>(2)</sup>	Exp	Cal	Exp	Cal	
6		0.4	0.5	3.2	0.6	4.8	0.7	
14		0.8	1.2	1.8	1.4	7.6	1.6	
20		1.3	1.7	1.6	2.1	12.0	2.3	
27		2.3	2.3	4.3	2.8	6.5	3.0	
43		3.3	3.6	4.9	4.4	5.4	4.8	
54		4.5	4.5	5.3	5.5	5.6	6.1	
62		1.9	5.2	6.1	6.4	3.2	7.0	
76		5.9	6.3	11.9	7.8	9.2	8.6	
83		7.3	6.9	10.1	8.5	16.3	9.4	

 $M_{abal}$   $(\alpha) = 10^{-4}$ 

<sup>(1)</sup>. Experimental data are the average of duplicate samples. <sup>(2)</sup>. Calculated data based on the estimated permeance constant.

Table 20. Total toluene uptake by chocolate for Saran coated OPP, Acrylic coated OPP and Metallized PET/OPP based package structures as a function of time (Experimental and calculated data)

	Total Quantity (g) $\times 10^{-4}$						
Time (days)	Saran OPP		Acryl	Acrylic OPP		Met PET/OPP	
	Exp <sup>(1)</sup>	Cal <sup>(2)</sup>	Exp	Cal <sup>(3)</sup>	Exp	Cal <sup>(3)</sup>	
11	0.5	0.002	0.2	-	0.3	-	
19	1.4	0.004	0.6	-	0.4	-	
35	2.7	0.007	0.2	-	0.4	-	
56	2.7	0.012	0.9	-	2.9	-	
79	3.1	0.017	3.5	-	2.2	-	

<sup>(1)</sup>. Experimental data are the average of duplicate samples. <sup>(2)</sup>. Calculated data based on the estimated permeance constant.

(3). No estimated permeance constant available for calculation.





Source	df	Sum of Square	Mean Square	F value <sup>(1)</sup>	
Total	47	512.36			
Film	5	178.04	35.61	10.13*	
Time	3	155.00	51.67	14.70*	
Film x Time	15	94.94	6.33	1.80	
Error	24	84.37	3.52		

Table 21. Analysis of variance (ANOVA) for toluene uptake for product/package systems

<sup>(1)</sup>. F table value:  $F_{0,05(5,24)}=2.62$ ;  $F_{0.05(3,24)}=3.01$ ;  $F_{0.05(15,24)}=2.11$ \* = significant difference at p ≤ 0.05 sided Dunnett's t-tabulated values (Gill, 1987). Table 22 shows the comparison of the various package/product systems with the control group. The detailed statistical analysis is presented in Appendix VI.

A statistically significant difference between the control system (i.e. OPP/product) and the comparison product/package system at the 95% confidence level is indicated for cases where the Dunnett's calculated t-values exceeds the Dunnett's table t-value.

Based on the statistical analysis, there was no statistically significant difference between the performance of the control package system and the comparison package system with respect to toluene uptake over the storage time, except for the Glassine/package system. Based on statistical analysis of the toluene permeance values for (i) Oriented Polypropylene; (ii) High Density Polyethylene; (iii) Glassine; and (iv) Saran OPP, determined on flat sheet stock, a statistically significant difference between the toluene barrier properties of the respective film structures was found. These findings indicate that the barrier performance of the film structures showed significant differences. However, as indicated above, the films barrier characteristics are negated following their fabrication to a package structure. This suggests that toluene uptake by the packaged product is the result of toluene ingression through the cold seal area as the predominant mechanism and not the

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Control: OPP/product

- 1 : HDPE/product
- 2 : Glassine/product
- 3 : Saran OPP/product
- 4 : Acrylic OPP/product
- 5 : Met PET/product

Table 22. Statistical comparison of toluene uptake for six package/product systems

