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EVALUATION OF THE EFFECT OF RELATIVE HUMIDITY ON THE PERMEATION OF TOLUENE VAPOR THROUGH BARRIER FILMS

By Kenny Jae-Kae Liu

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To My Parents and Lovely Wife

ABSTRACT

EVALUATION OF THE EFFECT OF RELATIVE HUMIDITY ON THE PERMEATION OF TOLUENE VAPOR THROUGH BARRIER FILMS

By Kenny Jae-Kae Liu

The effect of relative humidity on the diffusion of toluene vapor through a multi-layer coextrusion film structure containing moisture sensitive hydrophilic barrier layers (i.e. nylon and EVAL) was evaluated. Two experimental test methods were developed. In method I, the effect of relative humidity on the diffusion of toluene vapor was evaluated, when the test film was preconditioned to a fixed water activity prior to test. In method II, the effect of water vapor as a co-permeant was evaluated. Studies carried out by method I showed the concentration dependency of the diffusion process and the importance of relative humidity on the diffusion of organic vapor through barrier structures. Water vapor was found to exhibit strong interactive effects with the moisture sensitive polymer layers of the laminate which resulted in an increase in the diffusion of toluene vapor through the barrier structure.

When the effect of water vapor as a co-permeant was evaluated (method II), the direction of permeation(i.e. surface exposed to high relative humidity and vapor concentration) markedly influenced the resultant barrier properties.

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INTRODUCTION

Due to considerations of convenience and economy, polymeric packaging materials are increasingly put to use for all kinds of food products through storage and distribution and estimates for future usage show continued growth. Knowledge of the transmission rates of permeants such as carbon dioxide, oxygen and water vapor through polymeric packaging films have been utilized in selecting packaging systems which would prevent or inhibit deterioration of food products.

In contrast to the extensive studies conducted on the permeability of non-interactive gases (i.e. oxygen) and water vapor through plastic packaging films, data describing the permeability of organic vapors are limited. 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 transport properties of polymeric packaging systems to organic vapors and aroma constituents. For food products packaged in polymeric materials, the permeability of the packaging system with respect to organic vapors becomes increasingly more important, as the loss of specific aroma constituents or the gain of unexpected odors, as a result of diffusion during storage or distribution, can result in product quality loss.

The permeation studies here are designed to develop a better understanding of the effect of factors such as water vapor (or relative humidity) on the diffusion of organic vapor molecules through polymer film samples. Specifically, the diffusion of organic vapors through a coextrusion structure containing moisture sensitive layers (i.e. nylon and ethylene-vinyl alcohol copolymer (EVAL)) was evaluated at low penetrant levels (i.e. below 100 ppm, wt/v). The studies on the test film have both practical and theoretical importance. The effect of water vapor on the permeation rate (P), permeability constant ($\bar{P}$) and lag time (Θ) was also determined.

LITERATURE REVIEW

5-1 Permeation Theory

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). Permeability is often referred to as the ease of transmission of the penetrants (i.e. gases, vapors or liquids) through some resisting material without consideration of the actual mechanism involved. The transmission mechanism of gases or vapors through homogeneous amorphous plastic materials is the activated diffusion type, i.e., a process in which the gas or vapor dissolves into the polymer at the inflow surface, diffuses through the polymer under a concentration gradient, and evaporates from the surface at the lower concentration (Stannett, Yasuda 1965). The diffusion flow or flux, F , of a substance in a mixture with other substances is defined as the amount passing during unit time through a surface of unit area normal to the direction of flow, independent of the state of aggregation of the mixture. This is described by the expression,

$$F = Q/A \cdot t \qquad (1)$$

Where Q is the total amount of substance which has passed through area A during time t. The mathematical theory of diffusion is based on the hypothesis that the rate of transfer of a diffusing substance through a unit area of a section is proportional to the concentration gradient measured normal to the section. This can be expressed by Fick's law (Crank, 1975):

$$F = -D \cdot (dc/dx) \qquad (2)$$

Where D is the diffusion constant, and dc/dx is the concentration gradient in the direction of flow. If D is independent of the concentration, this expression may be integrated to give:

$$F = D \cdot (C1 - C2)/L \qquad (3)$$

Where C1 and C2 are the steady state concentrations of gas in the inflow and outflow surfaces of the film and L is the film thickness.

The gas concentrations (i.e. C1 and C2) are usually expressed in terms of the pressure, p, of the gas above each surface. These quantities may be related to Henry's law (equation 4) which describes a linear relationship between the concentration of the penetrant in the polymer and the penetrant concentration in the gas or vapor phase in contact with the polymer.

$$C = p \cdot S \tag{4}$$

Where p is the concentration of permeant in the gas phase, S is the solubility coefficient for the particular gas or vapor in the polymer and C is the concentration of the penetrant in the polymer.

Substitution into equation (3) yields:

$$F = D \times S\ (p1 - p2)/L = \overline{P} \cdot (p1 - p2)/L \tag{5}$$

Where $\overline{P} = D \times S$ is usually referred to as the permeability constant. This value is a constant at a given temperature when Henry's law is obeyed, and when the diffusion constant is independent of the gas concentration. However, if Henry's law is not obeyed , or if the diffusion process is concentration dependent, P is no longer constant and the flux (F) depends nonlinearly on the pressure difference (Barrer 1939).

Many techniques have been used to measure the transmission rate of low-molecular-weight penetrants through a polymer film which forms a partition between two test chambers (Barrer, 1958; Newns, 1950; Rogers, 1956a; Hilton and Nee, 1979; Zobel, 1982). One chamber usually is initially free of penetrant. Most of the methods for determining the amount of penetrant which has passed through the film in unit time involve measuring the concentration of the substance as a function of time. Several of the more common experimental methods have for initial conditions the relationship, $p1 > p2 = 0$, so that Q/t can be calculated from $p2/t$, obtained from a plot of the pressure increase at the low pressure side versus time. The permeability constant then is calculated as,

$$\bar{P} = Q \cdot L/t \cdot A \cdot p1 \qquad (6)$$

Where Q is the quantity of gas at STP which has permeated in the time interval t during steady-state flow, A is the effective area of the film, and L is the average film thickness. Typical units for the permeability constant are cubic centimeters of gas at standard temperature and pressure passing per second through a 1 sq. m area of a film 1 mil thick, when the pressure differential across the film is 1 atm.

When a penetrant diffuses through a film, there is an interval from the time the penetrant first enters the film until the steady state of flow is established. The intercept on the time axis of the extrapolated linear steady-state portion of the curve is called the lag time (Θ) (see Figure 1). Using appropriate solutions of the diffusion

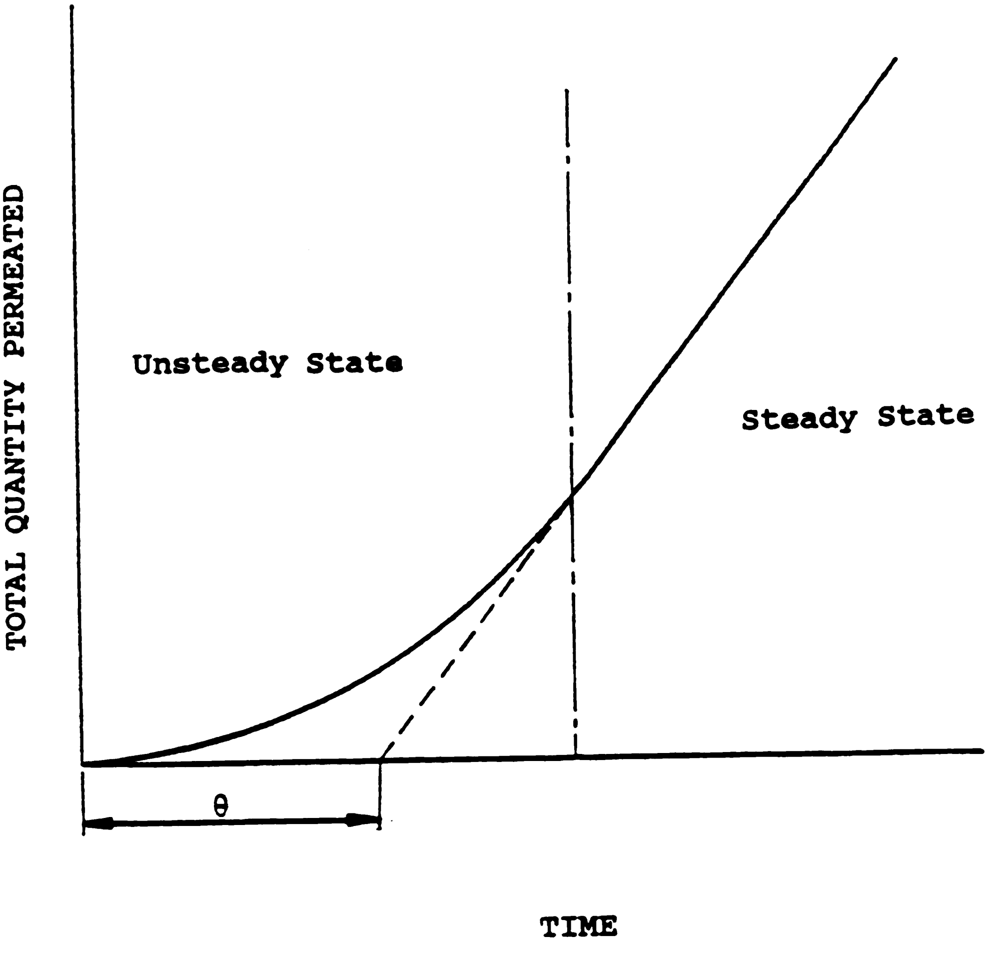


Figure 1 TRANSMISSION RATE PROFILE

equation, Barrer (1939) has shown that the time lag is directly related to the diffusion coefficient D. Using a pressure increase method or other appropriate techniques, data pertaining to the rate of attainment of steady-state flow can be readily obtained. The steady state measurements serve to determine the permeability constant $\bar{P}$, and the corresponding time lag from the same experiment serves as a means for calculation of D. Since $\bar{P}$ is defined as the product of D x S, the solubility coefficient S can also be calculated as the quotient, $\bar{P}/D$. This general method for the estimation of D and S from permeation time lag data is very convenient and is capable of giving accurate estimates of D and S for non-interactive penetrants (Crank 1975). In a typical experimental case (Rogers et al. 1956b), the film is initially free of penetrant, and diffusion flux occurs through the film into a reservoir of essentially zero concentration of penetrant, so that,

$$\theta = L^2 / 6 \cdot D \qquad (7)$$

5-2 The Effect of Penetrant Concentration on the Permeability of Organic Vapors

The diffusion of organic vapors in polymers differs from that of simple gases (i.e. helium, hydrogen, oxygen). For organic vapors, the diffusion coefficient (D) at a given temperature is not constant as in simple gases but is an increasing function of penetrant concentration (Pace et al., 1979).

Several investigations have shown that the diffusion of simple gases (i.e. helium, argon, oxygen and hydrogen) in rubber (Barrer, 1939) and plastics (Reitinger, 1944) obeys Henry's law, with a diffusion coefficient independent of concentration. The ideality of the diffusion process with simple gases is due to their relative insolubility, so that at ordinarily accessible concentrations the quantity of gas dissolved in the polymer is insufficient to alter its properties to any observable extent and encounters between gas molecules within the polymer are rare (Meares, 1954). This contrasts with the behavior of organic vapors which have strongly concentration-dependent diffusion coefficients. Several investigations of the diffusion of organic vapors in polymers have established that in most systems the diffusion process is strongly dependent on the concentration of the penetrants in the polymer (Barrer, 1957; Prager et al, 1951; Meares, 1958).

Meares (1965) indicated that organic vapors are usually freely absorbed by polymers, and the absorbed molecules diffuse by a random exchange of vapor causing the polymer to swell and to change the configuration of the polymer molecules. These configurational changes are not instantaneous : they are controlled by the retardation time of the chains. If these are long, stresses may be set up which relax slowly. Thus, the absorption of a vapor is accompanied by time-dependent processes in the polymer which are slower than the micro-Brownian motion which promotes diffusion.

There are a number of literature references describing the phenomenon of the concentration dependent permeation of organic vapor through barrier films. Zobel (1982) described such finding in studies carried out on the diffusion of benzyl acetate through coextruded oriented polypropylene and Saran coated oriented polypropylene, at various penetrant concentrations. Baner (1985) in studies carried out with toluene vapor with a Saran and with a Saran coated-oriented polypropylene found similar results, with the permeability constant ($\overline{P}$) increasing with an increase in penetrant concentration. Figure 2 shows a plot of the

permeability constant ($\bar{P}$) as a function of toluene vapor concentration for polypropylene, Saran, and Saran-coated polypropylene and illustrates such a concentration dependency.

