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The Effect Of Temperature And Sorbed Water On The Permeation Of Acetone Vapor Through Amorphous Polyamide Film

presented by

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M.S. degree in Packaging

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# THE EFFECT OF TEMPERATURE AND SORBED WATER ON THE PERMEATION OF ACETONE VAPOR THROUGH AMORPHOUS POLYAMIDE FILM

by

Suresh Nagaraj

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# A THESIS

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

MASTER OF SCIENCE

School of Packaging

#### ABSTRACT

# THE EFFECT OF TEMPERATURE AND SORBED WATER ON THE PERMEATION OF ACETONE VAPOR THROUGH AMORPHOUS POLYAMIDE FILM

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#### Suresh Nagaraj

The permeability of acetone vapor through amorphous polyamide films, under both dry and humidified conditions, was determined utilizing an isostatic test procedure. The test system which was designed and assembled, allowed permeability studies to be carried out as a function of temperature, vapor concentration and water activity.

Experiments were conducted at 60, 75, 85 and  $95^{\circ}$ C, at a constant penetrant concentration of 290 ppm (wt/v). For studies carried out under humidified conditions, the relative humidity of the penetrant stream was maintained at 70% R.H., measured at 23°C. The results of this study showed a temperature dependency for the permeation of acetone vapor through amorphous nylon, over the temperature range studied. Sorption of water vapor resulted in an increase in permeability, as compared to dry conditions, with an increase of approximately 1.5 times being observed.

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Dedicated to my grandfather, E.B.P. Haran.

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## NOMENCLATURE

<u>Symbol</u>	
a	calibration factor to convert detector response to units of mass of permeant / unit of volume.
Α	area
Ъ	driving force given by the concentration or partial pressure gradient
c	vapor concentration
°,	concentrarion at $x - L$ in equilibrium with the penetrant flow
° <sub>1</sub>	concentration of permeant in the face of the film in contact with the permeant
°2	concentration of permeant in the face of the film in contact with low permeant vapor concentration
D	differential diffusion coefficient
f	flow rate of sweep gas
G	response units from detector output at steady state
gms	grams
L	thickness of film
m	meters
mils	0.001 inch
mmHg	millimeters of Mercury
Р	rate of permeation or flux
Р <sub>1</sub>	partial pressure of permeant on high pressure side
P <sub>2</sub>	partial pressure of permeant on low pressure side
Q	total amount of permeant
R.H.	relative humidity
S	solubility coefficient
· t	time

t 1/2	time required to reach a rate of transmission equal to half the steady state value.
т <sub>g</sub>	glass transition temperature
x	distance travelled by permeant
$(\Delta M/\Delta t)$	transmission rate of the penetrant at time t
$(\Delta M/\Delta t)$	$\infty$ transmission rate of penetrant at steady state

# POLYMERS

Co-VDC vinylidene chloride copolymer

- EVOH Ethylene vinyl alcohol
- PE Polyethylene

PET Poly(ethylene) terephthalate

PVDC poly vinylidene chloride

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#### INTRODUCTION

Polymeric packaging materials are increasingly put to use in the areas of food, beverage and pharmaceutical packaging, due to considerations of convenience, economy and an increasing variety to meet specific needs. Estimates for future usage show continued growth. Knowledge of the transmission rates of gases and organic vapors through polymers play an important role in the selection of an appropriate packaging system.

It is of importance to determine the permeability of a polymeric packaging system used for food products, as the loss of specific aroma constituents, or gain of off odours, due to diffusion, can result in the loss of product quality and shelf life. Polyamides ( Nylons ) have gained importance in food packaging because of their aroma barrier properties. While there is data on the diffusion of oxygen and water vapor through polyamides, there exists a limited amount of data on the diffusion of organic penetrants in polyamides, with no data reported for the permeation of organic vapors through amorphous nylon, since it is a relatively new material in the market.

The purpose of this study was to develop a more operator-independent method to measure the permeation of organic vapors through amorphous nylon film, at different temperatures.

The specific objectives of this study wore as follows :

- Assemble a continuous-flow, automatic sampling system to measure the diffused permeant.
- 2. Carry out permeation experiments on the acetone vapor amorphous

nylon film system, at different temperatures.

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3. Evaluate the effect of sorbed water vapor on the permeation of the acetone vapor - amorphous nylon film system.

#### LITERATURE REVIEW

# The Importance of Studying the Permeation of Organic Vapors Through Polymeric Packaging Materials

The shift from absolute barrier packaging systems, such as metal cans and glass bottles, to semi-permeable plastic packages has created a need to develop a better understanding of the mass transfer properties of polymeric packaging systems to organic vapors and aroma constituents.

When selecting a package system for a food product, it is important to know the product's characteristics and what effect the gain or loss of organic vapor, due to sorption and permeation during storage and distribution, has on product quality.

The gain or loss of organic vapors by a product in a package occurs by two mechanisms: the mass transfer or permeation of the vapor into or out of the package, and the sorption or desorption of organic volatiles by the packaging material. This study deals with the measurement of mass transfer or permeation of an organic vapor through a polymeric packaging film.

# The Permeation Mechanism for the Transfer of Organic Vapors Through Polymers

Mass transport through polymeric materials occurs by a diffusion process (Lebovitz, 1966). Diffusion is the process by which matter is

transported from one part of a system to another as a result of random molecular motion (Crank, 1975). For permeation to occur, the permeant molecule has to undergo these three steps in succession:

(i). Dissolution of the penetrant molecule into the surface of the polymeric film;

(ii) Diffusion of the penetrant molecule through the polymer matrix; and (iii) desorption of the penetrant molecule from the other surface of the film (Lebovitz, 1966).

The sorption or dissolution process depends on the chemical nature of the penetrant molecule and the polymer.

The diffusion process is able to take place because polymer molecules have a random kinetic agitation or heat motion. The polymer chains undergo vibrational, rotational and translational motions that continually create "holes" in the polymer matrix. The penetrant molecules are able to move through the "holes" in the direction of the concentration gradient. The rate of diffusion depends on the temperature, chemical composition and morphology of the polymer and the concentration gradient of the permeating molecule across the polymer (Mears, 1965a).

Small penetrant gas molecules such as oxygen, nitrogen and carbon dioxide do not interact with the polymer matrix, as their kinetic agitations are rapid compared to those of the polymer chains. The rate of diffusion of these molecules is controlled by their agitation which is governed by the energy in the systems (Mears, 1965a). The permeation of organic molecules is more complicated, as it depends on the motion of both the polymer and the penetrant molecule. If the organic molecule is

soluble in the polymer, the polymer can undergo swelling, resulting in changes in the physical characteristics of the polymer. Organic molecules sorbed by polymers act as plasticizers, lowering the glass transition temperature and increasing the polymer free volume, which further increases plasticization and swelling (Mears, 1965b), thereby resulting in an increase in diffusion and permeability.

In a permeation experiment, the penetrant flow or the total amount flowed through a polymeric film is measured as a function of time under a constant concentration gradient (Fujita, 1961).

The permeability coefficient  $(\overline{P})$  is the steady state rate of transfer of a substance through a material, and is expressed as the quantity of permeant that passes through a material of unit thickness, per unit time, per unit surface area for a given concentration or pressure gradient of the permeant (eg. gms. mils / m<sup>2</sup>. day. mmHg).

#### Permeability Theory for Organic Vapor permeation in a sheet

When a polymer is in contact with an organic vapor on one side, the organic vapor is sorbed into the polymer. Then, as the concentration gradient changes across the polymer, the organic vapor moves across the polymer and desorbs from the other surface. After a given period of time, a steady state rate of flow is reached, provided the pressure differential across the polymer is maintained constant. The rate of permeation (P) or flux is defined as the amount of penetrant passing, during unit time, through a surface of unit area normal to the direction of flow (Rogers, 1964):

$$\mathbf{P} = \mathbf{Q} / \mathbf{A} \mathbf{t} \tag{1}$$

where Q is the total amount of penetrant which has passed through area (A) during time (t).

Summarizing from Rogers (1964):

Consider a unit area of film L (cms) thick exposed to a penetrant at partial pressure  $p_1$  on one side and a lower pressure  $p_2$  on the other side. The concentration of the penetrant in the first layer of film (x = 0) is  $c_1$  and in the last layer (x = L) is  $c_2$ . When the rate of permeation through a plane at a distance x from the high pressure surface is P, the rate through a plane at a distance x + dx will be P +  $(\delta p/\delta x)$  dx. Therefore, the amount retained per unit volume of polymer is equal to the rate of change of concentration with time:

$$-\delta P/\delta x = \delta c/\delta t \tag{2}$$

In the steady state of flow,  $\delta c/\delta t$  is zero, P is constant and the rate of permeation is directly proportional to the concentration gradient as expressed by Fick's First Law of Diffusion:

$$\mathbf{P} = -\mathbf{D} \quad \delta \mathbf{c} \ / \delta \mathbf{x} \tag{3}$$

where D is the differential diffusion coefficient. Assuming D to be constant, this can be integrated between the two concentrations  $c_1$  and  $c_2$  to give:

$$P = D (c_1 - c_2) / L$$
 (4)

The steady state concentrations  $c_1$  and  $c_2$  of penetrant in the polymer can be related to the partial pressures  $p_1$  and  $p_2$  in the gaseous phase by Henry's Law:

$$c = S p (5)$$

where S is the solubility coefficient of the penetrant in the polymer

and c is the vapor concentration in the polymer. When Henry's Law is obeyed, there is a linear relationship between concentration and pressure, and S is a constant, so that:

$$P = D \cdot S (p_1 - p_2) / L$$
 (6)

or 
$$\overline{P} = D$$
.  $S = P$ .  $L / (p_1 - p_2)$  (7)

where  $\overline{P}$  is the permeability constant. This value is a constant at a given temperature when Henry's Law is obeyed, and when the diffusion coefficient is independent of the concentration, which is the case with permeant - polymer systems involving gases such as oxygen and hydrogen. However, if Henry's Law is not obeyed, or if the diffusion coefficient is concentration dependent, which is the case with most organic vapor - polymer systems,  $\overline{P}$  is no longer constant and the flux depends nonlinearly on the pressure difference (Barrer, 1939).