Comparison group	Dunnett's t-value <sup>(1)</sup> (calculate)
1 vs Control	2.142
2 vs Control	3.445*
3 vs Control	1.290
4 vs Control	1.975
5 vs Control	1.826

<sup>(1)</sup>. Dunnett's t-table value:  $t_{p,0.05,m=5,\nu=24} = 2.70$ \* = significant difference at p ≤ 0.05 primary result of diffusion through the package structure. This hypothesis is supported by the fact that the metallized PET/OPP based packaging system showed comparable levels of toluene uptake by the product, as compared with the polypropylene package system, while no measurable rate of permeation was observed for the metallized PET/OPP flat sheet structure.

Based on the assumptions described in the Section "Predicted Uptake Levels of Toluene Vapor by the Packaged Confectionery Product as a Function of Time (24°C)", the calculated values of total quantity of toluene uptake for the respective product package systems at 24°C and a = 0.0015 were obtained and compared to the experimentally determined values. The results are summarized in Table 19 and 20, respectively. For better illustration, the experimental and calculated toluene uptake values obtained for the OPP, HDPE, Glassine and Saran/OPP package systems are presented graphically in Figures 30 - 33, respectively.

As shown, for the OPP, HDPE and Glassine package systems, the calculated toluene uptake values were similar to those determined experimentally, while for the Saran/OPP package system, the calculated (estimated) toluene uptake values were significantly higher than the values determined experimentally. With respect to the Saran/OPP package system and the lack of agreement between the estimated and experimentally determined toluene uptake values; like any



Figure 30. Comparison of estimated and experimental values for toluene uptake by the OPP/product system at a = 0.0015 (24°C)













other predictive model, the validity of the estimation method will only be as accurate as the assumptions made in developing the model. Implicit in the estimation method used to calculate toluene uptake levels is the assumption that the package system is hermetically sealed and that diffusion through the package structure, as described by Fick's First and Second Laws, is the principle mechanism resulting in toluene ingression. Since the calculated toluene uptake values for the Saran/OPP package system were significantly higher than the uptake values determined experimentally, the assumption that vapor sorption is a function of permeation of toluene through the barrier structure is not valid. Thus, as indicated above, a mechanism involving flow or transfer through microvoids in the cold seal closure area is the predominant mechanism of toluene ingression and not the result of diffusion through the package structure.

### Part III. Seal Integrity Evaluation of the Cold Seal Closure for Packaged Confectionery Systems

The seal integrity tests were performed with a Nikka Packaging Leak Tester (PLT-3501) (Nikka Densok U.S.A., Inc., Lakewood, CO). The average leak test values obtained for the respective packages provided are summarized in Table 23. In performing the leak tests, the Nikka Packaging Leak Tester Model PLT-3501 was found to have limitations when evaluating package systems, such as the Glassine structure, which had

Table 23. The average values for leak testing by using Nikka Packaging Leak Tester (PLT-3501)

 Film Structures	Leak	test <sup>(1)</sup>	(mm-H <sub>2</sub> O)
OPP		25.4 ±	6.2
HDPE		32.4 ±	6.1
Glassine <sup>(2)</sup>			
Saran OPP		25.0 ±	6.2
Acrylic OPP		21.9 ±	3.3
Metallized PET/OPP		24.3 ±	3.2

- (1). Average for each product/packaging system, based on 20 replication testing samples.
   (2). Glassine packages exhibited very poor seal properties as
- (2). Glassine packages exhibited very poor seal properties as well as poor mechanical characteristic. The values of glassine package system were found over the limitation of leak tester machine.

serious leakage or seal integrity problems. For package systems with poor seal quality, which could be seen by visual inspection, the leak tester output gave values indicative of a well sealed package system. Therefore, prior to preforming a seal integrity test on the package system, all packages were examined visually for the presence of major defects in the seal area.