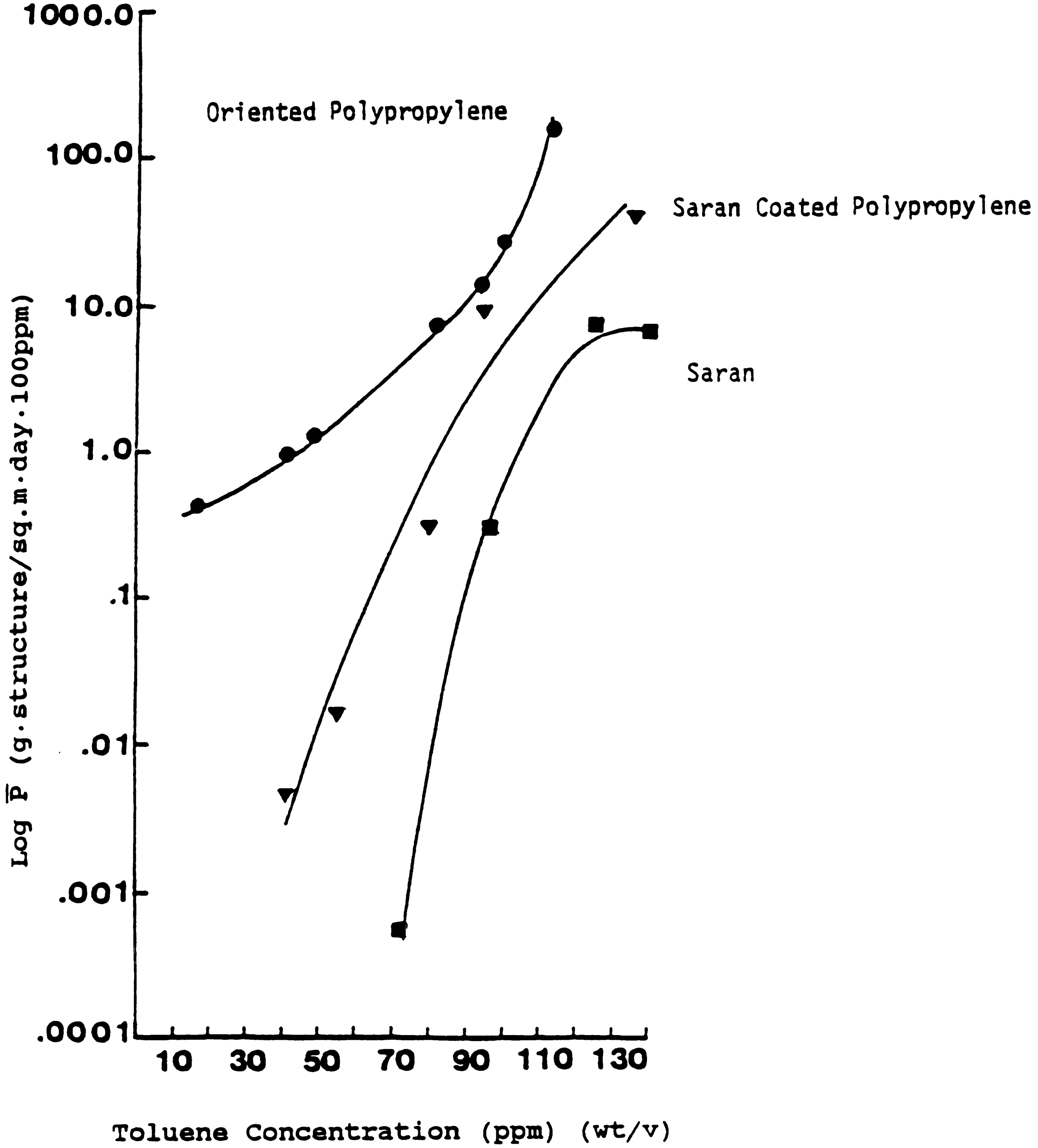


Figure 2 THE EFFECT OF TOLUENE VAPOR CONCENTRATION ON THE Log $\overline{P}$ FOR POLYPROPYLENE, SARAN AND SARAN-COATED POLYPROPYLENE (Baner, 1985)

5-3 The Effect of Water Vapor on the Permeability of Permeant Gas and Organic Vapor through Barrier Films

The presence of water vapor often accelerates the diffusion of gases and vapors in polymers with an affinity for water (Barrie, 1968).

The effect of water vapor on the gas transmission for a large number of polymer-gas systems has been studied by Simril and Hershberger (1944). The results obtained with nylon, at varying relative humidities, have shown that the presence of water vapor can markedly affect the rate of transmission of various gases such as nitrogen, oxygen and carbon dioxide.

The effect of relative humidity on the permeability of nitrogen, oxygen and carbon dioxide through polyethylene (PE), polyethylene terephthalate (PET) and the hydrophilic film , nylon 6 was studied by Meyer et al.(1957). These investigators found little effect of relative humidity on the gas permeability of PE and PET films(Table 1).

Table 1 The effect of Water Vapor on Gas Transmission at $30^\circ C$. (Meyer et al, 1957)

Film	Gas	RH%	$\bar{P}$ (cc·mm / sq. cm·sec·cmHg)
PE	Nitrogen	0	2.1
		36	2.1
		56	2.2
		63	2.6
	Oxygen	0	6.6
		32	6.2
		66	6.6
	Carbon Dioxide	0	26
		35	26
		61	28
PET	Nitrogen	0	5.9×10^{-3}
		35	6.0×10^{-3}
		61	6.1×10^{-3}

The results obtained for nylon 6 with carbon dioxide as the penetrant are given in Table 2. It is interesting to note that for the hydrophilic film the transmission rate of gases increases with an increase in relative humidity.

Table 2 The Effect of Water Vapor on Gas Transmission Through Nylon 6 Film At 25°C (Meyer et al. 1957)

Film	Gas	%RH	$\overline{P}$(cc·mm / sq. cm·sec·cmHg)
Nylon 6	Carbon Dioxide	0	0.12
		42	0.17
		97	0.28
		100	0.28

Pilar (1960) also found that an increase of relative humidity from 0 to 100 % RH resulted in a 200-fold increase in the permeation constant of cellophane to oxygen. Figure 3 showed the profound effect of relative humidity on the permeability constant of oxygen through cellophane. As shown, at a relative humidity range of 70-80%, the permeability constant increases in an exponential manner. This corresponds to the results of Simril and Smith (1942) who showed that around this value of relative humidity, the mechanism of water sorption appears to be changing and is accompanied by extensive structural changes within the polymer. Similar studies were carried out by Kunz and Cornwell (1962) who found that an increase in the relative humidity caused an increase in permeability of oxygen through cellophane films.

In general, polymers which swell greatly in water

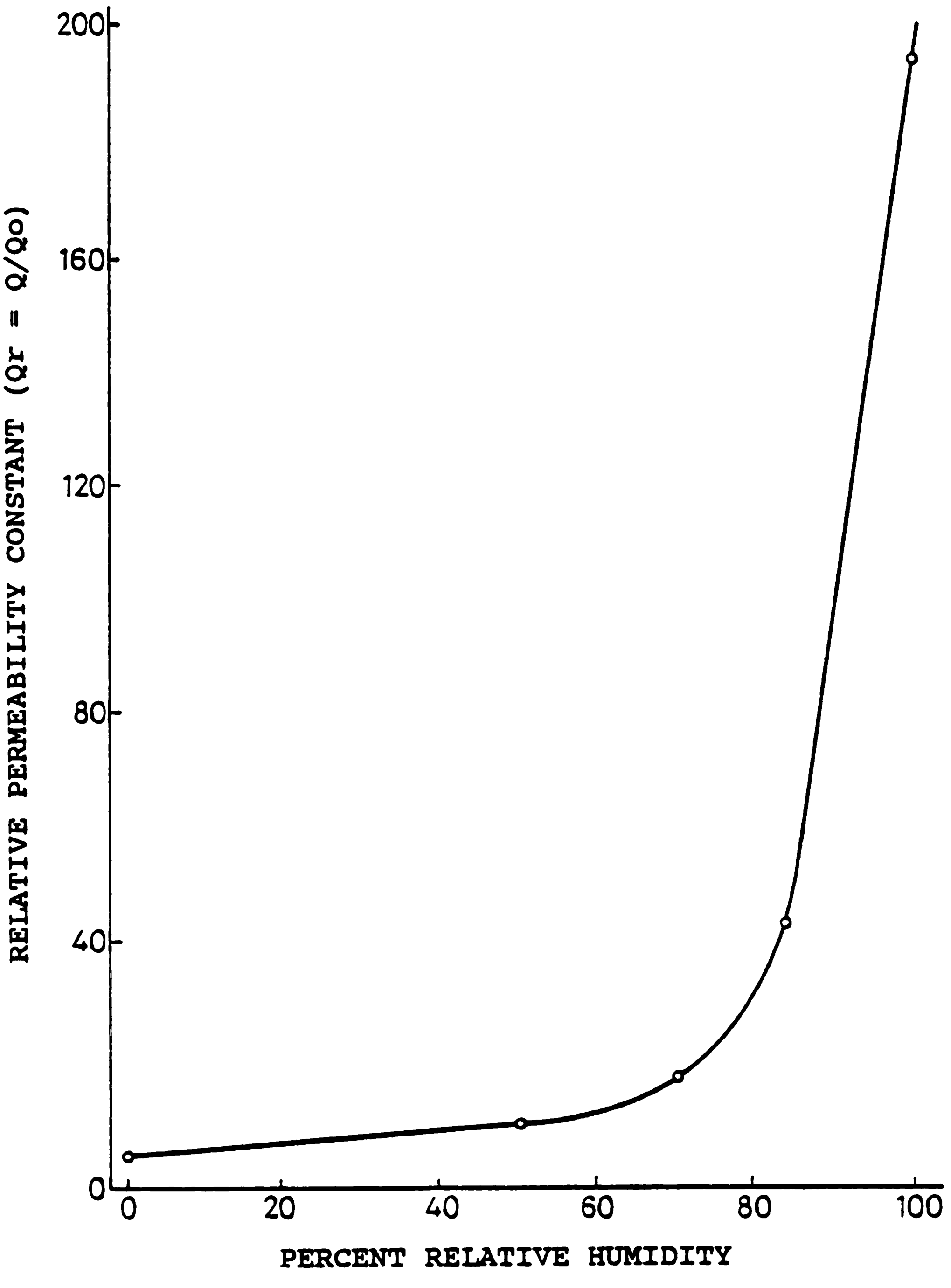


Figure 3 THE RELATIVE PERMEABILITY CONSTANT OF CELLULOSE FILMS AT 25 °C TO OXYGEN AS A FUNCTION OF RELATIVE HUMIDITY. (Pilar, 1960)

Q = $\bar{P}$ at a given relative vapor pressure
Qo= $\bar{P}$ of the dry film

will always show increasing diffusivity with increasing relative humidity.

For nylon and polyvinyl alcohol (PVOH) this is illustrated by the results of Ito (1961), summarized in Table 3. It is apparent that when water is highly sorbed, as in nylon 6 and polyvinyl alcohol, the film is plasticized by the water, which leads to greatly increased permeability rates. Crank and Park (1968) also indicated that the addition of water vapor, like the addition of a plasticizer to a polymer, decreases the cohesive forces between the polymer chains resulting in an increase in polymer chain segmental mobility.

Jabarin and Lofgren (1986) found that water absorbed by high barrier acrylonitrile-based polymers influences both mechanical and thermal properties of the polymers. They proposed that water decreases the effectiveness of the intermolecular forces in the polymer, and therefore reduces the rigidity of the three dimensional structure. The plasticizer (water) then reduces the polymer intermolecular forces by neutralizing the polymer polar groups with its own polar group or by increasing the distance between polymer molecules. This suggests that the glass transition temperature (Tg) is then greatly reduced. The reduction in Tg is directly proportional to the amount of absorbed water. It is clear that this should result in an increased rate of diffusion and a lower activation energy for the diffusion process.

Table 3 The Effect of Relative Humidity on the Diffusion of Gases in Polymers (Ito, 1961)

Polymer	Gas	T (°C)	%RH	$\bar{P} \times 10^{11}$ (a)
Nylon 6	Carbon Dioxide	30	0	1.0
		30	44	1.7
		30	95	2.9
Polyvinyl Alcohol	Carbon Dioxide	23	0	0.01
		23	84	52
		23	94	119

(a) $\bar{P}$ = cc·(STP)/sq. cm · sec·cmHg

Notley (1963) has also measured the effect of water vapor on the oxygen permeability of cellophane laminates. Similarly, large increases in the permeability of oxygen through the cellophane laminates were obtained when water was present (see Figure 4). Notley proposed that water vapor causes swelling of the cellophane structure and consequently increases the permeability of gases through cellophane films. Kamiya and Takahashi (1977) used a laminate composed of cellophane and a hydrophobic polymer film (i.e. polyethylene) for studying the permeability of moistened cellophane to gases. They found that the effect of water vapor on the films permeability, as shown in Figure 5,