Several investigators have established the concentration dependency of the diffusion process in an organic vapor - polymer system (Barrer, 1957; Prager et al., 1951; Mears, 1958 and 1965; Baner, 1987; Zobel, 1982).

## Effect of glass transition temperature on Permeation

The glass transition temperature  $(T_g)$  of a polymer marks the change in polymer properties from glassy type structure properties to amorphous type structure properties as the temperature increases, marking the onset of polymer segmental mobility for a polymer (Rodriguez, 1970).

Mears (1954) has described the importance of  $T_{p}$  in the diffusion

process in polymers. The diffusion of organic vapors in polymers is largely dependent on the segmental mobility of the polymer chains at a given temperature. The glass transition temperature for a polymer in the absence of plasticizing agents, depends on the cohesive energy density, which is a quantitative measure of the attractive forces holding the polymer chains together in the polymer matrix. The increased flexibility of the polymer chains is caused by the unfreezing (on heating) of micro brownian motion of polymer chain segments (Boyer, 1977). The increase in polymer chain segmental mobility above the glass transition temperature corresponds to an increase in permeability and diffusion.

#### Organic vapor permeation measurement techniques

Different techniques have been used to measure the permeation of organic vapors through polymer films. Lebovitz (1966) placed a film in a sealed cup containing the liquid penetrant and measured the weight loss of the permeant. This gravimetric method has limitations due to the limited vapor pressure range and the inability to evaluate co-permeants.

A number of theoretical studies of permeation and diffusion of organic vapors through polymers have used the absolute pressure method (Rogers, 1964).

A manometric or volumetric technique is used to measure the permeant in the absolute pressure method. A pressure gauge, such as MacLeod gauge, is used to measure pressure in the pressure differential method, and a calibrated capillary tube containing mercury for volumetric measurements, is used for the volume differential method. The permeation

cell has two chambers, a high pressure and a low pressure chamber. The sample is clamped between the two chambers. Steady state permeation is attained when there is a constant increase in pressure or volume, with time, in the low pressure chamber. Modifications of this method have been used by Rogers et al. (1956), Meyers et al. (1957), and Mears (1958a) to measure the permeation or diffusion of organic vapors through polymeric films. This method has the following limitations: (i) copermeants cannot be used, as the detector system cannot differentiate between them; (ii) due to the high pressure differential, some kind of film support is required for thin and pressure sensitive films; and (iii) the apparatus used is complex.

Researchers have described the isostatic and quasi-isostatic methods for studying permeation and diffusion of organic vapors through polymer films, using gas chromatography analysis for quantification (Stannett et al 1972; Zobel, 1982; Baner et al., 1986; Hernandez et al., 1986; DeLassus, 1986). In these methods the partial pressure differential of the test vapor provides the driving force, with the total pressure on both sides of the film being one atmosphere. This allows study over a range of permeant concentrations and film thickness.

An isostatic system allows for the continuous monitoring of the transmission of an organic vapor through barrier films from the initial time zero to steady state conditions, as a function of temperature and permeant concentration. The film is clamped in a permeation cell and the desired permeant concentration in a carrier gas, is flowed continually over one side of the film. An inert carrier gas stream (same as the penetrant carrier gas) is flowed simultaneously over the low

concentration side of the film, carrying the permeant vapor to a detector. The steady state permeation rate is equal to the steady state concentration of permeant in the sweep gas stream times the sweep gas flow rate.

Davis (1946) developed an isostatic method that used chemical sorption of the permeating gases for quantification. This method lacks sensitivity. Ziegel et al. (1969) and Pastenak et al. (1970) used thermal conductivity detectors with an isostatic system to measure the increase of permeant in the sweep stream. Small thermistors were used by Yasuda and Rosengren (1970); and Giacin and Gyeszly (1981) to detect the permeant in the sweep gas stream in an isostatic test method. Thermal conductivity detectors and thermistors however are unable to detect copermeants in the sweep gas stream. Further, there are problems of calibrating these detectors for the specific permeant vapor concentration, and there are also problems with the effect of sweep gas flow rate on calibration. Zobel (1982) used a flame ionization detector as the detection system in an isostatic method to measure (FID) permeability of polymeric films to organic vapor. Pye et al. (1976) used two gas chromatographs interfaced to a permeation cell to study the diffusion of organic vapors through polymer films using an isostatic test method. One chromatograph was equipped with a flame ionization detector and the second with a thermal conductivity detector. This enabled the study of the transport of both organic vapors and gases through polymer films. An isostatic system was used to measure the transmission rates for mixtures of organic vapors through polymer films as a function of penetrant concentration, temperature and relative

humidity (Niebergall et al., 1978). Hernandez (1984) and Baner et al. (1986) employed an isostatic procedure for determining the diffusion coefficient from permeability data of organic vapors through barrier films. Analysis of penetrant was based on a gas chromatographic technique using a flame ionization detector. DeLassus (1986) used photoionization and atmospheric pressure ionization techiques to study the transport properties of barrier films using an isostatic system.

The quasi-isostatic test method is a variation of the isostatic method. The low concentration chamber of the isostatic permeation cell is initially filled with the inert sweep gas and sealed, instead of having the sweep gas flowing through, as in the isostatic system. The accumulation of permeant in the low concentration chamber is then measured as a function of time.

In earlier studies using a static system, researchers mounted a polymer film in a permeation cell above a reservior of liquid permeant. The permeating vapor accumulates above the film in the low concentration chamber. The penetrant is sampled using a gas tight syringe and injected into a gas chromotograph with FID detector for quantification (Gilbert and Pegaz, 1969; Hilton and Nee, 1978; Murray and Dorschner, 1983). This method is limited to testing only at the saturation vapor pressure of the liquid penetrant at a given temperature.

Gilbert et al. (1983), and Baner et al. (1986) used a quasiisostatic system to evaluate the barrier properties of films to various organic penetrants. They continually flowed a penetrant vapor stream through the high concentration cell chamber to provide a partial pressure gradient, so that the net movement of the penetrant is from

high partial pressure to low partial pressure. The diffused vapor was quantified by gas chromatographic analysis using a flame ionization detector.

#### Permeability Measurements

Isostatic method

A typical transmission rate profile curve for describing the transport of a penetrant through a barrier film by an isostatic method is shown in Figure 1.

The permeability coefficient, P, can be calculated from the isostatic method by substitution in Equation (8).

$$\overline{P} = \frac{a.G.f.L}{A.b}$$
(8)

where:

a - calibration factor to convert detector response to units of mass of permeant/unit of volume [(mass/volume)/signal units]

G = response units from detector output at steady state (signal units)

- f = flow rate of sweep gas conveying penetrant to detector (volume /
   time)
- A area of film exposed to permeant in the permeability cell (area units)
- L film thickness (thickness units)



Figure 1. Generalized Transmission Rate Profile Curve for the Isostatic Test Method.

b - driving force given by the concentration or partial pressure gradient (pressure or concentration units).

Summerizing from Hernandez et al. (1986), solution to Equation (3) depends on the boundary conditions of the experiment, which in this study is given by:

$$c = c_{1}$$
 at  $x = 0$   $t = 0$   
 $c = c_{0}$  at  $x = L$   $t > 0$   
 $c = c_{2}$  (L-x)/L at  $0 < x < L$   $t = \infty$  (9)

where L is the thickness of the film,  $c_0$  is the concentration at x-L in equilibrium with the penetrant flow. These boundry conditions represent the change from one steady state, t=0 and  $c_1$  to the final concentration  $c_2$  at t- $\infty$ , with the partial pressure of the permeant on the downstream side of the membrane always kept at zero since pure nitrogen gas is continuously flowed.

A solution to Equation (3) subject to boundry conditions given by Equation (9) was presented by Pasternak et al. (1970) and is given as a first approximation in Equation (10).

$$\frac{(\Delta M/\Delta t)_{t}}{(\Delta M/\Delta t)_{m}} = \begin{bmatrix} 4 & L^{2} & -L^{2} \\ [-2mm] - [-2mm] & [-2mm] & -L^{2} \\ [-2mm] - [-2mm] & -L^{2} \\ [-2mm] & -L^{2} \\ [-2mm] & -L^{2} \\ [-2mm]$$

where  $(\Delta M/\Delta t)_t$  and  $(\Delta M/\Delta t)_{\infty}$  are the transmission rate of the penetrant at time t and at steady state, respectively, t is time and L is the thickness of the film.