In this study, it was found that a large number of the Glassine packages had serious visually observed structural defects in both the seal area and the package itself, although the test output gave values indicative of a well sealed package. Even when an effort was made to leak test Glassine packages which showed no visual indication of structural defects, it was evident that under the applied vacuum, there was no pressure differential created between the package internal and external environments, which is the principle upon while the test is based. Because of this finding, the leak test values for the glassine package are not presented in Table 23. The results obtained from evaluating the integrity of the glassine packages were consistent with the finding of the toluene uptake studies, in that the glassine package system showed the highest level of toluene ingression and was the package system showing the poorest seal quality.

The various other package structures, showed no visible evidence of structural or seal defects and the leak test

values for the OPP, HDPE, Saran OPP, Acrylic OPP and Metallized PET/OPP package systems were assumed to be reliable and indicative of the seal integrity of the respective packages. As shown in Table 23, the leak test values determined for OPP, Saran OPP, Acrylic OPP and Metallized PET/OPP package systems were similar, while the value for the HDPE package system was higher.

Since the leak test values are inversely related to seal quality, the higher value obtained for the HDPE package system is representative of a package with a lower seal integrity, as compared to the other package systems evaluated. The results obtained from the package integrity studies for the OPP, Saran OPP, Acrylic OPP, Metallized PET/OPP and HDPE package systems were consistent with the finding of the toluene ingression studies.

As described in the Materials and Methods Section, leak test values for packaged samples removed from the permeation test chambers were determined directly upon their removal and prior to opening for product sampling and analysis of sorbed toluene. Summarized in Appendix VII are the seal integrity values obtained for the packaged samples and the corresponding toluene uptake levels as a function of storage time. As shown in Appendix VII, in general, package systems exhibiting leak test values above the mean and standard deviation for the specific package structures showed higher toluene ingression levels, as compared to replicate samples

which gave leak test values within the expected range. These finding are consistent with the hypothesis that a mechanism involving flow or transfer through microvoids in the cold seal closure is the predominant mechanism of toluene uptake by the packaged product.

#### SUMMARY AND CONCLUSION

For a series of commodity films, permeance values were obtained from permeability studies based on an isostatic procedure utilizing the MAS Technology Model 2000 Permeability Test System. Parameters evaluated included vapor activity and temperature. For each temperature, three vapor activity levels were evaluated. Permeability studies were carried out at three temperatures to allow evaluation of the Arrehenius relationship. In addition, the respective commodity films were used to package a confectionery product via a cold seal closure technology. To evaluate the integrity of the cold seal closure, with respect to organic vapor ingression, package permeability studies were carried out. Toluene was selected as the organic permeant. Package permeability was evaluated based on the level of permeated vapor sorbed by the packaged confectionery product.

The results of this study are summarized below:

 The temperature dependency of the transport process associated with the respective barrier membranes, over the temperature range studied, was found to follow well the Arrehenius relationship.

2. From this study, the metallized PET/OPP based structure

was found to exhibit the best organic vapor barrier properties among the six polymer membranes evaluated, when tested in film form. Based on statistical analysis, there are statistically significant differences between the toluene barrier properties of the respective polymer structures, in flat sheet form. The barrier properties of the six polymer membranes evaluated, in order of decreasing barrier performance, are as follows: Metallized PET/OPP, Acrylic OPP, Saran OPP, OPP, Glassine, and HDPE.

- 3. By application of the Arrehenius Equation, expressions describing the relationship between permeance and temperature were derived for the respective toluene vapor activity levels evaluated. Based on the linear expressions derived, permeance values at ambient temperature (24°C) were estimated for the respective vapor activity levels evaluated. Permeance values varied as a function of the vapor activity levels. The relationship between the permeance constants and vapor activity for the respective films evaluated at 24°C was described by mathematic expressions derived from a least squares fit.
- 4. Based on statistical analysis, there was no statistically significant difference between the performance of the control package system and the comparison package systems, with respect to toluene uptake, except for the