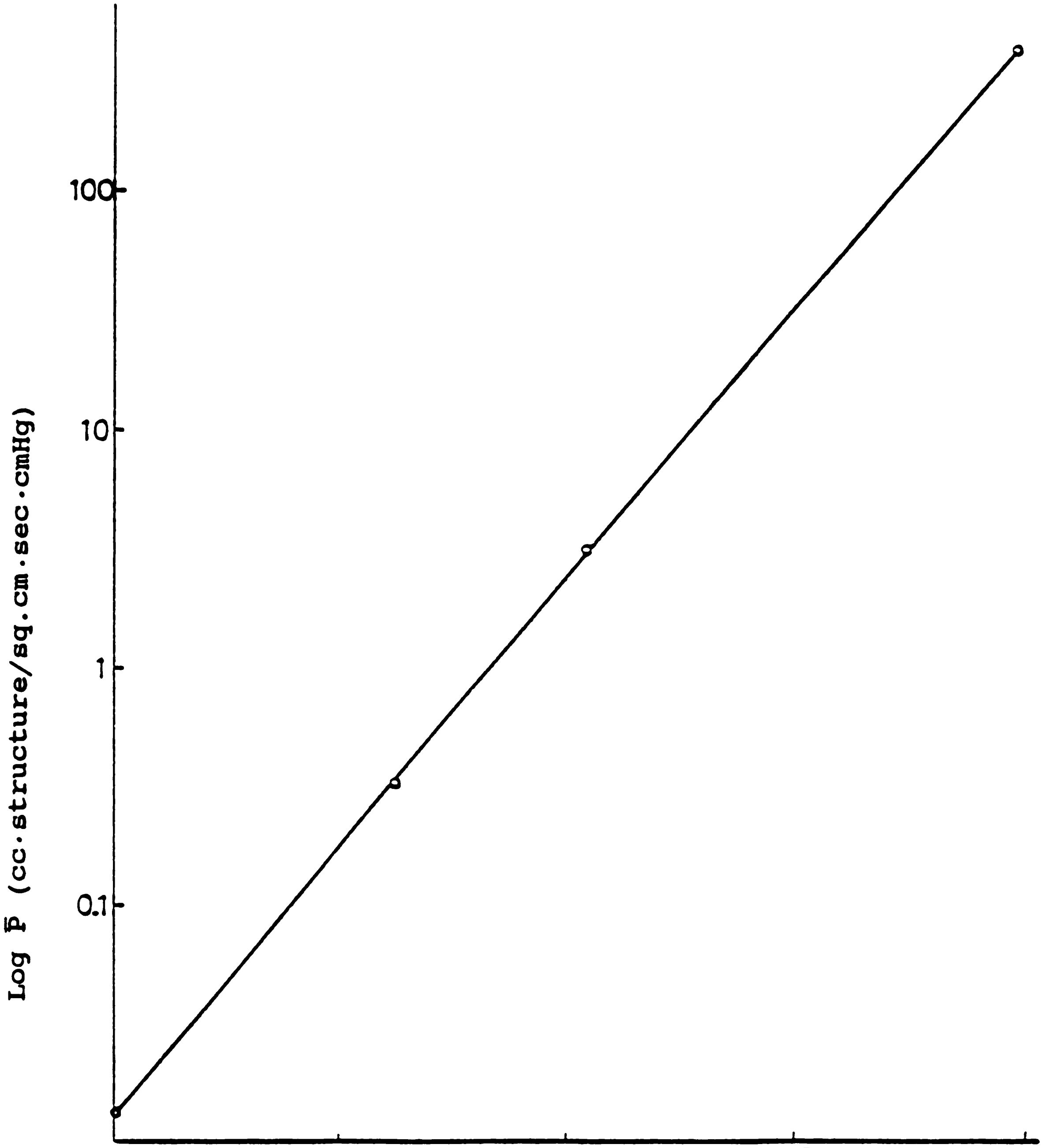


Figure 4 PERMEABILITY AS A FUNCTION OF RELATIVE HUMIDITY FOR POLYTHENE/CELLOPHANE/NITROCELLULOSE. (Notley, 1963)

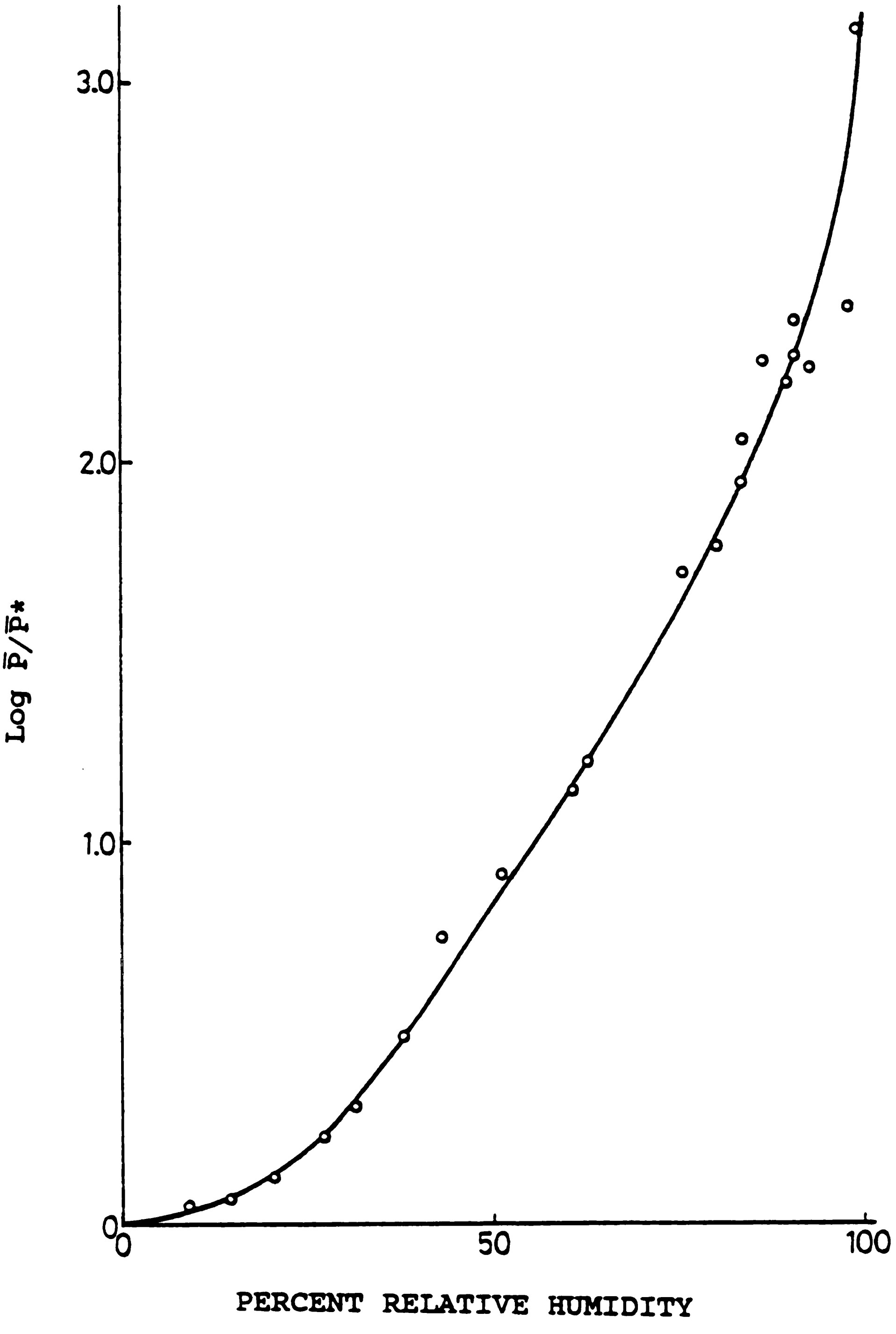


Figure 5 RELATIVE PERMEABILITY OF CELLOPHANE TO HYDROGEN AS A FUNCTION OF RELATIVE HUMIDITY. (Kamiya & Takahashi, 1977)

$\bar{P}$ = PERMEABILITY COEFFICIENT AT VARYING RH
$\bar{P}*$= PERMEABILITY COEFFICIENT AT 0% RH

was very similar to the effect obtained by Pilar (1960). Also, Petrak et al. (1980) measured oxygen permeability through a number of hydrophilic films (i.e. polyacrylic acid, polyvinyl alcohol, carboxylcellulose, etc.) at varying relative humidities. They reported a similar effect, namely a large increase in the permeability coefficient is observed because of the plasticizing effect of water on hydrophilic polymers.

Long and Thompson (1953, 1955) found that organic vapor diffused more rapidly into polymers containing sorbed water vapor than into the dry polymer, provided the polymer absorbed water to an appreciable extent. They point out that the most plausible explanations for the accelerating effect of water vapor are : (a) the water vapor diffuses rapidly into the polymer and (b) water present in the polymer acts as a plasticizer and leads to a higher diffusion coefficient for the organic vapor than would be found for the dry polymer.

Watt (1964) has determined the rates of diffusion of ethyl alcohol in keratin at various level of swelling with the use of water vapor as a swelling agent. He showed that swelling of the polymeric material by water vapor resulted in an increase in the rate of diffusion of the ethyl alcohol. A plot of calculated diffusion coefficients as a function of the percentage volume swelling is shown in Figure 6.

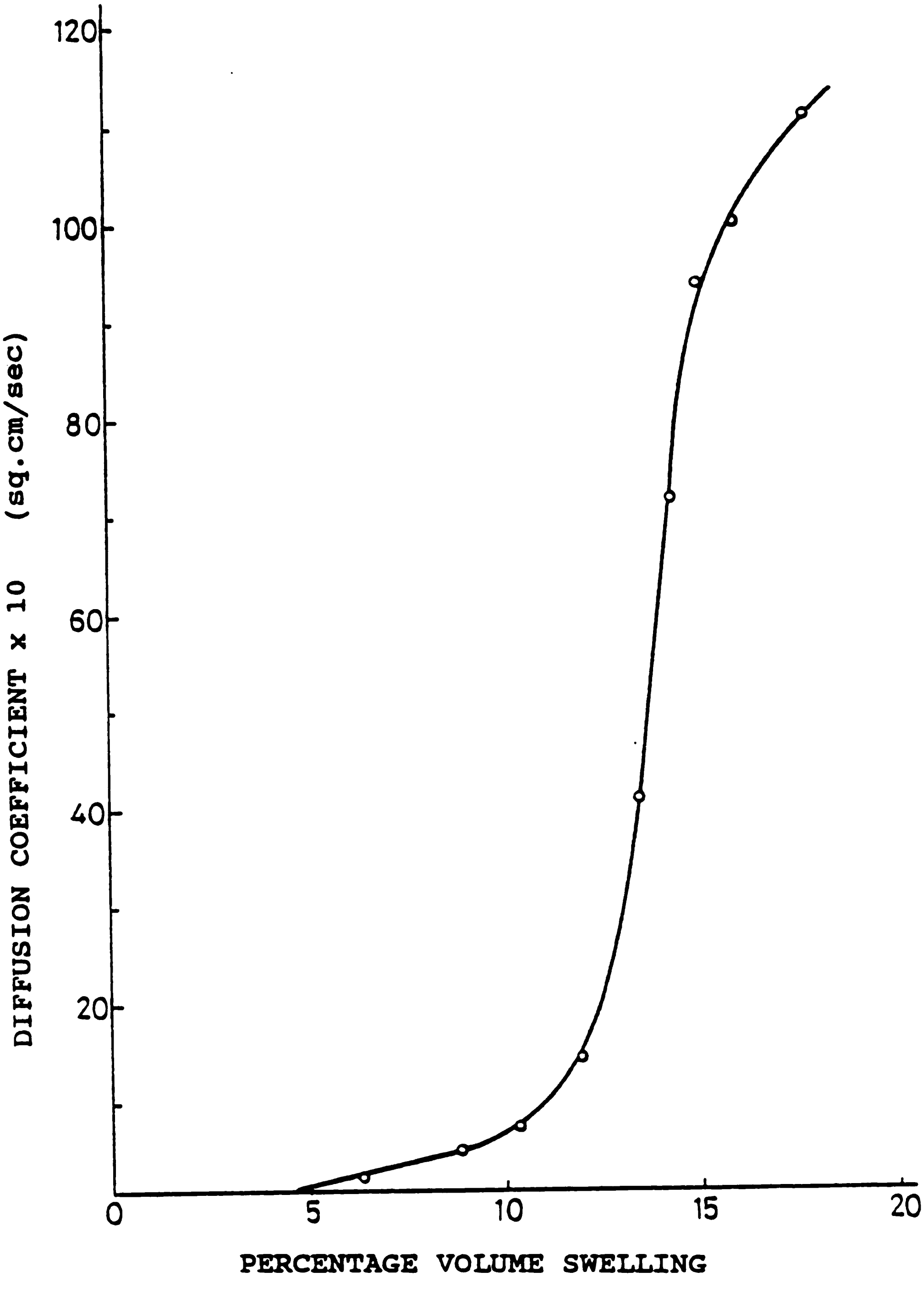


Figure 6 DIFFUSION COEFFICIENT OF ETHYL ALCOHOL IN KERATIN AT 35 °C AS A FUNCTION OF VOLUME SWELLING. (Watt, 1964)

Different results were obtained by Pye et al. (1976) who found that water vapor reduced the permeability of gases through amorphous aromatic polyimides. The experimental data indicated that there was a significant reduction in the permeability of methane and hydrogen gases through wet films, relative to the dry structure. A possible explanation for the observed permeability reductions is that a small amount of water binds to active sites (Carbonyls) within the polymer bulk phase which effectively reduces the microvoid content of the films and the available diffusion paths for the nonreactive gases. Such interaction may also reduce the solubility of the penetrant at elevated relative humidity levels.

It has long been known qualitatively that the presence of water vapor can have a marked accelerating effect on the rate of diffusion of organic vapors in certain polymers (Long et al., 1953; Praeger et al., 1951). However, there is a paucity of literature data available which describes in detail the effect of water vapor upon the permeability of organic vapors through polymeric materials and elucidates the mechanism of the effect of water vapor on the barrier properties of multi-layer laminate structures containing a hydrophilic barrier layer.

MATERIALS AND METHODS

Film Sample :

Barrier film to be tested was supplied by the Cryovac Division of W. R. Grace & Company (P. O. Box 464, Duncan, SC 29334), coextrusion film sample FDX 1570 (100 gauge film, PE/nylon/EVAL/nylon/PE). The diagram of the cross section view of the coextrusion film is presented in Appendix A.