For each value of  $(\Delta M/\Delta t)_t/(\Delta M/\Delta t)_{\infty}$  a value of  $L^2/4Dt$  can be calculated, and by plotting  $(4Dt/L^2)$  as a function of time, a straight line is obtained. From the slope of this graph, the diffusion

coefficient (D) is calculated by substitution in Equation (11).

$$D = \frac{\text{slope} \cdot L^2}{4} \tag{11}$$

From a different general expression for  $(\Delta M/\Delta t)_t/(\Delta M/\Delta t)_{\infty}$ , Ziegel et al (1969) derived Equation (12) to solve for D:

$$D = \frac{L^2}{7.199 t_{1/2}}$$
(12)

where t is the time required to reach a rate of transmission  $(\Delta M/\Delta t)_t$  equal to half the steady state  $(\Delta M/\Delta t)_m$  value.

## Quasi-Isostatic Method

In this method, the permeated gas or vapor is accumulated and monitored as a function of time. Figure 2 shows a transmission rate profile curve describing the transport of a permeant through a polymer membrane by the quasi-isostatic method. As shown, the amount of vapor, q, which has passed through a unit area of film during time, t, is plotted as a function of time. Typically, the plot is convex towards the time axis and asymptotically approaches a straight line as the time increases (Fujita, 1968). When the asymptotic portion of the curve gives a rate of permeation dq/dt, which is independent of time, the permeation is said to be in steady state.

The steady state permeability coefficient,  $\overline{P}$ , can be determined from the quasi-isostatic method by substitution into Equation (13).

$$\overline{P} = \frac{y \cdot L}{A \cdot b}$$
(13)



Figure 2. Generalized Transmission Profile Curve for the Quasi-Isostatic Test Method.

where:

- y = the slope of the straight line portion of the transmission rate curve (mass/time)
- L = thickness of film
- A = area of film exposed to the permeant in the permeability cell
- b = driving force given by the concentration or partial pressure
  gradient

#### Permeation studies at elevated temperatures

Barrier polymers such as copolymers of polyvinylidene chloride (PVDC), ethylene vinyl alcohol copolymers (EVOH), polyethylene terephthalate (PET) and polyamides, offer an excellent barrier to gases and organic vapors. To study the transport properties of organic vapors through these high barrier polymers at room temperature takes an extended period of time. Experiments at room temperature would yield a very low signal after many weeks, as the permeability and diffusion coefficients are very low at ambient temperatures. Elevated temperatures can be used to accelerate the experiments.

DeLassus et al.(1988) conducted permeability experiments at several elevated temperatures to study the transport of trans-2-hexenal through vinylidene chloride copolymers (co-VDC) and EVOH barrier films. They found both the films to be excellent barriers when dry. The authors used an Arrhenius plot (log P vs. 1/T ) to calculate the activation energies associated with the diffusion and permeation of trans-2-hexenal through the barrier films, and also to interpolate the data to room temperature.

Shirakura (1987) conducted permeability experiments at several elevated temperatures to study the effect of temperature on the diffusion of ethyl acetate through PET films oriented at different temperatures. He reported a strong temperature dependence of the permeation of ethyl acetate through oriented PET film over the temperature range investigated, with the temperature range being well below  $T_g$  for the PET samples.

### Temperature Dependance of permeability

In general, an increase in temperature results in an increase in the segmental mobility of the polymer chains, thereby resulting in an increased rate of transmission of penetrants through the polymer film. The temperature dependence of the diffusion coefficient (D) over small ranges of temperature can be described by an Arrhenius type relation (Barrer, 1939; Van Amerongen, 1946):

$$D = D_{o} \exp\left(-E_{p}/RT\right)$$
(14)

where  $D_{o}$  is the pre-exponential diffusion term related to entropy,  $E_{D}$  is the activation energy of diffusion. T is the absolute temperature and R is the gas constant.

The solubility coefficient (S) is also related to temperature by an Arrhenius type relation (Michaels and Parker, 1959):

$$S = S_{o} \exp \left(-H_{s}/RT\right)$$
(15)

where S is the pre-exponential solubility term and H is the heat of solution. Combining Equation (14) and Equation (15) gives:

$$\overline{P} = DS = \overline{P}_{o} \exp (E_{p}/RT)$$
 (16)

where  $P_{o}$  is the pre-exponential term of permeability and  $E_{p}$  is the pre-exponential term of permeability and  $E_{p}$  is the apparent activation energy for permeation. It follows that:

$$E_{p} = E_{D} + H_{s}$$
(17)

# The Effect of water vapor on the permeability of gases and organic vapors through barrier films

The transmission of gases and vapors through hydrophilic polymers is often accelerated in the presence of water vapor (Barrie, 1968).

Pilar (1960) found a 200-fold increase in the permeation constant of cellophane to oxygen when relative humidity increased from 0% to 100 % . Figure 3 shows the profound effect of relative humidity on the permeability of oxygen through cellophane. The permeability constant increases exponentially between the range of 70 to 80% R.H. Simril and Smith (1942) showed that within this range of relative humidity, the mechanism of water sorption appeared to be changing and was accompanied by extensive structural changes within the polymer. Kunz and Cornwell (1962) also found an increase in oxygen permeability through cellophane with an increase in relative humidity. Notley (1963) and Kamiya and Takahashi (1977) studied the transmission of gases through a cellophane laminate and found similar effects - an increase in permeability. Notley proposed that water vapor causes swelling of the cellophane structure, and consequently increases the permeability of gases through cellophane films.



Figure 3. The Relative Permeability Constant of Cellophane Films at 25 C to Oxygen as a function of Relative Humidity (Pilar, 1960).



In general, polymers which swell greatly in water will show an increase in permeability with an increase in relative humidity.

Simril and Hershberger (1944) have studied the effect of water vapor on the gas transmission rates for a number of polymer - gas systems. Studies with nylon, at varying relative humidities, showed that the presence of water vapor increased the transmission rate of gases such as oxygen, nitrogen and carbon dioxide.

Meyer et al (1957) studied the effects of relative humidity on the permeability of oxygen, nitrogen and carbon dioxide through polyethylene (PE), polyethylene terephthalate (PET) and a hydrophilic film, nylon 6. These studies showed little or no effect on the gas permeability of PE and PET due to changes in relative humidity. However, the transmission of carbon dioxide through Nylon 6 increased with an increase in relative humidity.

Ito (1961) found an increase in the permeability of carbon dioxide, with an increase in relative humidity, through Nylon 6 and polyvinyl alcohol. When water is highly sorbed by a polymer film, water plasticizes the film, leading to an increased rate of permeation, as is the case with Nylon 6 and EVOH. The sorbed water vapor acts as a plasticizer to the polymer, decreasing the cohesive energy forces of the polymer chains, thereby resulting in an increase in polymer chain segmental mobility (Crank and Park, 1968). Petrak et al. (1980) also noted a similar effect in their study of the permeation of oxygen through several hydrophilic films.

Water sorbed by a hydrophilic polymer weakens the intermolecular forces in the polymer chain by hydrogen bonding to the polar groups of

the polymer, or by increasing the distance between polymer molecules, thereby reducing the glass transition temperature of the polymer. The reduction in T is directly proportional to the amount of water absorbed (Jabarin and Lofgren, 1986). The reduction in T g, decreases the activation energy required for diffusion, thereby leading to increased permeation.

Pye et al. (1976), studying the transport of hydrogen and methane through amorphous aromatic polyimides, found permeability to decrease when the film was exposed to water vapor, as compared to when the film was dry. This could be due to a small amount of water binding to the active carbonyl sites within the polymer bulk phase and effectively reducing the microvoid content of the films, and thus the available diffusion paths for the nonreactive gases. Chern et al. (1983) also found that  $CO_2$  permeability through kapton polyimide decreased, when exposed to water vapor.

Hernandez (1989) studying the permeation of oxygen through glassy amorphous polyamide found similar results. He reported a decrease in permeability with an increase in water content of the polymer, and proposed that the decrease in permeability is due to water molecules being bound to the amide groups of the polymer through hydrogen bonding, with the saturation of the amide active sites being completed before the relative humidity reaches a value of 10 % RH. He also proposed that both water and oxygen compete for active sites and with an increase in relative humidity, there is a decrease in the number of active sites for oxygen, thereby resulting in an increase in the activation energy for the diffusion process. The presence of water vapor accelerates the diffusion of organic vapors in certain polymers (Praeger et al., 1951; Long et al., 1953). Long and Thompson (1953, 1955) found that organic vapor diffused more rapidly into polymers containing sorbed water vapor than into dry polymers, provided the polymer absorbed water to an appreciable extent. These investigators proposed that the increased diffusion is due to water plasticizing the polymer.

Watt (1964) found an increase in the diffusion of ethyl alcohol through keratin in the presence of water vapor. Water vapor caused the polymer to swell, thereby resulting in increased diffusion.