Glassine/package system. The oriented polypropylene (OPP) package/product system was assigned as the control group. Based on statistical analysis of the toluene permeance values for (i) polypropylene; (ii) polyethylene; (iii) Glassine; and (iv) Saran OPP, determined on flat sheet stock, a statistically significant difference between the toluene barrier properties of the respective film structures was found. These findings indicate that the barrier performance of the film structures showed significant differences, when evaluated as flat sheet stock. This suggests that toluene uptake by the packaged product is the result of toluene ingression through the seal area as the predominant mechanism, and not the primary result of diffusion through the package structure. This hypothesis is supported by the fact that the metallized PET/OPP based packaging system showed comparable levels of toluene uptake by the product, as compared with the polypropylene package system, while no measurable rate of permeation was observed for the metallized PET/OPP flat sheet structure.

#### FUTURE STUDIES

Since cold seal closures are widely employed in food packaging applications, evaluation of seal performance or seal integrity for the cold seal closure warrants further investigation. Based on the results of the present study, other issues that have potential for further investigation include:

- Identity and evaluate alternate adhesive formulations, which have utility as a cold seal pattern adhesive, to be used in formation of a cold seal closure. Also consider increasing the jaw pressure or jaw configuration in effecting the cold seal closure.
- 2. Future studies may also include seal performance evaluation, with other permeants, such as water vapor, oxygen and additional organic vapors to develop a better understanding of the seals overall vapor barrier performance. Studies may also include determination of seal properties, such as seal strength, or peel strength.
- 3. This study has focused on a packaged confectionery product and the extent of toluene vapor ingression and

subsequent sorption by the product. Other product/package systems may also be of importance and warrant investigation. Further, the cold seal integrity, as a function of temperature, may also effect the barrier performance of the package system. This can be very important for some packaged frozen food products. APPENDICES





Figure 34. Calibration curve for Ethyl Acetate by GC - FID

Quantity (g)	Area Response
0	0
8.94 x 10 <sup>-9</sup>	5746
17.88 x 10 <sup>-9</sup>	14157
35.76 x 10 <sup>-9</sup>	35158



Figure 35. Calibration curve of Toluene by GC - FID

Quantity (g)	Area Response
0	0.0
$3.46 \times 10^{-9}$	42712.0
8.67 x 10 <sup>-9</sup>	124476.5
$17.34 \times 10^{-9}$	274730.3
34.68 x 10 <sup>-9</sup>	502068.0

Appendix II



Figure 36. Calibration curve of Toluene by GC/MS -Thermal desorption unit (SIM Mode)

Quantity (g)	Area Response
0	0
3.46 x 10 <sup>-9</sup>	1051470
8.67 x 10 <sup>-9</sup>	2512015
17.34 x 10 <sup>-9</sup>	5378503
34.68 x 10 <sup>-9</sup>	9167813

# Appendix III

Standard Toluene Mass Spectrum



Species: Toluene, Formula: C7H8 Contributor: D.HENNEBERG, MAX-PLANCK INSTITUTE, MULHEIM, WEST GERMANY

ID#	4614	(	CAS#	108-8	8-3		EPA#	61278		MW 92	Qual	Idx 812
Ten	Largest	Ma	BSes	and A	bund	ances						
91	92		39		65	51		63	50	27	93	90
999	725		204	4	136	10	9	105	74	63	53	51
				•	100	10	-	105	<i>,</i> .	•••		
56	Masses	and	Abur	ndance	s							
2	2 5	43	22	63	105	83	1					
12	2	44	8	64	23	84	3					
13	3	45	44	65	136	85	8					
14	5	46	29	66	18	86	in					
15	24	50	74	67	1	87	6					
25	3	51	100	60	1	07	1					
26	30	57	26	20	1	00	10					
20		52	20	/0	1	89	40					
21	03	53	12	71	1	90	51					
28	6	55	4	73	3	91	999					
29	3	56	2	74	13	92	725					
39	204	57	2	75	8	93	53					
40	23	60	3	76	5	94	1					
41	24	61	25	77	14		-					
42	3	62	50	79	1							
		52	50	Graph	ics,	List,	Str	ucture,	Names,	Quit		

## Appendix IV

The analysis of variance (ANOVA) table of permeance for toluene using the MSTAT (ver 4.0, 1987) microcomputer statistical program.