Toluene :

Toluene with purity greater than 99.8%, boiling point of 110-110°C, from Burdick and Jackson Laboratory Inc. was used as the permeant.

Nitrogen :

High purity dry nitrogen 99.98% was provided by Union Carbide Corporation, Linde Division, Daudery, Connecticut.

6-1 Analytical

Analysis for penetrant concentration was based on a gas chromatographic procedure. In all cases, a standard curve of response vs. penetrant concentration was constructed from standard solutions of known concentration. The penetrant concentration was determined by reference to the calibration curve. Analyses were carried out on a Hewlett Packard Model 5890 Gas Chramatography, equipped with flame ionization detection. The gas chromatographic conditions are presented below :

Injection Temperature: 200°C
Column Temperature: 125°C
FID Temperature: 350°C
Area Reject: 0
Carrier Gas Flow Rate: 30 cc/min (Nitrogen)
Column: 6'x 1/8" O.D. stainless steel, packed with 5% SP2100 on 100/120 mesh Supelcoport (Supelco, Inc. Bellfonte, PA)

To elute toluene at 0.56 min.

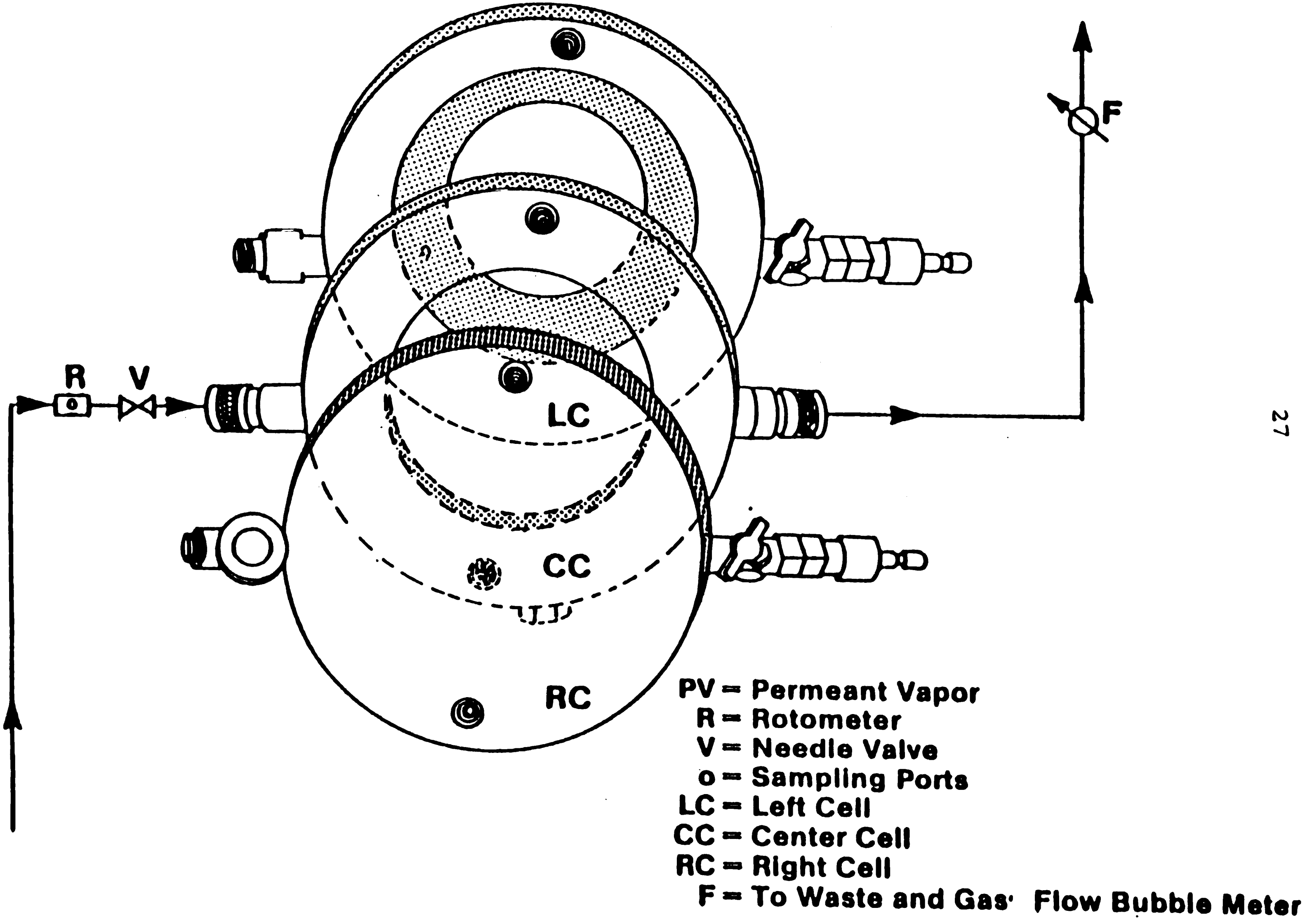
6-2 Procedure

Two test methods were developed for considering the effect of water vapor on the diffusion of organic vapor through barrier films. In Method I, the effect of relative humidity on the diffusion of organic vapor through barrier membranes is considered and the film to be tested is preconditioned to the required relative humidity employing a preconditioning system prior to test. In Method II, the effect of water vapor as a co-permeant on the diffusion of organic vapor is evaluated. In both methods, analysis is based on an accumulation or quasi-isostatic procedure and utilizes gas chromatographic analysis for quantifying the amount of organic vapor that permeated through the film sample.

The permeability cells are of our own design and are constructed of either stainless steel or aluminum; the cells are composed of two cell chambers and a hollow center ring. A schematic diagram of the permeability cell is shown in Figure 7. The right and left cell chambers each have a volume of 50 cc, while the volume of the center cavity is approximately 50 cc. In operation, the test films are placed in the cell so that the film effectively isolates the center cell chamber (i.e. the high concentration cell chamber) from the low concentration cell chambers. Hermetic isolation is achieved by the compression of overlapping Viton "O" rings on the film specimen. Viton is a fluorocarbon elastomer which is resistant to attack and swelling by most organic vapors. As shown in Figure 7, both cell chambers and the center ring are equipped with inlet and outlet valves and a sampling port. The films to be tested are mounted in the permeability cell and the cell assembled. A constant low partial pressure of permeant vapor, adjusted to the desired relative humidity, is then flowed continuously through the cell chamber. This allows the permeability of two film specimens to be determined concurrently under identical conditions.

Figure 8 presents a schematic diagram of the permeation test apparatus designed for this study. As shown, to perform multiple runs concurrently, a series of four cells can be attached to a dispensing manifold. This allows

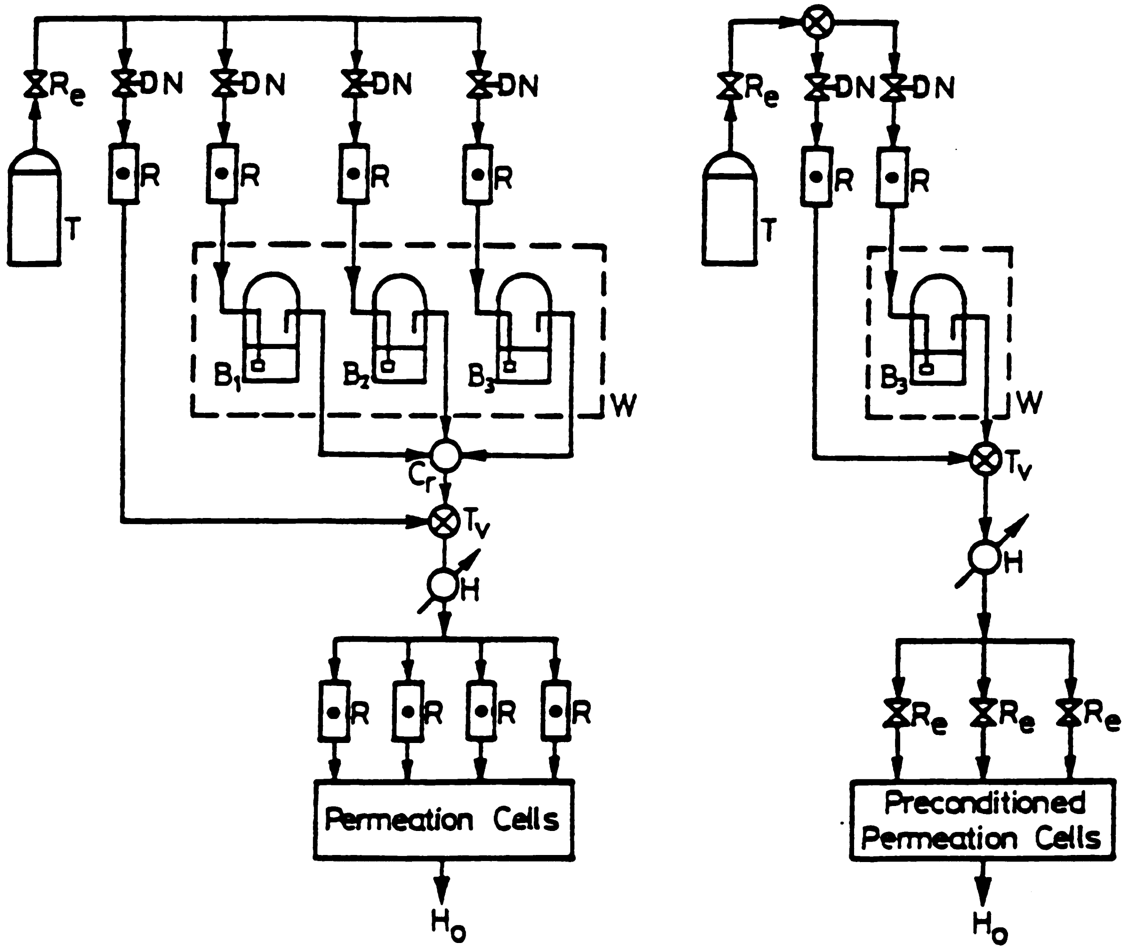
Figure 7 PERMEATION CELL SYSTEM



delivery of a constant concentration of permeant vapor to each cell. To deliver a constant low partial pressure of humidified permeant vapor to the permeability cells, a vapor generator system was designed. As illustrated in Figure 8, the vapor generator system consisted of three gas washing bottles with fritted dispersion tubes, connected as shown. One gas washing bottle (B1) contained the pure organic liquid penetrant. A second gas washing bottle (B2) was filled with a mixture of distilled water and the organic liquid penetrant. Gas washing bottle B3 contained pure distilled water. Flow meters were used to provide a continuous indication that a constant rate of nitrogen flow was maintained through the respective gas washing bottles. Gas flows were regulated with NU PRO needle valves, type B-2SG. When the vapor generator system is assembled as shown, this design allows for evaluation of the diffusion of organic penetrants over a broad range of organic vapor concentrations and relative humidity values. To obtain a lower than saturation concentration of penetrant vapor, the humidified organic vapor stream is mixed with another stream of pure carrier gas (nitrogen). The vapor generator system was mounted in a constant temperature water bath maintained at 1°C above ambient temperature so as to avoid condensation after the permeant vapor stream passed through the glass reservoirs.

For studies carried out to evaluate the effect of

SCHEMATIC OF PERMEATION TEST APPARATUS FOR EVALUATING THE EFFECT OF RELATIVE HUMIDITY ON THE PERMEATION OF ORGANIC VAPOR



(a) (b)

B_1-Organic vapor bubbler
B_2-Organic/water vapor bubbler
B_3-Water bubbler
C_r-Four way valve
H - Hygrometer
H_o-Hood

N - Needle valve
R - Rotameter
R_e-Regulator
T - Nitrogen tank
T_v- Three way valve
W - Water bath

Figure 8

relative humidity on the diffusion of organic vapor through a barrier film, the film samples to be tested were preconditioned to the required relative humidity employing a preconditioning system (see Figure 8). To precondition the test films, the film samples are mounted in the permeability cells and are equilibrated to the required relative humidity by continuously flowing a humidified nitrogen stream through the test cell for a period of time (i.e. approximately 1-2 weeks) considered appropriate to have equilibrated the film to the surrounding relative humidity level. The permeation cells containing the preconditioned film samples are then removed from the preconditioning system and affixed directly to the permeability test apparatus. The organic vapor stream which is flowed continuously through the high concentration cell chamber is adjusted to the same relative humidity to which the film sample was preconditioned and the rate of diffusion of the organic penetrant determined by the lag time diffusion method. In this study, the high and low concentration cell chambers and the test film are maintained at a constant relative humidity throughout the period of test.

To evaluate the effect of water vapor as a co-permeant in the diffusion of organic vapor through barrier membranes (i.e. Method II), the film sample to be tested is stored over a desiccant prior to initiating the permeability studies. The film sample is then mounted in the permeability cell and the cell affixed to the organic vapor permeability test apparatus. The organic vapor stream, adjusted to the desired relative humidity, is then flowed continuously through the high concentration cell chamber of the permeation cells. Again, the permeation rate through the film, under the test conditions of a fixed relative humidity and organic vapor concentration, is determined by the lag time diffusion method. In Method II, both water vapor and the organic vapor permeate simultaneously and, therefore, the effect of water vapor as a co-permeant is evaluated.