Liu (1986) evaluated the effects of relative humidity on the permeation of toluene vapor through a multi-layer laminate structure containing nylon and ethylene vinyl alcohol (EVAL) as the hydrophilic barrier layers. Permeability increased with an increase in relative humidity. Figure 4 shows the effect of relative humidity on the permeability constant of toluene through the multi layered structure.

Delassus (1988) studied the effect of relative humidity on the transport of trans-2-hexenal through a vinylidene chloride copolymer (co-VDC) film and an EVOH film. Relative humidity had no effect on the co-VDC films, whereas the hydrophilic EVOH film showed a large increase in permeability due to the strong plasticizing effect from the moisture.


Figure 4. Permeability Constant Versus Relatine Humidity of Crayovac FDX 1570 Film at 81 ppm Tolune, 72 F (Liu, 1986)

#### MATERIALS AND METHODS

#### MATERIALS

#### Film Samples

The amorphous polyamide film samples were provided by E.I. Dupont de Nemours & Company.

This amorphous polyamide, Nylon 61/6T, is made from hexamethylenediamine and a mixture of isophthalic (70%) and terephthalic (30%) acids. The random placement of the acid isomers in the polymer chain prevents crystallization (Blatz and Talkowski, 1987).

The 1 mil film samples used in this study were stored in a desiccator, filled with CaSO desiccant.

# Acetone

Acetone with a purity of 99.6%, boiling point of 56.3°C from . Mallinkrodt Inc. (Paris, KY) was used as the permeant.

## Nitrogen

High purity dry nitrogen 99.98% by Union Carbide Corporation, Linde Division, (Danbury, CT) was used as the carrier gas.

#### METHODS

# Film Sample Handling Technique

Film samples taken from the desiccator were cut and placed in a vacuum oven for twelve hours at 90°C and 30 mmHg vacuum to ensure the sample was dry. The vacuum in the oven was replaced by dry nitrogen to avoid any moisture uptake by the film sample. The film sample was then taken from the oven and immediately clamped in the permeation cell.

Selection of organic penetrant

At the start of this study, several organic penetrants were screened to assist in the selection of a penetrant for further research. The procedure of the screening test and the penetrants evaluated are listed in Appendix B. Based on the results of the primary study, acetone was selected as the permeant. The selection of the penetrant was based on the rate of permeation of the penetrant through amorphous nylon film.

#### Experimental Procedure

Prior to the start of the experiment, the permeation cell, the cell parts and o-rings were baked out in a vacuum oven at 90°C and 30 mmHg vacuum for a period of twelve hours to remove any residual sorbed permeant from the previous experiment. After being removed from the oven, the cells were allowed to cool to ambient temperature before starting a new experiment.

A schematic diagram of the isostatic test apparatus is shown in Figure 5. The test system allows for the continuous collection of permeation data of an organic vapor through a film from initial time zero to steady-state conditions, as a function of temperature and permeant concentration. The test system also allows the effect of water vapor as a co-permeant to be evaluated. This system was designed to allow two film samples to be evaluated simultaneously.

The film to be tested was placed between the two stainless steel disk shaped plates forming a cell with two chambers, with each cell chamber having a volume of 5cc. The surface area of the film exposed to the permeant is 50 cm<sup>2</sup>. Hermetic isolation of the chambers from the



Figure 5. Schematic Diagram of the Isostatic Test Apparatus.

environment was achieved by the compression of overlapping Viton "O" rings on the film. Viton is a fluorocarbon elastomer which is resistant to attack and swelling by most organic vapors. A diagram of the permeation cell is shown in Figure 6.

The assembled cell and film was placed horizontally in an oven. which was maintained at a constant temperature. A constant concentration and constant flow of the permeant vapor was continually flowed through the upper (high concentration) cell chamber. Concurrently, a constant flow of nitrogen was passed through the lower cell chamber removing permeant vapor at a constant rate and conveying it to the detector apparatus. The high concentration stream from the upper cell chamber was connected to another permeation cell (shown in Figure 7) and the vapor concentration is quantified by withdrawing a sample from the sampling port with a gas tight syringe and injecting into the detector apparatus. This detection system consists of a gas chromatograph (GC), equipped with a flame ionization detector. The GC is interfaced to the permeation cell via a computer aided stream selection and gas sampling valves. At preselected time intervals the concentration of the penetrant in the nitrogen stream flowing through the low concentration cell chamber was determined and the transmission rate was continually monitored until steady state conditions were attained. The permeability coefficient values (P) was then computed by substitution into Equation (8).

A constant concentration of permeant vapor and relative humidity was produced by bubbling nitrogen gas at 1 atm through liquid acetone and distilled water. This was carried out by assembling a vapor generator consisting of two Pyrex glass gas washing bottles, 250mm long and 250mm



Figure 6. Schematic Diagram of Permeation Cell for the Isoststic Test Method.

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diameter, with fritted dispersion tube. One contained the organic liquid and the other distilled water. The organic vapor stream and water vapor stream can be mixed with another stream of pure carrier gas nitrogen to reduce the vapor concentration. Before being directed to the permeation cell, the organic vapor/water vapor stream was passed through a glass vial containing a hygrometer sensor, designed specifically for use in an organic vapor atmosphere (narrow range hygrometric sensor from Hydrodynamics Inc., Silver springs, MD), to measure the relative humidity.

When water vapor is used as a co-permeant, the sweep gas nitrogen stream was also humidified by bubbling nitrogen through distilled water in a gas washing bottle, as with the high concentration stream. The relative humidity of the sweep gas stream was measured using a hygrometer sensor before being directed to the lower chamber of the permeation cell.

Rotameters were used to provide a continuous indication that a constant rate of flow was maintained. Gas flows were regulated using Nupro "M" series needle valves. Accurate measure of the flow of gases was performed at atmospheric pressure by using a 10cc gas flow bubble meter from Supelco (Bellefonte, PA). A Casio stopwatch model HS-10W was used to measure the flow rate of gases. Temperatures in the oven were measured with a mercury thermometer to within  $0.5^{\circ}$ C.

Unless otherwise stated, 1/8" O.D. X 1.65mm I.D. copper refrigeration tubing was used to connect the different components of the test system. The connections between the cell and the stream selection valve, and from the stream selection valve to the gas sampling valve on

the chromatograph were made with stainless steel capillary tubing 1/16" OD and 0.762mm ID., with a total length of 40cm, giving a dead volume of 0.2cc. All fittings and tubing connections used were brass Swagelok fittings.

The high concentration stream was connected to the permeation cell shown in Figure 7. This cell has three chambers. The top and bottom cells are closed by placing aluminium foil disks. The volume in the center cavity is approximately 50cc, and a sample is withdrawn from the sampling port in this chamber. The permeant stream is then vented to the hood. The applicability of taking measurements of the high concentration stream through the sampling valves was ruled out, due to possible contamination and interference caused by sorption of acetone vapor by the tubing and sampling valves, followed by a slow rate of desorption.

A Hewlett-Packard 5830A gas chromatograph (GC) equipped with dual flame ionization detection, interfaced to a 18850A GC Hewlett-Packard terminal was used as a detection means. The 5830A GC is a keyboard controlled instrument with a multifunctional digital processor.

Working with values entered via a keyboard on the terminal unit, the processor established the required GC conditions for the analysis. A printed output with a plot of the amount of material detected as a function of time, the area under this curve (expressed in area units), and retention time was obtained.

1/16" OD stainless steel tubing was used to convey the diffusant from the cell to the stream selection valve (Multiposition automatic gas sampling valve model no. ACSF8P, Valco Instruments Co. Inc., Houston, TX) was used with a dead ended flowpath, which allows one stream at a









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time to flow to the gas sampling valve through a common outlet. A stream was selected in the clockwise direction every time the valve was actuated. Figure 8 shows the dead ended flowpath of the stream selection valve.

A 1/16" SS tubing was also used to connect the stream selection value to the automatic gas sampling 6-port value housed within the gas chromatograph. Figure 9 shows the connection between the sampling value and the sample stream during the fill position (de-actuated value) and the injection position (actuated value). The sampling loop in the value has a volume of 0.5 ml. Both the values are actuated by air actuators.

The column used in the gas chromatograph was a 1/8" OD X 6' stainless steel column packed with 5% SP-2100 on 100/120 mesh supelcoport ( Supelco SP-2100 methysilicone fluid, Supelco Inc., Bellefonte, PA). The GC analysis conditions are listed in Table 1.

TABLE 1. Conditions under which GC was run

Column temperature	150°C
Injection temperature	175°C
FID temperature	350°C
Oven maximum temperature	225°C
Helium carrier gas flow rate	28 cc/min

Operation

An experiment consisted of several runs. A run was considered as a



Figure 8. Schematic Diagram of Dead Ended Flow Path of the Stream Selection Valve.

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set of data taken from the moment the oven equilibrated at the required temperature and a constant concentration of the permeant flow, and where applicable, a constant relative humidity in the permeant stream, contacted the film, and until a steady state of permeation was clearly obtained, at a given temperature.