Table	24.	Analysis	of	variance	for	toluene	permeance
		constant					

Source of variance	Degree of freedom (df)	Mean Square	F value <sup>(1)</sup>
Polymer membranes (P)	3	10.426	4401.787*
Temperature (T)	1	0.917	386.964*
Vapor activity	(VA) 2	0.330	139.188*
РхТ	3	0.198	83.498*
P x VA	6	0.016	6.778*
T x VA	2	0.010	4.148*
P x T x VA	6	0.005	2.022
Error	24	0.002	

(1). F-table value at P  $\leq 0.05$ :  $F_{1,24} = 4.26$ ;  $F_{2,24} = 3.40$  $F_{3,24} = 3.01$ ;  $F_{6,24} = 2.51$ \* = significant difference at p  $\leq 0.05$  Significant differences between film composition, temperature and vapor activity levels were evaluated at the 95% confidence level ( $P \le 0.05$ ). The interaction between the polymer membranes and the temperature or vapor activity levels showed significant differences. The following t-test compares the respective polymer structures with OPP assigned as the control structure.

For each of the comparison groups the t-value was calculated from the linear Arrhenius Relationship by substitution into the following expression:

For 
$$T_1F_1$$
:  
 $\hat{Y}_1 = a_1 + b_1 X_L$   
 $T_2F_2$ :  
 $\hat{Y}_2 = a_2 + b_2 X_L$   
 $T_3F_3$ :  
 $\hat{Y}_3 = a_3 + b_3 X_L$   
 $t_{1,2} = \frac{\hat{Y}_1 - \hat{Y}_2}{\operatorname{se}(\hat{Y}_1 - \hat{Y}_2)} = \frac{\hat{Y}_1 - \hat{Y}_2}{[\operatorname{se}(\hat{Y}_1)^2 - \operatorname{se}(\hat{Y}_2)^2]^{1/2}}$ 

$$t_{1,3} = \frac{\hat{y}_1 - \hat{y}_3}{\sec(\hat{y}_1 - \hat{y}_3)} = \frac{\hat{y}_1 - \hat{y}_3}{[\sec(\hat{y}_1)^2 - \sec(\hat{y}_3)^2]^{1/2}}$$
$$var(\hat{u}_{y|x}) = \sigma^2 \left[\frac{1}{n} + \frac{(x^* - \bar{x})^2}{S_{xx}}\right]$$

 $se = [var(\hat{u}_{y|x})]^{1/2}$ 

where:  $X_1 = 1/T$  value at room temperature (24°C)

 $\hat{y}_1 = \log(P)$  value at room temperature for first polymer structure

se = standard error for 
$$\hat{y}_n$$

### Appendix V

Estimation of toluene uptake by the packaged confectionery product by a permeation mechanism.

$$P = \frac{Q}{A \times t \times \Delta P}$$

$$Q = Quantity \text{ permeated (kg) in time = t}$$

$$A = Package \text{ surface area} = 0.0122 \text{ m}^2$$

$$\Delta P = Vapor \text{ pressure at } a = 0.003, P = 9.8 \text{ Pa}$$

For shelf life estimation assume 20 ppm (g/g) as sensory threshold and total uptake is in chocolate layer. For product assumed chocolate layer = 28 g.

$$20 \times 10^{-6} (g/g) \times 28(g) = 560 \times 10^{-6} (g)$$
$$= 0.56 \times 10^{-6} (kg)$$

Time to equal or exceed concentration of 20 ppm (g/g) based on permeability for oriented polypropylene wrapper (assumes only ingression of toluene vapor is by permeation, no macrochannels through seal area, seal is hermetic).