As shown in Figure 8, the relative humidity of the organic vapor stream which is flowed through the high concentration cell chambers is monitored upstream from the three way valve (Tv) to the cell by using a special hygrometer sensor, designed for use in an organic vapor atmosphere (Hydrodynamic, Inc., Silver Springs, MD). Unless otherwise stated, permeability runs were carried out at 23 °C. All runs were carried out in duplicate. A low, but constant, penetrant concentration (i.e. less than 100 ppm, wt/v) was employed. Studies were carried out at four relative humidity conditions, namely 0% RH, 23% RH, 50% RH, and 85% RH. Unless otherwise stated, the upper surface (outer surface) is always exposed to the high concentration of toluene vapor.

Two methods were employed in these studies to determine the water content of the test films, namely gravimetric and titration procedures (Pande, 1974). Good agreement was obtained between these two methods.

The equilibrium sorption isotherm for the test film was determined according to ASTM E 104-51 standard method of test. Humidity conditioning was achieved by storing samples at ambient temperature in relative humidity chambers ranging from 12 to 93 percent RH. These humidity conditions were maintained using various standard salt solutions.

6-3 Operation

The quantity of permeant vapor that has permeated through the polymer membrane into the lower concentration chamber with time is quantified by gas chromatography with flame ionization detection. At predetermined time intervals, an aliquot (0.5 ml) of headspace gas is removed from the right and left cell chambers with a gas-tight syringe and injected directly into the gas chromatograph. A constant total pressure of 1 atm is maintained throughout the run in both the high and low permeant concentration cell chambers. A constant pressure in the high concentration cell chamber is maintained by continually flowing the vapor stream through the high concentration cell chamber and discharging it at atmospheric pressure. To maintain a constant total pressure in the low concentration cell chamber, the volume of headspace gas removed for analysis is replaced with an equal volume of humidified nitrogen gas removed from the preconditioning test system (see Figure 8b) for the studies. Residual levels of penetrant in the lower concentration cell chamber are checked before each run to ensure no interference. Samples are removed from the lower concentration cell chamber at predetermined time intervals and the permeation-time plot (i.e. transmission rate profile) monitored until a steady state permeation rate is obtained. The resultant transmission rate profile is related to the permeation rate of the film specimens. Measurements are continued until sufficient data is collected to ensure steady-state kinetics. Care is taken so that the permeant concentration in the lower concentration cell chamber does not exceed 3% of the permeant vapor concentration in the high concentration cell chamber (i.e. center chamber). This is done to assure a constant driving force of the penetrant throughout the course of the run.

RESULTS AND DISCUSSION

7-1 The Effect of Relative Humidity on the Permeation of Toluene Vapor through Cryovac Test Film FDX 1570 (Method I)

Table 4 and Figure 9 summarize the data which were obtained for the studies on the diffusion of toluene vapor (81 ppm, wt/v) through Cryovac FDX 1570 samples as a function of relative humidity. For this film sample, good agreement was obtained between replicate runs and the results reported are the average of replicate studies. The results indicated that the test film was an excellent toluene vapor barrier at 0% RH. However, as shown, the permeability constant ($\bar{P}$) for this film structure, was dependent upon relative humidity, with $\bar{P}$ increasing with an increase in relative humidity at a constant permeant level. To better illustrate the effect of RH on the transmission rate for the test films, the results are presented graphically in Figure 10, where the permeability constant is plotted as a function of relative humidity. Figure 10 serves to illustrate the profound effect of relative humidity upon the permeability of toluene vapor through the FDX 1570 film.

TABLE 4

THE EFFECT OF RELATIVE HUMIDITY ON THE DIFFUSION OF TOLUENE VAPOR THROUGH CRYOVAC FDX 1570 FILM AT 81 PPM, 72°F

RH (%)	P[a] Permeability Rate (g/hr/sq. m)	$\overline{P}$[a][c] Permeability Constant (g/sq. m·day·100ppm)	θ Lag Time (hr)
0	No Detectable Level[b]	------	---
23	2.7×10^{-3}	7.2×10^{-2}	6.9
	3.1×10^{-3}	8.4×10^{-2}	5.9
	x = $2.9 \times 10^{-3} \pm 0.2 \times 10^{-3}$	$7.8 \times 10^{-2} \pm 0.6 \times 10^{-2}$	6.4
49	6.4×10^{-3}	1.90×10^{-1}	1.1
	5.8×10^{-3}	1.70×10^{-1}	1.3
	x = $6.1 \times 10^{-3} \pm 0.3 \times 10^{-3}$	$1.8 \times 10^{-1} \pm 0.1 \times 10^{-1}$	1.2
85	1.08×10^{-2}	3.20×10^{-1}	0.8
	1.06×10^{-2}	3.12×10^{-1}	0.8
	x = $1.07 \times 10^{-2} \pm 0.1 \times 10^{-3}$	$3.16 \times 10^{-1} \pm 0.4 \times 10^{-2}$	0.8
89	1.98×10^{-2}	5.85×10^{-1}	0.6
	2.54×10^{-2}	7.49×10^{-1}	0.6
	x = $2.26 \times 10^{-2} \pm 0.28 \times 10^{-2}$	$6.67 \times 10^{-1} \pm 0.82 \times 10^{-1}$	0.6

(a) Average of Replicate Runs

(b) No Detectable Level of Permeation After 2 Weeks

(c) Permeability Coefficient Normalized to 100 ppm (wt/v) Toluene Vapor Concentration

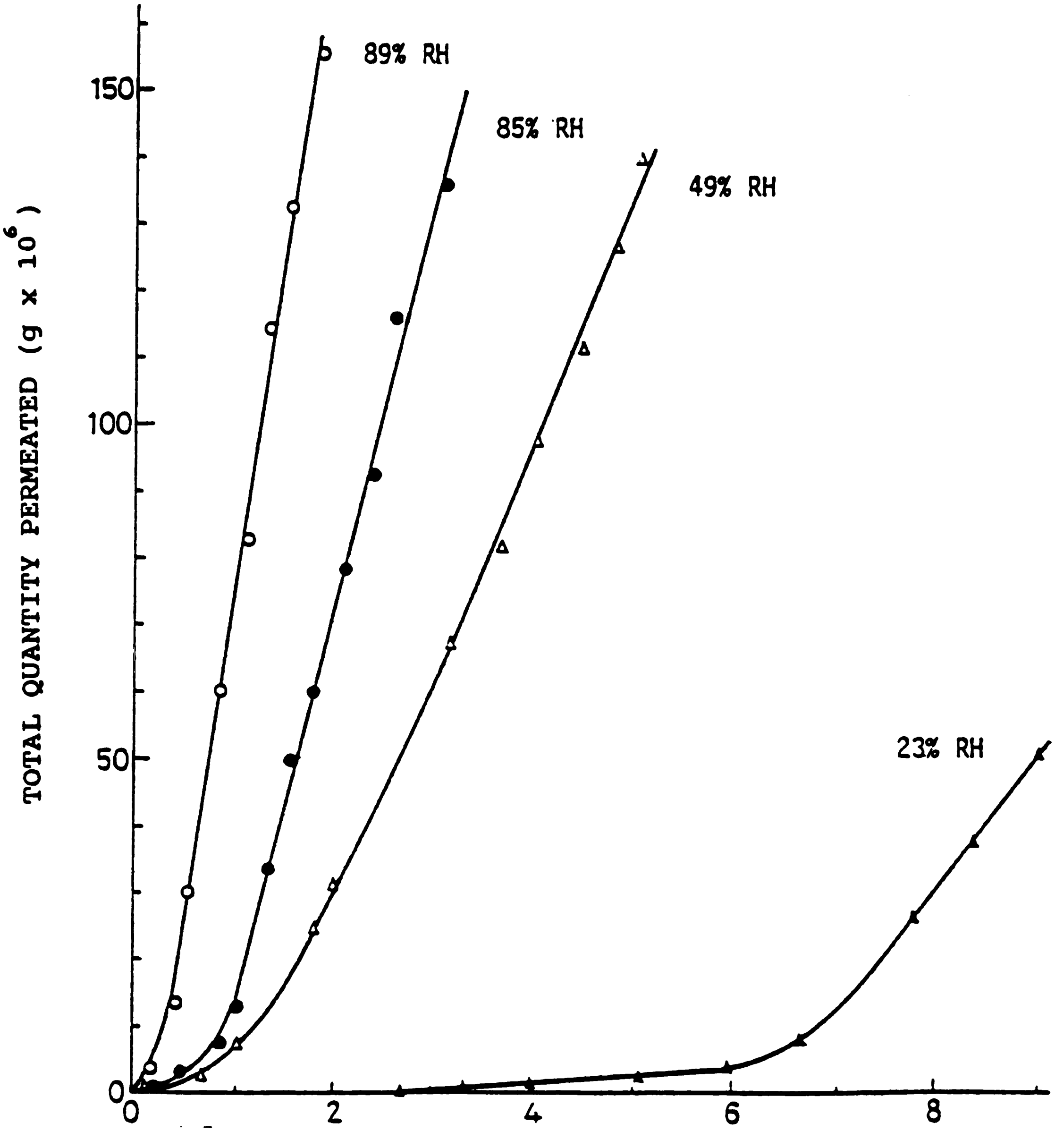


Figure 9 TRANSMISSION RATE PROFILE OF CRYOVAC FDX 1570 FILM AT 81 PPM, 72°F. (Method I)

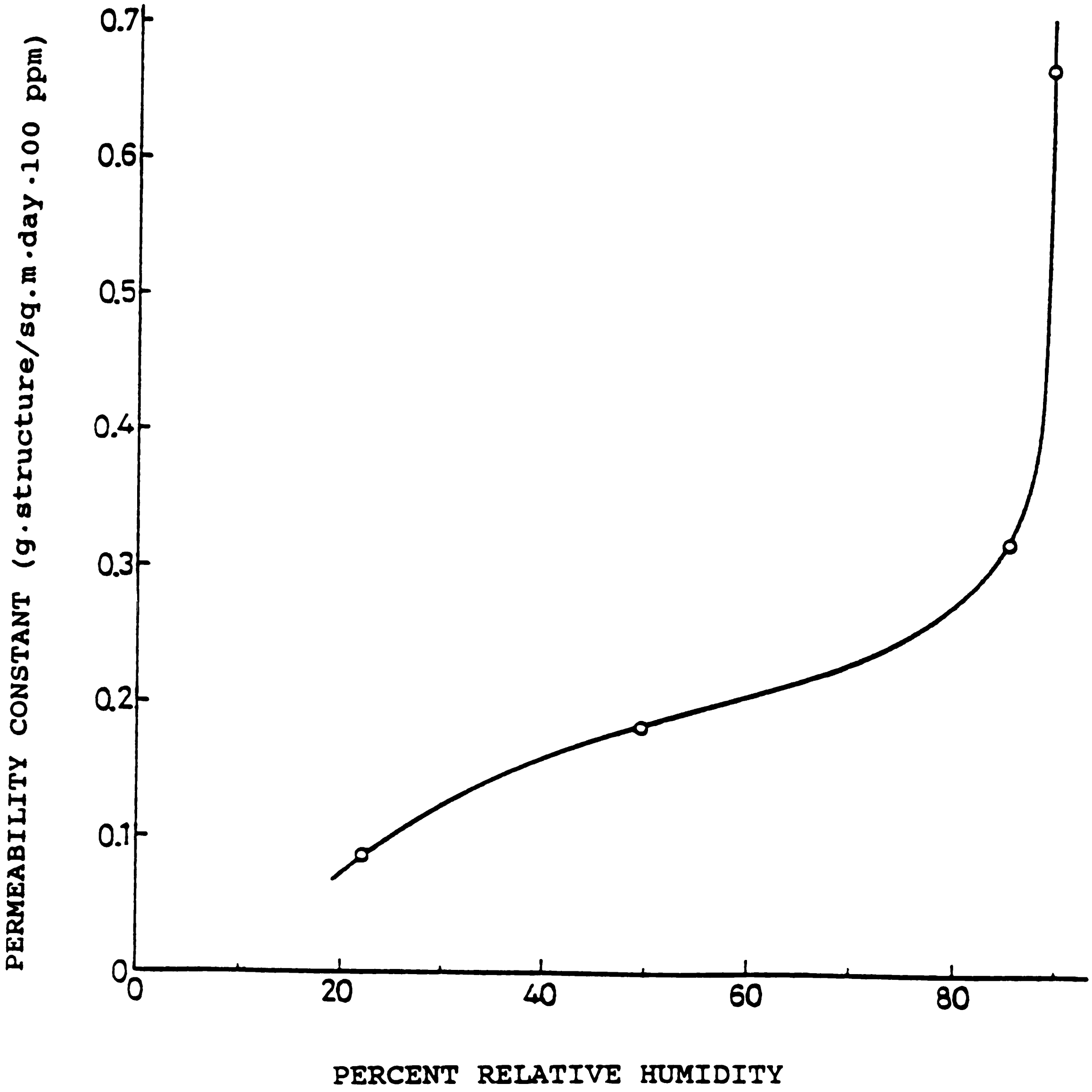


Figure 10 PERMEABILITY CONSTANT VERSUS RELATIVE HUMIDITY OF CRYOVAC FDX 1570 FILM AT 81 PPM, 72°F.

For the Cryovac FDX 1570 film, the relationship between the permeability constant for toluene vapor (81ppm) and the relative humidity of test is given by equation 8 which was derived by the cubic spline method. Equation 8 is a high order polynomial expression which gave a correlation coefficient of 99.9%.

$$Y = 5.18X^4 - 7.66X^3 + 2.96X^2 + 0.27X - 0.06 \qquad (8)$$

Further experiments were carried out at a lower (62 ppm, wt/v) concentration of toluene vapor with varying RH environments for the FDX 1570 film. A summary of the experimental results is given in Table 5.