Prior to starting an experiment, the oven was set to the desired temperature, and care was taken to purge the lower cell chamber, the capillary tubing, the sampling valve and the stream selection valve of acetone vapor. To accomplish this, an aluminium foil disk was mounted in the permeability cell and nitrogen was continually flowed through the lower chamber and both the valves. The system was considered "clean" when the signal from the GC was less than 500 area units, corresponding to an acetone vapor concentration of 0.003 ppm.

For experiments conducted under dry conditions (at 0% RH), the flow of the acetone vapor was adjusted to the required concentration. Nitrogen gas was continually passed through the vapor generator and the concentration monitored to insure a steady vapor and constant concentration of permeant vapor. Several days were required to attain and maintain a constant acetone vapor concentration. The concentration of the acetone vapor was monitored by removing a sample via a gas tight syringe from the sampling port of the cell shown in Figure 7, and analyzing the gas sample by direct on column injection into the GC. The flow rate of the nitrogen gas sweep stream was also concurrently adjusted to the required value by measuring with a bubble flow meter.

The dry film sample from the vacuum oven was mounted in the permeation cell and the cell was placed in the oven for two hours for

the film to equilibrate to the temperature before being connected to the permeant and sweep gas streams.

Preparation for experiments to evaluate the effect of water vapor as a co-permeant in the permeant stream, were very similar to the ones under dry conditions. Here the desired relative humidity was adjusted along with the required concentration in the permeant stream. The sweep gas stream was also humidified to the same value as the permeant stream. The humidities were measured by hygrometric sensors, at room temperature, before the streams were directed to the permeation cell in the oven. The film was mounted in the permeation cell and placed in the oven for two hours. The organic vapor flow was stopped (after the flow rate values were noted) and the permeation cell was connected to the humidified permeant and sweep gas streams. The film was conditioned at the required relative humidity for one week (considered appropriate to have equilibrated the film to the surrounding R.H. level). The acetone vapor was adjusted to the previously noted values. Approximately one hour was required before a steady acetone vapor concentration was attained in the permeant stream. The run was considered started from the moment the acetone vapor is introduced into the permeant stream.

Calibration of the gas chromatograph for acetone was done by constructing a standard curve of area response versus guantity injected. The calibration factor was calculated to be  $3.231 \times 10^{-12}$  gms/area units. The penetrant concentration was determined by reference to the calibration curve. The GC calibration procedure and data are reported in Appendix A.

The precision of the measurements for the permeation coefficient are

reported in Appendix C.

#### Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) measurements were conducted in order to determine the glass transition temperature  $(T_g)$  of amorphous nylon film following sorption by the penetrant vapor, and also when dry.

Film sample preparation for DSC studies were as follows:

film sample was cut into tiny pieces and a sample of The approximately 10 mg was placed into each DSC pan. A forecep was used to handle the samples and the pans. The pans along with the lids, were then placed in a vacuum oven for twelve hours at 90°C and 30 mmHg to ensure the samples were dry. The vacuum in the oven was replaced by dry nitrogen to avoid any moisture uptake by the samples. The pans were then taken from the oven and immediately placed in a permeation cell. The cell was then closed and connected to the permeant stream, adjusted to the same acetone concentration employed in the permeation studies. The samples were conditioned to the permeant stream for a period of two after which the  $T_{\sigma}$  of the film samples exposed to the acetone weeks, vapor stream were determined. DSC runs were conducted directly after the samples were taken out of the oven to estimate the  $T_{\sigma}$  of the dry film sample.

A DuPont Differential Scanning Calorimeter model 910 was used. For dry film samples, the temperature of the run was between 40 to  $140^{\circ}$ C with a heating rate of  $10^{\circ}$ C/min, and for film samples exposed to the permeant vapor, between 25 to  $140^{\circ}$ C, with a ramp of  $10^{\circ}$ C/min. The DSC plots are shown in Appendix D.

#### **RESULTS AND DISCUSSION**

The isostatic method was employed to determine the permeability coefficient of the amorphous nylon - acetone vapor system at a constant acetone vapor concentration, at a series of temperatures.

At the time this study was conducted, no permeation data for the acetone - amorphous nylon system was available in the literature. A considerable amount of time was therefore devoted to preliminary experiments, and in developing the test method used in this study.

Initially, inconsistent results were obtained using the quasiisostatic technique, and no measurable permeation was observed after a period of 45 days at ambient temperature, by this method. The experimental procedure used in this study was, therefore, developed in order to conduct more operator - independent experiments, having good control of the variables. Experiments were conducted at several elevated temperatures to accelerate the permeation process.

Film samples with a thickness of 1 mil were used for all experiments. The same film sample was used for all runs within an experiment. For an experiment, each run was maintained for a period of 8 to 14 days after steady state conditions were attained, to ensure the system was at equilibrium.

# Experiment 1. Effect Of Temperature On The Permeation Of Acetone Through Amorphous Nylon Film

The film sample used in this experiment was subjected to acetone

vapor for a period of 45 days at a temperature of 75°C prior to testing. The acetone vapor concentration was maintained at a constant value of 290 ppm (0.29 kg/m<sup>3</sup>) throughout the experiment, with the nitrogen gas sweep stream flow rate maintained at a constant value of 1.82 cc/min  $(3.03 \times 10^{-8} m^3/sec)$ .

The stream selection value was not used for this experiment. Therefore the permeation cell was connected directly to the automatic gas sampling value of the gas chromotograph. Table 2 gives a summary of the permeability values obtained.

Run	Temperature	$\frac{1}{p}$ (a)	Std.	P
No.	(°C)	(g.mil/m <sup>2</sup> .day.ppm)	Dev.	(kg.m/m <sup>2</sup> .sec.Pa)
1	75	$1.2 \times 10^{-4}$	0.035	7.2 x $10^{-20}$
2	85	$2.2 \times 10^{-4}$	0.042	$1.3 \times 10^{-19}$
3	60	$6.0 \times 10^{-5}$	0.000	$3.8 \times 10^{-20}$
4	95	$2.1 \times 10^{-4}$	0.028	$1.2 \times 10^{-19}$

TABLE 2. Data for Experiment 1.

(a) - average of replicate runs.

# Experiment 2. The Effect Of Temperature On The Permeability Of Acetone

# Through Amorphous Nylon Film

This experiment was designed to be a replicate of Experiment 1. However, in this experiment the stream selection valve was interfaced to the automatic gas sampling valve, and the film sample was not preexposed to acetone vapor, prior to initiating the experimental runs. The acetone vapor concentration was maintained at 290 ppm  $(0.29 \text{ kg/m}^3)$  with the nitrogen sweep stream flow kept at 1.74 cc/min  $(2.9 \times 10^{-8} \text{ m}^3/\text{sec})$ . For this experiment, good agreement was obtained between replicate runs, and the results reported are the average of replicate studies. Further, the permeability parameters obtained showed good agreement with those of Experiment 1. Table 3 summarizes the results of this experiment.

Run No.	Temperature (°C)	$\overline{P}$ (a)(g.mil/m².day.ppm)	Std. Dev.	P   (kg.m/m².sec.Pa)
1	60	$6.1 \times 10^{-5}$	0.000	$3.8 \times 10^{-20}$
2	75	$1.1 \times 10^{-4}$	0.031	$6.6 \times 10^{-20}$
3	85	$1.7 \times 10^{-4}$	0.068	9.9 x $10^{-20}$
4	95	$2.1 \times 10^{-4}$	0.044	$1.2 \times 10^{-19}$

TABLE 3. Data for Experiment 2.

(a) - average of replicate analyses.

A plot of GC area response values versus time for Run 1 (60°C) is shown in Figure  $\overset{10}{\mathscr{P}}$ . The time required to reach a rate of transmission, equal to half the steady state value, t<sub>1/2</sub> was determined from this plot. The diffusion coefficient was then calculated by substituting this value into Equation (12). The permeability parameters determined at 60°C are summarized in Table 4. TABLE 4. Permeability Parameter Values for Experiment 2 at 60°C.

Time required to reach half the steady state transmission rate,  $t_{1/2}$ , for run 1 - 21 days Diffusion Coefficient,  $D_{t1/2} = 0.49 \times 10^{-12} \text{ cm}^2/\text{sec}$  (4.9 x  $10^{-17} \text{ m}^2/\text{sec}$ ) Solubility Coefficient, S = 3.7 x  $10^{-4} \text{ g/cm}^3$ .ppm (7.9 x  $10^{-4} \text{ kg/m}^3$ .Pa) Permeability Coefficient,  $\overline{P} = 6.1 \times 10^{-5} \text{ g.mil/m}^2$ .day.ppm  $3.8 \times 10^{-20} \text{ kg.m/m}^2$ .sec.Pa

Yanezawa (1989) determined the solubility coefficient of acetone in the amorphous nylon film at 24°C to be 7.9 x  $10^{-4}$  g/cm<sup>3</sup>.ppm, (1.87 kg/m<sup>3</sup>.Pa) by using a microbalance gravimetric technique (Hernandez et al., 1986). Combining this value and the solubility coefficient calculated at 60°C, the enthalpy of sorption ( $\Delta H_s$ ) was determined by substitution into Equation (15), giving a value of  $\Delta H_s = -6.8$ kcal/mole. The solubility coefficient, was then calculated for 75°C. Using the expression  $\overline{P} = D.S$ , the diffusion coefficient at 75°C was also calculated. The values for the activation energy for permeation ( $E_p$ ) and the enthalpy of sorption ( $\Delta H_s$ ) were then substituted into Equation (17) to obtain the activation energy for diffusion. The values obtained are presented in Table 5.