$$P = \frac{Q}{A \times t \times \Delta P} \quad \text{or} \quad t = \frac{Q}{A \times P} \times \frac{1}{P}$$

$$t = \frac{0.56 \times 10^{-6} \text{ kg}}{0.0122 \text{ m}^2 \times 9.8 \text{ Pa}} \times \frac{1 \text{ m}^2.\text{sec.Pa}}{1.6 \times 10^{-12} \text{ kg}}$$
$$= 2.9274 \times 10^6 \text{ sec}$$

$$t_{(days)} = 2.9274 \times 10^{6} \sec x - \frac{1 \min 1 hr}{60 \sec 60 \min 24 hr} \times \frac{1 \dim 1}{24 hr}$$
  
= 34 days

To estimate quantity uptake as a function of time for oriented polypropylene at a = 0.003 and  $24^{\circ}C$ Selected time = 6 days

6 days x  $\frac{24 \text{ hr}}{\text{day}}$  x  $\frac{60 \text{ min}}{\text{hr}}$  x  $\frac{60 \text{ sec}}{\text{min}}$  = 518,400 sec P =  $\frac{Q}{A \text{ x t x } \Delta P}$ Q (kg) =  $\frac{1.65 \text{ x } 10^{-12} \text{ kg}}{\text{m}^2.\text{ sec. Pa}}$  x 518400 sec x 0.0122 m<sup>2</sup> x 9.8 Pa = 1.02 x 10<sup>-7</sup> kg = 1.02 x 10<sup>-4</sup> g

### Appendix VI

The statistical calculation for the comparison of toluene uptake by the packaged confectionery product

From the ANOVA Table (Table 21), no significant differences were found for the interaction between film and time. It only shows that there are statistically significant differences for the individual factors, which are film types and time. Therefore, the comparison group does not need to consider each individual sampling time, but rather the average toluene uptake data for each polymer membrane as the comparison group.

For each of the comparison groups, the Dunnett's tvalue was calculated by substitution into the following mathematic expression:

$$t = \frac{Y_i - Y_c}{(2MS_E/8)^{1/2}}$$

where: Y<sub>i</sub> = the mean average for the comparison package/product system, respectively.

- Y<sub>c</sub> = the mean average for the control package/product system, respectively.
- $MS_{F} = error mean square$

### Appendix VII

Table	25.	Leak test	values and	corresponding toluene	uptake
		levels as	a function	of time for OPP, HDPE	and
		Glassine 1	based packag	jing structures	