In over 14 days of continuous testing, there was no measurable permeation at relative humidities of 0%, 23% and 49%. The permeability coefficients at these relative humidities were below the detectable threshold level for this method, which is determined by the sensitivity of the gas chromatography flame ionization detector. However, an upper limit value was estimated and is presented in Table 5. The procedure of estimation is given in Appendix B.

As can be seen, the permeability constant is much lower than that for studies conducted at 81 ppm (wt/v) concentration of toluene vapor at comparable relative humidities. The vapor concentration dependency of the diffusion process is illustrated graphically in Figure 11, where the total quantity of toluene permeated (Q) is plotted as a function of time for studies carried out at 81 ppm (wt/v) and 62 ppm (wt/v) toluene vapor concentration respectively with both runs being carried out at 85-86% relative humidity.

As shown in Table 5, the effect of relative humidity on the diffusion of toluene vapor is similar to that obtained at 81 ppm (Table 4), namely, that the transmission rate increases with an increase in the relative humidity at which the test was performed. Further, at a constant RH of 85-86%, the diffusion process also appears to be dependent upon the concentration of penetrant vapor (from 62ppm to 81ppm, wt/v). The observed concentration-dependent permeability constant suggests penetrant/polymer interaction, resulting in configurational change and alteration of polymer chain configurational mobility and thus penetrant diffusivity.

TABLE 5

THE EFFECT OF RELATIVE HUMIDITY ON THE DIFFUSION OF TOLUENE VAPOR THROUGH CRYOVAC FDX 1570 FILM AT 62 PPM, 72°F

RH (%)	$P^{(a)}$ Permeability Rate (g/hr/sq. m)	$\bar{P}^{(a)(b)}$ Permeability Constant (g/sq. m·day·100ppm)	θ Lag Time (hr)
0	$P < 2.1 \times 10^{-6}$	$P < 8.4 \times 10^{-6}$ (c)	---
	No Detectable Level After 14 Days		
23	$P < 2.1 \times 10^{-7}$	$P < 8.4 \times 10^{-6}$ (c)	---
	No Detectable Level After 14 Days		
49	$P < 2.1 \times 10^{-7}$	$P < 8.4 \times 10^{-6}$ (c)	---
	No Detectable Level After 14 Days		
86	5.1×10^{-4}	1.94×10^{-2}	10
	9.1×10^{-4}	3.46×10^{-2}	7
x =	$7.1 \times 10^{-4} \pm 2.0 \times 10^{-4}$	$2.7 \times 10^{-2} \pm 0.76 \times 10^{-2}$	8.5

(a) Average of Replicate Runs

(b) Permeability Coefficient Normalized to 100 ppm (wt/v) Toluene Vapor Concentration

(c) Represents An Estimated Upper Limit Value

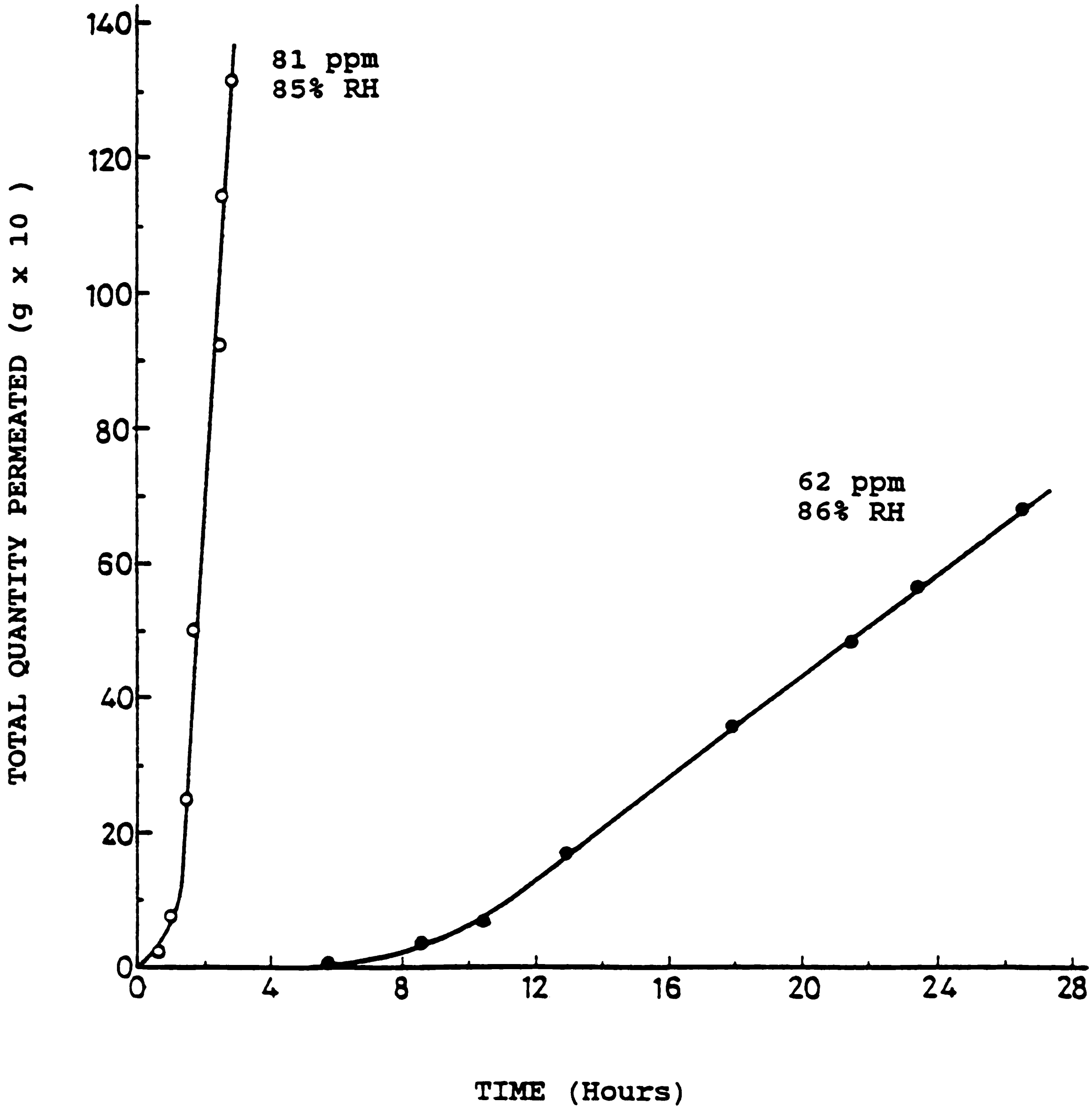


Figure 11 TRANSMISSION RATE PROFILE OF CRYOVAC FDX 1570 FILM AT 72°F, VARYING VAPOR CONCENTRATION.

7-2 Equilibrium Sorption Isotherm of Cryovac FDX 1570 Test Films

The equilibrium sorption isotherm of the FDX 1570 test film is presented in Figure 12. As shown, good agreement was obtained between the two test methods, namely the gravimetric and titration methods for quantitating moisture content (Pande, 1974). Table 6 gives a summary of the isotherm results. Since the test film (FDX 1570) contains the hydrophilic polymers nylon and EVAL in the coextrusion structure, it is necessary to obtain the isotherm in order to have a better understanding of the relationship between relative humidity and water vapor absorbed by the test film.

A high order polynomial equation describing the relationship between the equilibrium moisture content and the relative humidity (Figure 12), is given below :

$$Y = 30.85X^{4} - 23.00X^{3} + 6.77X^{2} + 0.33X \qquad (9)$$

Equation (9) gave a correlation coefficient of 99.9% (cubic spline method).

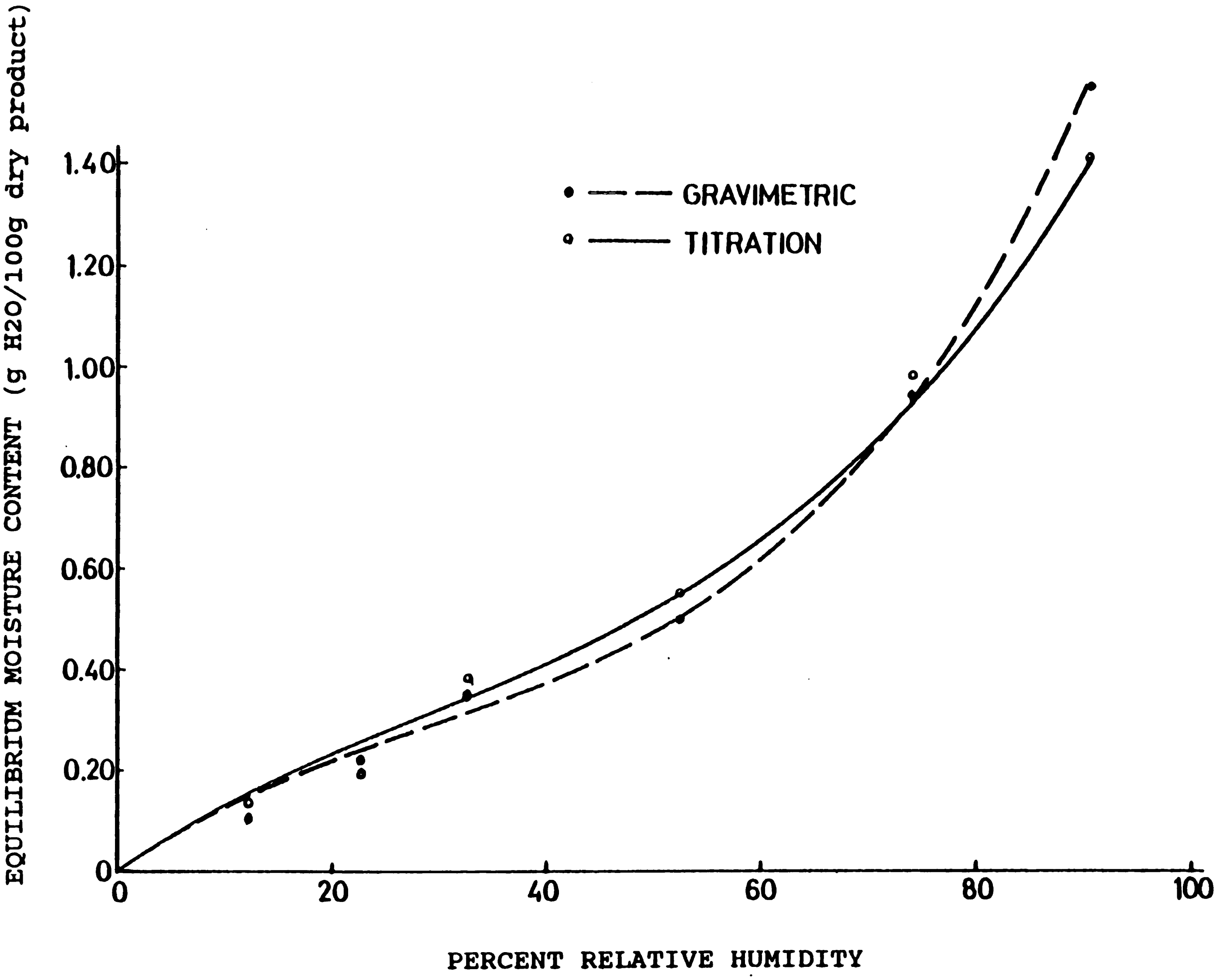


Figure 12 EQUILIBRIUM SORPTION ISOTHERM FOR FDX 1570 FILM AT 72°F.

TABLE 6

EQUILIBRIUM SORPTION ISOTHERM OF CRYOVAC FDX 1570 FILM AT 72°F

Saturated Salt Solution	RH%	Equilibrium Moisture Content(Meq%)[a] Gravimetric[b]	Titration[b]
LiCl H2O	12	0.11 ± 0.010	0.13 ± 0.007
KC2H3O2	23	0.22 ± 0.010	0.19 ± 0.010
MgCl2 6H2O	33	0.35 ± 0.008	0.37 ± 0.005
Mg(NO3)2 6H2O	53	0.50 ± 0.018	0.55 ± 0.005
NaCl	75	0.95 ± 0.009	0.97 ± 0.010
KNO3	93	1.56 ± 0.017	1.41 ± 0.005

(a) Meq% = (g moisture content/100 g dry product)

(b) Average of Triplicate samples.

7-3 Moisture Content Versus Exposure Time of Preconditioning Film

This aspect of the study was conducted to determine the moisture content of test films as a function of preconditioning time for the films equilibrated in a 86% relative humidity environment. The titration method was used to determine the moisture content of the test films. Table 7 provides a summary of the results and Figure 13 presents the moisture content gained as a function of preconditioning time at 86% relative humidity.

A high order polynomial equation for Figure 13, with correlation coefficient of 99.9%, is given below.

$$Y = 28.22X^5 - 60.30X^4 + 36.35X^3 - 2.86X^2 - 0.27X - 0.1 \qquad (10)$$

Apparently, the water content of the test film reached equilibrium after about 6 days preconditioning. The data shows what appears to be a smaller relative amount of slow sorption, followed by a rapid approach to apparent equilibrium. A plausible explanation of these results is that during the initial stage, water vapor is diffusing into the film which causes swelling of the nylon and EVAL layers. This swelling results in the rapid water absorption (exponential stage). It is proposed that the test films may absorb water much faster due to the increase in the water solubility caused by the swelling.