TABLE 5. Calculated values for Experiment 2 at 75°C.

Permeability Coefficient,  $\overline{P} = 1.1 \times 10^{-4} \text{ g.mil/m}^2 \cdot \text{day.ppm}$ = 6.6 x  $10^{-20} \text{ kg.m/m}^2 \cdot \text{sec.Pa}$ Solubility Coefficient, S = 1.47 x  $10^{-4} \text{ g/cm}^3 \cdot \text{ppm}$  (3.0 x  $10^{-4} \text{ kg/m}^3 \cdot \text{Pa}$ ) Diffusion Coefficient, D = 2.2 x  $10^{-12} \text{ cm}^2 / \text{sec}$  (2.2 x  $10^{-16} \text{ m}^2 / \text{sec}$ ) Time required to reach half steady state transmission rate,

Activation Energy for diffusion,  $E_{p} = 16.06 \text{ kcal/mole}$ 

# Experiment 3. The Effect Of Sorbed Water Vapor On The Permeability Of Acetone Through Amorphous Nylon Film.

This experiment was conducted to evaluate the effect of sorbed water vapor on the permeability of acetone through the amorphous nylon film. The acetone vapor was maintained at a concentration of 290 ppm (0.29 kg/m<sup>3</sup>), with the nitrogen sweep stream flow rate maintained at 1.82 cc/min.(3.03 x  $10^{-8}$  m<sup>3</sup>/sec). The relative humidity of the permeant stream was maintained at 70 % R.H. (0.025 kg H<sub>2</sub>0/m<sup>3</sup>), measured at 23°C for all the runs. Table 6 summarizes the results of this experiment. The permeability parameters determined at 75°C are summarized in Table 7. TABLE 6. Data for Experiment 3.

Run No.	Temperature (°C)	<pre></pre>	Std. Dev.	P (kg.m/m <sup>2</sup> .sec.Pa)
1	75	$1.9 \times 10^{-4}$	0.035	$1.1 \times 10^{-19}$
2	85	$3.0 \times 10^{-4}$	0.062	$1.7 \times 10^{-19}$
3	60	$8.0 \times 10^{-5}$	0.031	$5.0 \times 10^{-20}$

(a) - average of replicate runs.

**TABLE 7.** Permeability Parameter Values for Experiment 3 at  $75^{\circ}$ C.

Time required to reach half steady state transmission rate,  $t_{1/2}$ , for run 1 = 4.3 days Diffusion coefficient,  $D_{t1/2} = 2.41 \times 10^{-12} \text{ cm}^2/\text{sec} (2.41 \times 10^{-16} \text{ m}^2.\text{sec})$ Solubility coefficient = 3.6 x 10<sup>-4</sup> g/cm<sup>3</sup>.ppm (7.3 x 10<sup>-4</sup> kg/m<sup>3</sup>.Pa) Permeability coefficient = 1.9 x 10<sup>-4</sup> g.mil/m<sup>2</sup>.day.ppm = 1.1 x 10<sup>-19</sup> kg.m/m<sup>2</sup>.sec.Pa

Figure 10, the transmission rate profile curve for Run 3 at  $75^{\circ}$ C, was used to determine t<sub>1/2</sub>, and the value substituted in Equation (12) to obtain the diffusion coefficient.



Figure 11. Transmission Rate Profile Curve For Acetone Vapor Through Amorphous Nylon Film Sorbed by Water Vapor at 290 ppm and 75 C.

Table 8 presents a summary of the permeability coefficients for the three experiments at the temperatures tested. Experiments 1 and 2, were conducted under dry conditions, whereas, Experiment 3 was conducted at 70 R.H. (measured at 23°C).

	P (g.mil/m <sup>2</sup> .day.ppm)			
Temp. (°C)	Exp.1	Exp.2	Average	Exp.3
60	$6.0 \times 10^{-5}$	$6.1 \times 10^{-5}$	$6.05 \times 10^{-5}$	$8.0 \times 10^{-5}$
75	$1.2 \times 10^{-4}$	$1.1 \times 10^{-4}$	$1.15 \times 10^{-4}$	$1.9 \times 10^{-4}$
85	$2.2 \times 10^{-4}$	$1.7 \times 10^{-4}$	$1.95 \times 10^{-4}$	$3.0 \times 10^{-4}$
95	$2.1 \times 10^{-4}$	$2.1 \times 10^{-4}$	$2.10 \times 10^{-4}$	

TABLE 8. Summary of the permeability coefficients.

As shown in Table 8, sorption of water vapor resulted in an increase in the permeability coefficient values, as compared to dry conditions. The permeability coefficient values increased by an average of 1.5 times (average value for all temperatures). This is in contrast to what was reported by Hernandez (1989), who showed a decrease in the permeability of oxygen through the amorphous nylon film, following sorption of water vapor by the polymer. Hernandez interpreted these results within the framework of the dual mode sorption model, and proposed that both water and oxygen compete for active binding sites within the polymer bulk



phase, and there is a decrease in the number of active sites for oxygen, with an increase in the level of sorbed water. This resulted in a decrease in oxygen solubility in the polymer and a corresponding depression in the permeability coefficient. In the case of acetone as the penetrant, the observed increase in permeability supported that both water and acetone vapor simultaneously interact with the amorphous perhaps under the same competitive mechanism, polyamide, but to different degrees. This interaction of vapors with the polyamide is associated with a gradual relaxation of the polymer structure. This swelling-relaxation process leads to a significant increase in the mobility of the penetrant within the polymer bulk phase, resulting in an increase of penetrant flux, and therefore the permeability (Berens, 1977, Fujita, 1968). The results of thermal analysis suggested the proposed penetrant induced polymer chain relaxation and the resulting change in permeability of the polymer. These findings are discussed in detail in a subsequent section.

#### **Temperature** Dependency

Presented in Figure 11 is an Arrhenius plot of Log P vs. 1/T, for the mass transport studies carried out under dry and humidified conditions, respectively. The temperature dependency of the permeability coefficient, over the temperature range studied, can be represented by Equation (16). The following expressions were derived to describe the relationship between the permeability coefficient (P) and temperature, at a constant acetone vapor concentration of 290 ppm,

$$\overline{P} = 10^{1.908} - (2034 / T)$$
(18)

for experiments conducted under dry conditions, and

$$\overline{P} = 10^{-4.162} - (2748 / T)$$
(19)

for humidified experiments.

Where T = temperature in degree kelvin.

The activation energies for the permeation process  $(E_p)$  were determined from the slopes of the respective Arrhenius plots (Figure 11). An average of the permeability coefficients from Experiments 1 and 2 was used to represent experimental runs conducted under dry conditions, and the permeability coefficients from Experiment 3, for the humidified runs. The activation energy for the experiments conducted under dry conditions was calculated to be 9.3 kcal/mole, and for Experiment 3, where the effect of relative humidity was considered, the activation energy was calculated to be 12.5 kcal/mole.

Statistical analysis showed that the slopes of the respective Arrhenius plots were different, with a confidence level of 99.5%, thereby demonstrating a statistically siginficant difference between the permeability of the acetone vapor/amorphous polyamide, penetrant/polymer system, in the presence of sorbed water vapor. A similar increase in the activation energy was observed in the case of oxygen permeability, when comparing dry and humid conditions.

# Determination of glass transition temperature

As stated above, the results of Differential Scanning Calorimetry . (DSC) thermal analysis supported the proposed penetrant induced polymer chain relaxation, and the resulting change in permeability of the polymer, when comparing dry and humidified conditions. Using DSC thermal

analysis, the glass transition temperature  $(T_g)$  of the amorphous polyamide exposed to acetone vapor was determined. The T<sub>g</sub> of the polymer decreased from 125.8°C to about 41°C, when equilibrated with acetone vapor at a partial pressure of 92 mmHg and 23°C. The respective thermograms are shown in Figures 13 and 14, in Appendix D.

Hernandez (1989) determined the  $T_g$  of amorphous nylon film following exposure to water vapor at several relative humidities. The  $T_g$  of the polymer showed a steady decrease, with an increase in the level of sorbed water vapor. The DSC plots obtained by Hernandez (1989) are shown in Figure 15, (see Appendix D) for comparison. As shown, the observed trend in the reduction in  $T_g$  of the film sample following sorption by acetone vapor compares well with the results obtained following water sorption.

The permeability studies conducted at the test temperatures were thus well above the T<sub>g</sub> of the polymer, but can be used to approximate the upper limit of the barrier properties of the test film at room temperature. Extrapolating the permeability coefficient values to  $21^{\circ}$ C, the following values were obtained.

$$\bar{P} = 1.1 \times 10^{-5} \text{ g.mil/m}^2.\text{day.ppm}$$

for experiments conducted under dry conditions, and

$$\overline{P} = 0.81 \times 10^{-5} \text{ g.mil/m}^2.\text{day.ppm}$$

for the humidified experiment. Had these studies been conducted at room temperature, the temperature of test would have been below the  $T_g$  of the polymer, and so the extrapolated values represent upper limit approximations (DeLassus et al. 1988).