		OPP		HDPE	Glassine		
Time (day)	Leak test	Toluene uptake <sup>(2)</sup> (gram)	Leak test	Toluene uptake <sup>(2)</sup> (gram)	Leak test	Toluene uptake <sup>(2)</sup> (gram)	
6	84	0.57x10 <sup>-4</sup>	42	4.84x10 <sup>-4</sup>	-	8.60x10 <sup>-4</sup>	
	29	0.23x10 <sup>-4</sup>	22	1.46x10 <sup>-4</sup>	-	1.08x10 <sup>-4</sup>	
14	28	0.82x10 <sup>-4</sup>	28	1.96x10 <sup>-4</sup>	-	14.6x10 <sup>-4</sup>	
	27	0.78x10 <sup>-4</sup>	29	1.61x10 <sup>-4</sup>	-	0.63x10 <sup>-4</sup>	
20	25	$1.60 \times 10^{-4}$	36	$1.74 \times 10^{-4}$	-	20.9 <b>x</b> 10 <sup>-4</sup>	
	14	$1.02 \times 10^{-4}$	69	$1.44 \times 10^{-4}$	-	3.02x10 <sup>-4</sup>	
27	38	3.08x10 <sup>-4</sup>	39	2.57x10 <sup>-4</sup>	-	2.88x10 <sup>-4</sup>	
	29	$1.60 \times 10^{-4}$	49	5.99x10 <sup>-4</sup>	-	10.1x10 <sup>-4</sup>	
43	19	0.92x10 <sup>-4</sup>	90	5.73 <b>x</b> 10 <sup>-4</sup>	-	6.03x10 <sup>-4</sup>	
	37	5.70x10 <sup>-4</sup>	54	3.96x10 <sup>-4</sup>	-	4.76x10 <sup>-4</sup>	
54	28	4.07x10 <sup>-4</sup>	65	$5.74 \times 10^{-4}$	-	5.54x10 <sup>-4</sup>	
	90	4.92x10 <sup>-4</sup>	53	4.90x10 <sup>-4</sup>	-	5.73x10 <sup>-4</sup>	
62	68	$0.78 \times 10^{-4}$	36	$7.10 \times 10^{-4}$	-	5.25x10 <sup>-4</sup>	
	60	2.94x10 <sup>-4</sup>	35	5.06x10 <sup>-4</sup>	-	1.06x10 <sup>-4</sup>	
76	36	7.39x10 <sup>-4</sup>	28	$12.4x10^{-4}$	-	14.2x10 <sup>-4</sup>	
	33	4.36x10 <sup>-4</sup>	64	$11.4x10^{-4}$	-	4.24x10 <sup>-4</sup>	
83	58	$7.20 \times 10^{-4}$	128	10.6x10 <sup>-4</sup>	-	13.2x10 <sup>-4</sup>	
	64	$7.32 \times 10^{-4}$	35	11.1x10 <sup>-4</sup>	-	19.4x10 <sup>-4</sup>	

 (1). Unit of leak test is in mm-H<sub>2</sub>O.
 (2). Unless otherwise stated values are the average of replicate analysis from individual product/package samples.

Table 26. Leak test values and corresponding toluene uptake levels as a function of time for Saran OPP, Acrylic OPP and Metallized PET/OPP based packaging structures

	Sar	an OPP	Acry	vlic OPP	Met PET/OPP	
Time (day)	Leak test	Toluene uptake <sup>(2)</sup> (gram)	Leak test	Toluene uptake <sup>(2)</sup> (gram)	Leak test	Toluene uptake <sup>(2)</sup> (gram)
11	26	$0.62 \times 10^{-4}$	23	$0.13 \times 10^{-4}$	23	0.21x10 <sup>-4</sup>
	47	$0.44 \times 10^{-4}$	28	0.17 <b>x</b> 10 <sup>-4</sup>	31	0.36x10 <sup>-4</sup>
19	45	1.66x10 <sup>-4</sup>	22	$0.31 \times 10^{-4}$	27	0.66x10 <sup>-4</sup>
	30	$1.17 \times 10^{-4}$	28	0.93x10 <sup>-4</sup>	31	0.05x10 <sup>-4</sup>
35	31	$1.14 \times 10^{-4}$	18	$0.21 \times 10^{-4}$	22	0.37x10 <sup>-4</sup>
	50	4.31x10 <sup>-4</sup>	22	$0.28 \times 10^{-4}$	32	0.40x10 <sup>-4</sup>
56	29	0.52 <b>x</b> 10 <sup>-4</sup>	27	1.39x10 <sup>-4</sup>	33	0.53x10 <sup>-4</sup>
	35	4.89x10 <sup>-4</sup>	20	0.33x10 <sup>-4</sup>	52	5.18x10 <sup>-4</sup>
79	27	2.44x10 <sup>-4</sup>	35	3.67 <b>x</b> 10 <sup>-4</sup>	25	0.43x10 <sup>-4</sup>
	25	3.70x10 <sup>-4</sup>	24	3.39x10 <sup>-4</sup>	53	4.01x10 <sup>-4</sup>

<sup>(1)</sup>. Unit of leak test is in  $mm-H_2O$ . <sup>(2)</sup>. Unless otherwise stated values are the average of replicate analysis from individual product/package samples.

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