TABLE 7

MOISTURE CONTENT OF CRYOVAC FDX 1570 FILM VERSUS TIME OF PRECONDITIONING AT 85% RH, 72 °F

Equilibration Time (days)	Meq%[a] (g moisture content/100g dry product)	
1	x = 0.08 ± 0.010	(0.085, 0.090, 0.065)
2	x = 0.16 ± 0.014	(0.150, 0.180, 0.149)
3	x = 0.40 ± 0.011	(0.383, 0.410, 0.405)
4	x = 0.98 ± 0.030	(1.000, 1.000, 0.890)
5	x = 1.20 ± 0.030	(1.180, 1.240, 1.170)
6	x = 1.24 ± 0.013	(1.220, 1.240, 1.260)
7	x = 1.22 ± 0.020	(1.250, 1.210, 1.240)

(a) Average of Triplicate samples.

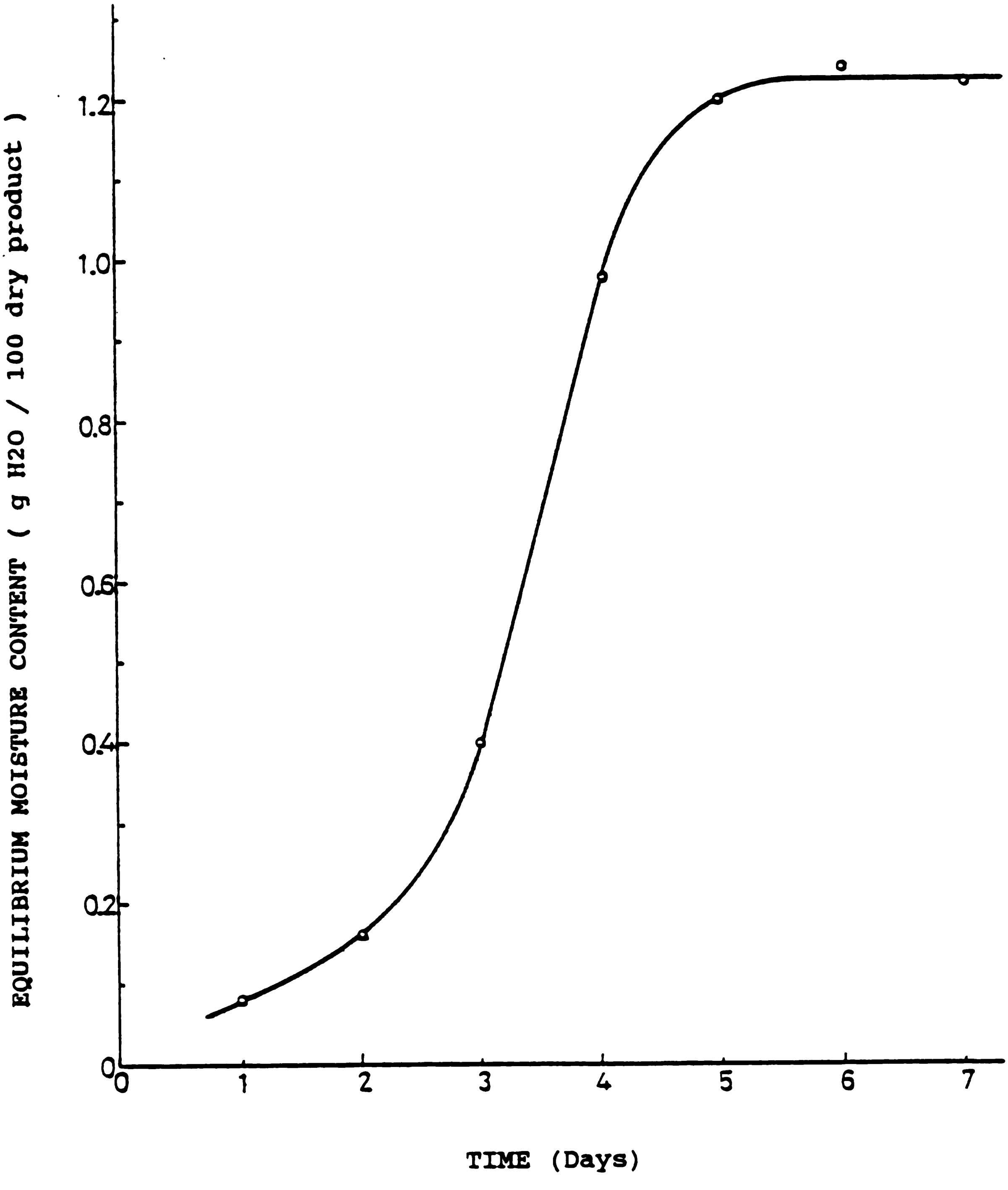


Figure 13 MOISTURE CONTENT OF CRYOVAC FDX 1570 FILM VERSUS PRECONDITIONING TIME AT 72°F.

7-4 The Permeability Constant ($\overline{P}$) Versus Exposure Time of Preconditioning Film

This experiment was intended to determine the permeability constant of the test films as a function of the preconditioning time. The experiment was carried out at 86% relative humidity and 81 ppm (wt/v) of toluene vapor concentration. The results are tabulated in Table 8 and presented graphically in Figure 14, where the permeability constant ($\overline{P}$) is plotted as a function of equilibration time. As shown, the permeability constant increases with an increase in time for preconditioning the test films. For the Cryovac FDX 1570 film structure, the relationship between the permeability coefficient ($\overline{P}$) and equilibration time, within the linear portion of the curve, is given,

$$Y = 0.08X - 0.07 \qquad (11)$$

During the course of the runs described, it is assumed that the moisture content of the test films remained relatively constant. This is based on the fact that, for Cryovac FDX 1570 film, a 6-7 day period was required for the samples to reach equilibrium moisture content at 86% RH. While the permeability studies were

TABLE 8

PERMEABILITY CONSTANT OF TOLUENE VAPOR THROUGH CRYOVAC FDX 1570 FILM VERSUS TIME FOR PRECONDITIONING AT 86% RH,81 PPM,72°F

Equilibration Time (days)	(c) Meq%	$\bar{P}^{(a)(b)}$ Permeability constant (g·structure/sq. m · day·100ppm)	θ Lag Time (hr)
		0.87×10^{-2}	7.1
		1.13×10^{-2}	5.1
1	0.08	$x=1.00\times10^{-2} \pm 0.13\times10^{-2}$	5.6
		1.15×10^{-1}	2.2
		0.85×10^{-1}	2.6
2	0.16	$x=1.00\times10^{-1} \pm 0.15\times10^{-1}$	2.4
		1.52×10^{-1}	1.7
		1.96×10^{-1}	1.5
3	0.40	$x=1.74\times10^{-1} \pm 0.22\times10^{-1}$	1.6
		3.23×10^{-1}	1.0
		3.17×10^{-1}	1.0
4	0.98	$x=3.20\times10^{-1} \pm 0.03\times10^{-1}$	1.0
		2.81×10^{-1}	1.2
		3.11×10^{-1}	1.0
5	1.20	$x=2.96\times10^{-1} \pm 0.15\times10^{-1}$	1.1
		3.24×10^{-1}	0.9
		3.08×10^{-1}	0.9
6	1.24	$x=3.16\times10^{-1} \pm 0.08\times10^{-1}$	0.9

(a) Average of Replicate Runs

(b) Permeability Constant Normalized to 100 ppm (wt/v) Toluene Vapor Concentration

(c) Meq% = (g moisture content/100 g dry product)

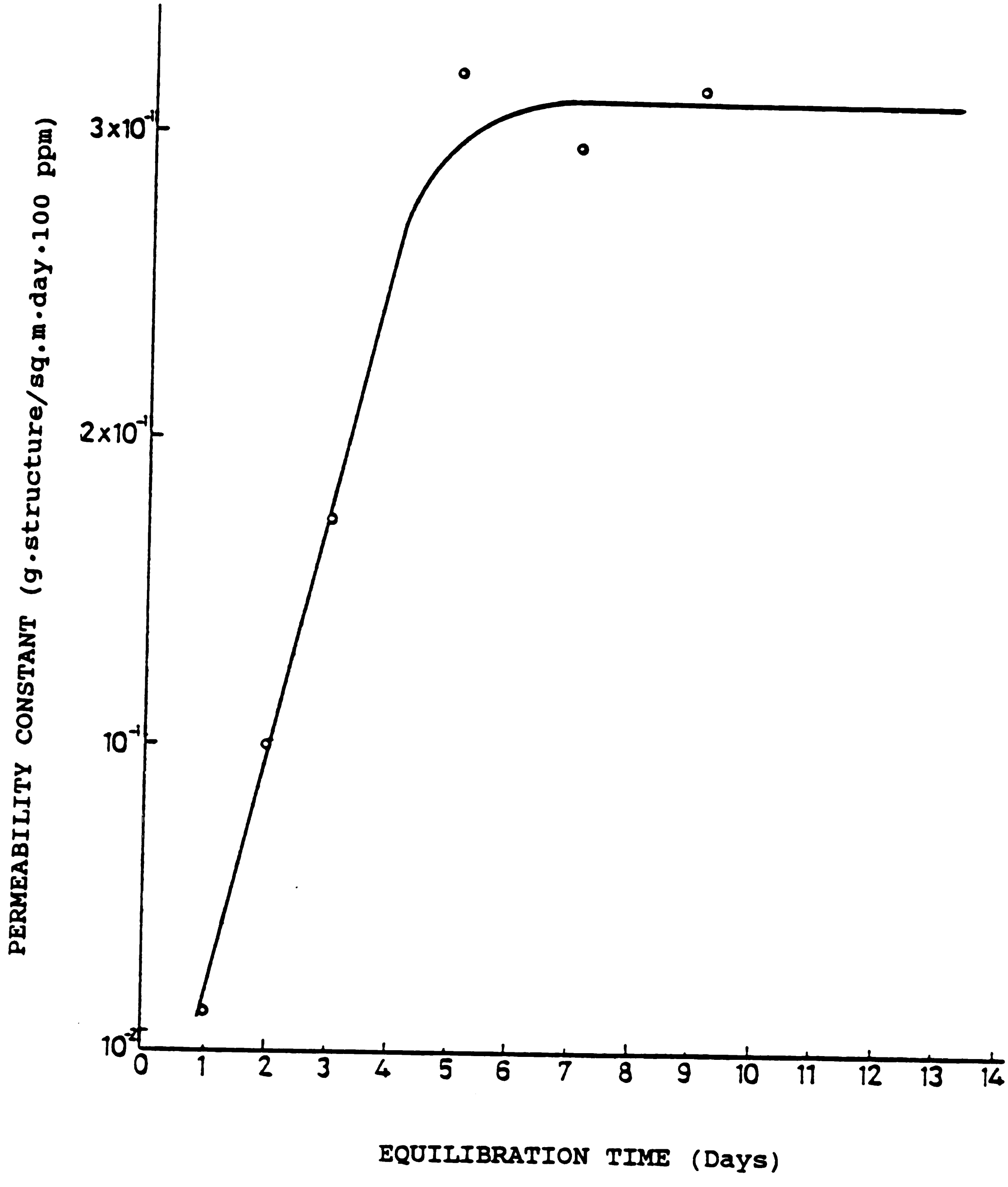


Figure 14 PERMEABILITY CONSTANT OF CRYOVAC FDX 1570 FILM VERSUS PRECONDITIONING TIME AT 72 °F.

conducted within hours. The slight increase of moisture gained by the films during the test period was considered negligible.

On the basis of the above experimental results, a mechanism to explain the water vapor effect on toluene vapor permeating through Cryovac FDX 1570 film samples may be proposed as follows.

The increase in the diffusivity of toluene vapor at a low level of sorbed water can be attributed to a weak enhancement of the segmental motion of the polymer chains, which is commonly called the plasticizing effect of sorbed water (Long et al., 1953). In addition, the diffusion process appears to be dependent upon the concentration of penetrant vapor (from 62 ppm to 81 ppm, wt/v) (see Figure 11). The water vapor effect at high levels of sorbed water (at 85 % RH) is related to swelling, which greatly increases the polymer chain segmental mobility. This leads to a significant increase in toluene vapor diffusivity. It is quite possible that the test films are in a glassy state (i.e. above Tg) when dry and become non-glassy at 70 to 80 % RH because of plasticization by water vapor (i.e. reduction in Tg). This behavior stems from the very nature of the polymer itself. Cryovac FDX 1570 films contain EVAL and nylon middle layers which are semi-crystalline polar polymers. There is little or no permeation through the crystalline regions, which is true for any polymer (Wachtel et al., 1984). When dry, there is little permeation through the amorphous regions because the interchain hydrogen bonding reduces the mobility of the polymer chain segments preventing the diffusion of toluene vapor. When moisture is present, it plasticizes the EVAL and nylon layers and reduces the amount of hydrogen bonding. At high water activities (which are accompanied by high moisture content in the EVAL and nylon layers), the middle or barrier layers are plasticized and swell to the point where the glass transition temperature (Tg) of the coextrution barrier polymer can approach room temperature (Wachtel et al., 1984; Tan, 1986). It appears that the nylon and EVAL components of the coextrusion structure may experience a change from the glassy to the rubbery state at about 70 to 80 % RH and the permeability constant increases rapidly at these relative humidities.