APPENDICES

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# APPENDIX A

#### CALIBRATION OF GAS CHROMATOGRAPH FOR ACETONE

#### Materials

HPLC grade Acetone

HPLC grade ortho-dichlorobenzene as solvent

## Equipment

100 ml volumetric flasks with stoppers

10  $\mu$ l liquid sampling syringe

Analytical balance

#### Procedure

1. Volumetric flasks and syringe are baked out in an oven prior to use to remove any residual solvent. These are then taken out and allowed to cool to room temperature.

2. The purity of the solvent was evaluated using the gas chromatograph to ensure that there are no interfering peaks at the permeant retention time.

3. Various dilutions of acetone were prepared using orthodichlorobenzene as the solvent, by following these steps:

a. the volumetric flasks are partially filled with the solvent.

b. tare the flask and the solvent.

c. the desired quantity of permeant was added.

d. the flask is reweighed to determine the actual amount of permeant added to the flask.

e. the flask was filled to the volumetric line with the solvent.

f. the flask's contents are mixed well.

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4. The gas chromatograph conditions used are listed in Table 1.

Acetone retention time 0.40 min.

5. 1  $\mu$ l of the sample was injected into the GC.

6. A plot of the GC area unit response versus quantity of acetone injected was made. The slope of this curve equals the calibration factor. The standard calibration curve is shown in Figure 12.

7. Sample calculations:

Dilution #1 : 0.0049 g permeant diluted in 100 ml solvent.

concentration = 
$$4.9 \times 10^{-5}$$
 g/ml

typical injection :

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 $4.9 \times 10^{-5}$  g/ml x 0.001 ml injection volume -

0.049x10<sup>-6</sup> g permeant injected

TABLE 9. Acetone standard calibration curve data

Quantity Injected (gms x 10 <sup>-6</sup> )	Area response
0.049	18166.25
0.108	38270.00
0.223	65170.00
0.306	101900.00
0.494	153522.22

Resulting line slope equation

 $Y = 1.97X10^3 + (3.095x10^{-5}) X$ 



# APPENDIX B

# INITIAL SCREENING TESTS

#### Organic Compounds

The following are the organic penetrants evaluated in preliminary screening tests:

- 1. Methyl Ethyl Ketone
- 2. Acetone
- 3. Ethyl Acetate
- 4. Benzene
- 5. Limonene
- 6. Toluene
- 7. Hexane
- 8. Heptane
- 9. Xylene

Analysis of the penetrant concentration was based on gas chromatographic procedure. The GC conditions are listed in Table 1.

# Procedure

The procedure was a quasi-isostatic method for determining the organic vapor permeability of the film samples.

A petri-dish containing approximately 2 grams of the organic compound was placed in the lower cell chamber of the permeability cell. The permeability cell used is shown in Figure 7. The film sample is then mounted between the two cell chambers, and the permeability cell

assembled. The organic compound volatilizes in the lower chamber and thus equilibrates to a steady state concentration, creating a constant partial pressure gradient between the two cell chambers. The vapor permeating into the lower concentration cell chamber is monitored as a function of time until the permeation rate reaches a steady state.

Prior to conducting the permeability studies, appropriate care was taken to ensure no organic residue was present in the permeation cell. The procedure followed is described below.

- the permeation cells were baked in a vacuum oven at 90°C and 30mmHg vacuum for 6 hours.
- the cells were assembled and flushed with nitrogen for 2 days.
- the inlet values and outlet values were then closed and the cells were allowed to stand for two days. The lower concentration cell chamber was then sampled and analysed for residual organics.

In the above mentioned procedure, an aluminium foil sheet was placed between the high and the low concentration chambers. If residual organics were detected, the above procedure was repeated.

Once the cells were shown to be devoid of residual organics, the cell was disassembled and the test film mounted and the cell reassembled. The permeability of the test organics through the film sample was evaluated according to the procedure described above. Results of the initial screening tests are listed in Table 10.

Penetrant	Observed Permeation
Methyl Ethyl Ketone	Yes
Acetone	Yes
Ethyl Acetate	No
Benzene	No
Limonene	No
Toluene	No
Hexane	No
Heptane	No
Xylene	No

TABLE 10. Results of the priliminary tests.

Yes - measurable rate of permeation was observed.

No - no measurable permeation after a period of 45 days.

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#### APPENDIX C

#### PRECISION OF MEASUREMENTS

To estimate the uncertainity in the permeability coefficient, it was necessary to have an estimate of the uncertainity in the measurements performed by the apparatus, i.e., the error associated for each value of the organic vapor concentration determined by the gas chromatograph (expressed in area units), as a result of the continuous diffusion process and mixing with the sweeping stream of nitrogen.

The error analysis had to include an evaluation of the incidence of at least the following factors (Hernandez, 1984):

- Uncertainty of the permeant concentration in the cell (depending on temperature, bubbling nitrogen flow, bubble diameter, height of organic liquid in the cylinder, etc.).
- 2. Uncertainity of the amount of nitrogen flowing through the lower chamber.
- 3. Uncertainity in the sampling values (volume and pressure).
- 4. Uncertainity in the detector unit.
- 5. Temperature fluctuations.

Considering that most of these variations are random and independent, some compensatory effects take place. A simple way to measure these uncertainties is to analyse the steady state portion of a run, since it includes all the parameters infuuencing the system (Hernandez, 1984).
Twenty five sample points, randomly chosen from the steady state transmission region of experiment 2, run 2, gave the following values:

Average concentration	0.085 ppm
Standard deviation	0.0025 ppm
Standard deviation of the mean	5 x 10 <sup>-4</sup> ppm
Percentage of uncertanity	0.59 %

Values of the high concentration permeant stream measured with the syringe were:

Average concentration	290	ppm
Standard deviation	10.1	ppm
Standard deviation of the mean	2.02	ppm
Percentage of uncertanity	0.69	8

Values for the flow rate of the nitrogen stream sweeping the lower cell chamber were:

Average	1.74	cc/min
Standard deviation	0.03	cc/min
Standard deviation of the mean	0.006	cc/min
Percentage of uncertanity	0.34	£

APPENDIX D



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## APPENIX E

## STATISTICAL ANALYSIS

The purpose of this analysis was to determine the significance of sorbed water vapor on the permeability coefficient of acetone vapor through the amorphous nylon film.

The slope of line for the humidified experiment was compared to the slope of the line for the experiment under dry conditions from the Arrhenius plot shown in Figure 11, to see if the humidified experiment was significantly different.

H: slope of humidified experiment - slope of dry experiment

$$t = \frac{bA_1 - bB_1}{\int (SE \ bA_1)^2 + (SE \ bB_1)^2}$$
  
v = (r<sub>1</sub> - 1) + (r<sub>2</sub> -1)  
bA<sub>1</sub> = slope of line for dry experiment  
bB<sub>1</sub> = slope of line for humidified experiment  
SE bA<sub>1</sub> = slope variance for slope of line for dry experiment  
Se bB<sub>1</sub> = slope variance for slope of line for humidified experiment

BIBLIOGRAPHY

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## BIBLIOGRAPHY

- Baner, A. L., "Diffusion and Solubility of Toluene in polymeric Films", IAPRI Annual Award, 13th Annual IAPRI Symposium, Oslo, Norway (1986).
- Baner, A. L., "The Measurement and Analysis of the Diffusion of Toluene in Polymeric Films", M.S. Thesis, Michigan State University, E. Lansing, MI. (1987).
- Baner, A. L., Hernandez, R. H., Jayaraman, K., Giacin, J. R., "Isostatic and Quasi-Isostatic Methods for Determining The Permeability of Organic Vapors through Barrier Membranes", Current Technologies In Flexible Packaging. ASTM STP 912. (1986).
- Barrer, R.M., "Permeation, Diffusion and Solubility of Gases in Organic Polymer", Trans. Faraday Soc. 35: 628 (1936).
- Barrer, R.M., Barrer, J., Slater, J., "Sorption and Diffusion in Ethyl Cellulose, Part I. History - Dependence Sorption Isotherms and Permeability Rates", J. Polym. Sci. 2:315 (1958).
- Barrie, J.A., "Water in Polymers", <u>Diffusion in Polymers</u>, Edited by J. Crank and G. S. Park. Academic Press, New York, N.Y. (1968).
- Blatz, P., and Talkoesky, C., Personnel Communication. (1987).
- Boyer (ed) <u>Encyclopedia of Polymer Science and Technology</u>, Supplement No.2, J. Wiley & Sons, New York (1977).
- Chern, R.T., Koros, W.J., Sanders, E.S., and Yui, R., "Second Component" Effect in Sorption and Permeation in Glassy Polymers, J. Membrane Sci., 15 157-169 (1983).
- Crank, J., <u>The Mathematics of Diffusion</u>, 2nd Edition, Clarendon Press, Oxford, (1975).
- Crank, J., Park, G. S., <u>Diffusion in Polymers.</u> Academic Press, New York, N.Y. (1968).
- Davis, D. W., "Gas Permeability, An Isostatic Test Method", Modern Packaging. May:145, (1946).
- DeLassus, P.T., "Transport of Unusual Molecules in Polymer Films", TAPPI Proceedings. Polymers, Laminations and Coatings Conference. Sept, 1986.
- DeLassus, P.T., Tou, J.C., Babinec, D.C., Rulf, D.C., Karp, B.K., Howell, B. A. " Transport of Apple Aromas in Polymer Films", ACS Symposium Series No. 365, Food and Packaging Interactions. Ed. Hotchkiss, J. H., Dec., 1987.

- Fujita, H., "Diffusion In Polymer-Diluent Systems. Forschr. Hochpolym. Forsh. 3(9):1. (1961).
- Fujita, H., "Organic Vapors Above the Glass Transition Temperature", Ch.3 in <u>Diffusion in Polymers</u>, Crank, J. and Park, G.S. (eds.) Pg. 75. Academic Press, N.Y. (1968).
- Giacin, J. R., Gyeszly, S. W., "The Permeability of Organic Vapors Through Barrier Packaging Materials : Theoretical and Pratical Considerations." Plastic Materials in Food Packaging. Proceesings of a symposium in Polymerteknisk Selskab #2. May 5, 1981.
- Gilbert, S. G., Pegaz, D., Package Engineering, 14:661. (1969).
- Gilbert, S. G., Hatzidimitiu, E., Lai, C., Passey, N., "The Study of Barrier Properties of Polymeric Films to Various Organic Aromatic Vapors.", Instrumental Analysis of Foods, 1:405. (1983).
- Hernandez Macias, R. J. "Permeation of Toluene Vapor Through Glassy Poly(ethylene) Terephthalate Films." M.S. Thesis. Michigan State University, E. Lansing, MI. (1984).
- Hernandez, R. J. "Modeling the Sorption of Water, and the Effect of Sorbed water on the Solubility and Diffusivity of Oxygen in an Amorphous Polyamide." Ph.D. Dissertation. Michigan State University, E. lansing, MI. (1989).
- Hernandez, R. J., Giacin, J. R., Baner, A. L., "The Evaluation of The Aroma Barrier Properties of Polymer Films", J. Plastic film anf Sheeting, 2(3):187. (1986).
- Hilton, B. W., Nee, S. Y., "Permeability of Organic Vapor through Packaging Films", Ind. Eng. Chem. Prod. Res. Dev. 17(1):80 (1978).
- Ito, Y., "Effect of Water Vapor on Permeation of Gases through hydrophilic Polymers", Chem. High. Polym. (Japan) 18:158 (1961).
- Jabarin, S. A., Lofgren, F. A. "Effect of water absorption on Physical Properties of high Nitrile Barrier Polymers", Polym. Eng. Sci. 26(6):405 (1986).
- Kamiya, Y., Takahashi, F., "Effect of Water on Permeation, Diffusion and Soluton of Gas in Cellophane", J. Appl. Polym. Sci. 21:1945 (1977).
- Kunz, W. B., Cornwell, R. T. K., "Oxygen Permeability of Cellophane", TAPPI 45(7):583 (1962).

Lebovits, a., "Permeability of Polymers to Gases, Vapors and Liquids",

Modern Plastics. 43:139. (1966).

- Liu. K., "Evaluation of the Effect of Relative humidity on the Permeation of Toluene Vapor Through Barrier Films", M.S. Thesis, Michigan State University, E. Lansing, MI. 1986.
- Long, F. A., Thompson, L. J., "Water Induced Acceleration of the Diffusion of Organic Vapors in Polymers", J. Polym. Sci. 8:321 (1953).
- Long, F. A., "Diffusion of Water Vapor in Polymers", J. Polym. Sci. 15:413 (1955).
- Mears, P., "The Diffusion of Gases through Polyvinyl Acetate", J. Am. Chem. Soc. 76:3415 (1954).
- Mears, P., Diffusion of Allyl Chloride in Polyvinyl Acetate Part I. The Steady State of Permeation", J. Polym. Sci. 27:391 (1958a).
- Mears, P., Diffusion of Allyl Chloride in Polyvinyl Acetate Part I. The Transient State of Permeation", J. Polym. Sci. 27:405 (1958b).
- Mears, P., <u>Polymers: Structure and Bulk Properties</u>, Van Nostrand & Co. LTD, London. (1965a).
- Mears, P., "Transient Permeation of Organic Vapors through Polymer Membranes", J. Appl. Polym. Sci. 9:917 (1965b).
- Meyer, J. A., Rogers, C., Stannett, V., Szwarc, M., "Studies in the Gas and Vapor Permeability of Plastic Films and Coated Papers, Part III." The Permeation of mixed Vapor and Gases. TAPPI 40(3):142 (1957).
- Michaels, A.S. and Parker, G.J., J. Polym. Sci. 41:53 (1959).
- Murray, L. J., Dorschner, R. W., "Permeation Speeds Tests, Aids choice of Exact Material", Package Engineering, 76, March, 1983.
- Niebergall, W., Humeid, A., Blochl, W., "The Aroma Permeability of Packaging Films and its Determination by means of a newly Developed Measuring Apparatus", Lebensm-Wiss U. Tecnol. 11(1):1 (1978).
- Notley, N. T., "Permeability of Oxygen of Cellophane Laminates", J. App. Chem. (London), 13:107 (1963).
- Pasternack, R. A., Schimsheimer, J. F., Heller, J., "A Dynamic Approach to diffusion and Permeation Measurement", J. Polymer Sci. Part A-2, 8:467, (1970).

Petrak K., Pitts, E., "Permeability of Oxygen through Polymer II, The

Effect of Humidity and Film thickness on the Permeation and Diffusion Coefficients", J. Appl. Polym. Sci. 25:879 (1980).

- Pilar, F. L., "The Flow of Gases through High Polymer Films in Equilibrium with Sorbed Vapors", J. Polym. Sci. 45:205 (1960).
- Prager, S., Long, F. A., "Diffusion of Hydrocarbons in Polyisobutylene", J. Am. Chem. Soc. 73:4072 (1951).
- Pye, D. G., Hoehn. H. H., Panar, M., "Measurement of Gas Permeability of Polymers II. Apparatus for Permeabilities of Mixed Gases and Vapors", J. Appl. Polym. Sci., 20:287 (1976).
- Rodriguez, F., <u>Principles of Polymer Systems</u>, McGraw-Hill Book Co., N.Y., (1970).
- Rogers, C. E., Meyer, J. A., Stannett, V. T., Szwarc, M., "Studies in the Gas and Vapor Permeability of Plastic Films and Coated Papers Part I. Determination of the Permeability Constant. TAPPI, 39(11):737 (1956a).
- Rogers, C. E., Meyer, J. A., Stannett, V. T., Szwarc, M., "Studies in the Gas and Vapor Permeability of Plastic Films and Coated Papers Part I. Some Factors Affecting the Permeability Constant. TAPPI, 39(11):741 (1956b).
- Rogers, C. E., Permeability and Chemical Resistance of Polymers. Ch 9 in <u>Engineering Design for Plastics.</u> Baer, E. (ed) Rheinhold, N.Y. (1964).
- Rogers, C. E., Solubility and Diffusivity. Ch 6 in <u>Physics and Chemistry</u> <u>of the Organic Solid State Vol 2</u> Fox, D., Labes, M. M. and Weissberger, A. (ed.) J. Wiley & Sons. N. Y. (1965).
- Shirakura, A., "The Effect of Temperature on the Diffusion of Ethyl Acetate through Oriented Polyethylene Terephthalate Films of Varying Thermomechanical History", M.S. Thesis. Michigan State University, E.Lansing, MI. (1987).
- Simril, V. L., Smith, S. E., "Sorption of Water by Cellophane", Ind. Eng. Chem. 34:226 (1942).
- Simiril, V. L., Hershberger, A., "Permeability of Polymeric Films to Gases", Mod. Plast., 22(11):155 (1944).
- Stannett, V., Hopfenberg, H. B., Petropoulos, J.H., Diffusion in Polymers. Ch 8 in <u>Macromolecular Science</u>, Baum, C. E. (ed). (1972).

Van Amorengen, G.W., J. Appl. Phys. 17:972 (1946).

- Watt, I. C., "Determination of Diffusion Rate in Swelling Systems", J. Appl. Polym. Sci., 8:2835 (1964).
- Yasuda, H. and Rosengren, K., "Isobaric Measurement of Gas Permeability in Polymers", J. Appl. Polym. Sci. 11(14):2839 (1970).
- Ziegel, K. D., Frensdorff, H.K., blair, D. E., "Measurement of Hydrogen Isotope Transport in Polyvinyl Flouride Films by Permeation Rate Method", J. Polymer Sci., A2. 7:809 (1969).
- Zobel, M. G. R., "Measurement of Odor Permeability of Polypropylene Packaging films at Low odourant Levels." Polymer Testing, 3: 133 (1982).
- Zobel, M. G. R., "The Odor Permeability of Polypropylene Packaging Film." Polymer Testing, 5:153 (1985).