7-5 The Effect of Water Vapor as a Co-Permeant on the Diffusion of Toluene Vapor through Cryovac FDX 1570 Film (Method II)

In the studies described in the preceding sections, all the films to be tested were preconditioned to the required relative humidity, employing a preconditioning system prior to test (Method I). Since the test film Cryovac FDX 1570 contains moisture sensitive components in the coextrusion structure (nylon and EVAL), preconditioning provides for moisture equilibration of the film with the surrounding relative humidity and minimizes the effect of the direction of permeation. This is particularly important if the film is not balanced. By preconditioning, similar results were obtained regardless of which surface was exposed to the high penetrant concentration.

In addition to evaluating the effect of relative humidity on the permeability of toluene vapor through the test film, the effect of water vapor as a co-permeant (Method II) in the diffusion of toluene vapor was also evaluated. Here the film samples to be tested were stored over a desiccant prior to test so as to maintain the films at a low relative humidity level prior to initiating the permeability studies. To evaluate the effect of permeation direction, the two different surfaces of the test film (FDX 1570), were exposed to the high concentration chamber. It is interesting to note that different permeability constants were obtained from this study depending upon which surface of the structure was exposed to the high concentration chamber. The results are tabulated in Table 9 and presented graphically in Figure 15, where the total quantity of toluene permeated (Q) is plotted as a function of time for both directional permeations. As shown for film FDX 1570, where the effect of water vapor as a co-permeant was evaluated, the direction of permeation (i.e. surface exposed to high relative humidity and vapor concentration) markedly influences the resultant barrier properties.

While these finding are not fully understood, this could be explained in part by the following. The outer and inner surfaces of the coextrusion are polyolefins and are assumed to have similar affinities for water vapor. However, the nylon and EVAL components of the coextrusion are in distinct layers and would be expected to exhibit different affinities for water vapor and thus would be affected differently by the sorption activity, in terms of barrier reduction. The relative position of the nylon and EVAL layer would therefore be expected to affect the permeability constant for toluene vapor, while water vapor was a co-permeant. It is presumed that the higher rate of diffusion of water vapor results in higher plasticizing or swelling of the barrier component of the laminate structure, thus enhancing the rate of permeability of toluene vapor through the test film.

TABLE 9

THE EFFECT OF WATER VAPOR AS A CO-PERMEANT ON THE DIFFUSION OF TOLUENE VAPOR THROUGH CRYOVAC FDX 1570 FILM AT 72°F

Toluene Vapor Concentration ppm (wt/v)	RH (%)	$\bar{P}^{(a)(c)}$ Permeability Constant (g·structure/sq. m · day·100ppm) Lower Surface (d)	Upper Surface (e)
97	61	1.42×10^{-4}	0.74×10^{-4}
97	61	1.58×10^{-4}	0.88×10^{-4}
97	61	$x=1.50\times10^{-4} \pm 0.08\times10^{-4}$	$0.81\times10^{-4} \pm 0.07\times10^{-4}$
97	45	0.96×10^{-5}	
97	45	1.20×10^{-5}	No Detectable Level (b)
97	45	$x=1.10\times10^{-5} \pm 0.12\times10^{-5}$	

(a) Average of Replicate Runs

(b) No Detectable Level After 2 Weeks

(c) The Permeability Coefficient normalized to 100 ppm (wt/v) Toluene Vapor Concentration

(d) Lower Surface Defined As the inner surface as wound

(e) Upper Surface Defined As the outer surface as wound

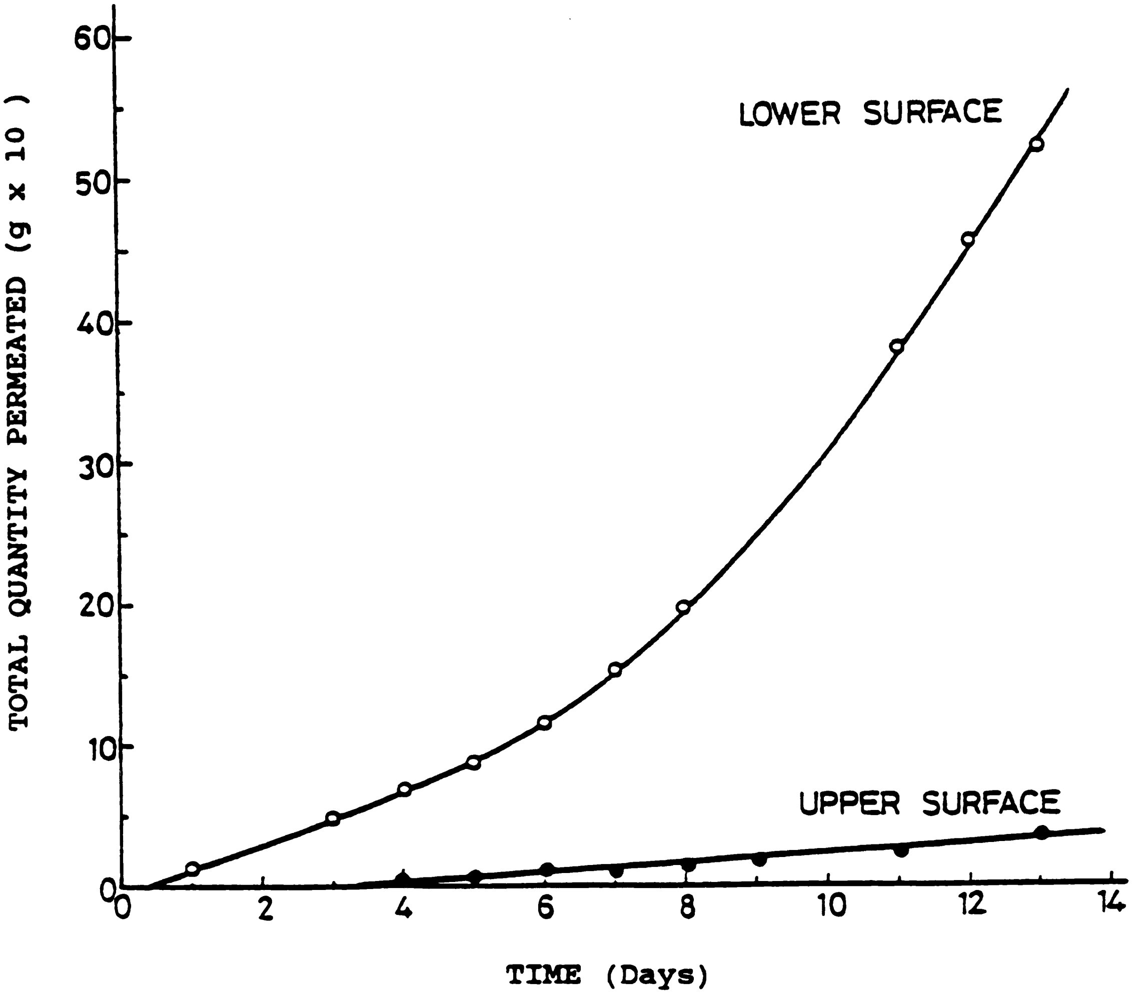


Figure 15 TRANSMISSION RATE PROFILE OF CRYOVAC FDX 1570 FILM AT 97 PPM, 61% RH, 72°F. (Method II)

7-6 WVTR of Cryovac FDX 1570 Film (ASTM E96-80)

Similar studies were carried out to evaluate the effect of permeation direction on water vapor permeation through the FDX 1570 film. The water vapor transmission rate (WVTR) studies performed on the FDX 1570 film were carried out at 23%, 50% and 80% RH at ambient temperature (72 F). Table 10 and Figure 16 give a summary of the experimental data. As shown, the direction of permeation (i. e. surface exposed to high relative humidity) markedly influenced the water vapor barrier characteristics of the test film.

These findings provide supporting evidence for the observed effect of permeation direction for the studies previously described on the effect of water vapor as a co-permeant on the diffusion of toluene vapor through the test film. The results also suggest a strong relative humidity dependence for the permeation of water vapor through the FDX 1570 film samples, with increasing relative humidity resulting in a higher WVTR.

TABLE 10

THE WATER VAPOR TRANSMISSION RATE OF CRYOVAC FDX 1570 FILM (a)

RH (%)	LOWER SURFACE (d)		UPPER SURFACE (e)	
	WVTR (b)	$\bar{P}$ (c)	WVTR (b)	$\bar{P}$ (c)
23	0.45	0.094	0.31	0.067
23	0.51	0.106	0.27	0.061
23	0.48	0.100	0.35	0.080
23	x=0.48±0.02	0.100±0.004	0.31±0.03	0.070±0.007
50	3.71	0.371	0.89	0.087
50	3.16	0.316	1.45	0.143
50	3.93	0.393	1.02	0.102
50	x=3.60±0.29	0.360±0.029	1.12±0.22	0.110±0.021
80	6.85	0.438	1.97	0.127
80	6.47	0.414	2.30	0.149
80	5.91	0.378	1.74	0.114
80	x=6.41±0.33	0.410±0.021	2.01±0.20	0.130±0.013

(a) Average of 3 Replicate Samples

(b) WVTR = g/sq. m·day

(c) $\bar{P}$ = g·structure/sq.m·day·mmHg

(d) The Lower Surface Defined As the inner surface as wound

(e) The Upper Surface Defined As the outer surface as wound

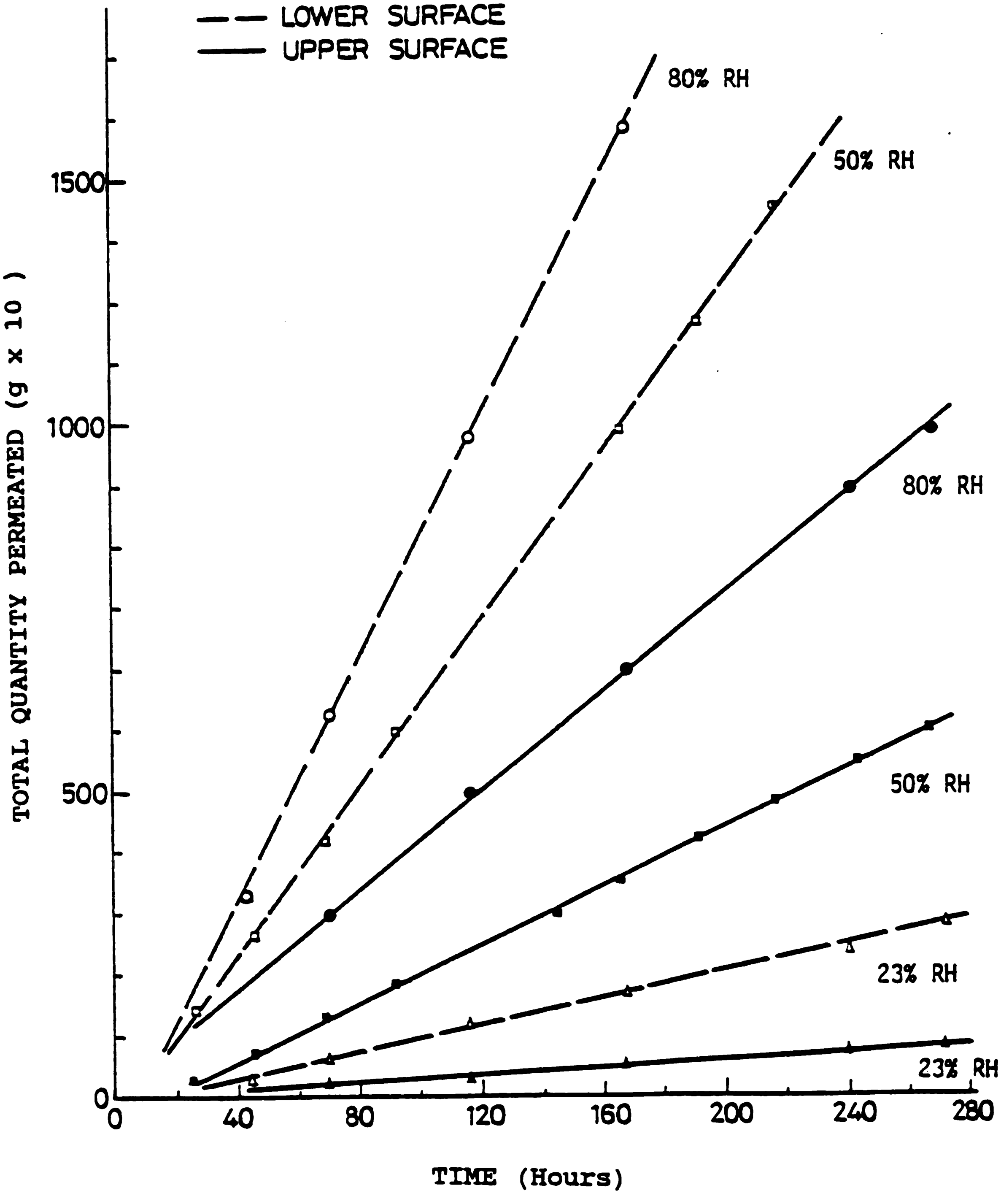


Figure 16 WATER VAPOR TRANSMISSION RATE OF CRYOVAC FDX 1570 FILM AT 72°F, VARYING RELATIVE HUMIDITY.

7-7 Calculated Results

Some calculated results can be obtained on the basis of the experimental data above. Figure 17 shows a plot of the permeability constant ($\bar{P}$) as a function of relative humidity, calculated from equation 9 (Figure 12, RH% vs. Meq%), equation 10 (Figure 13, Meq% vs. Time), and equation 11 (Figure 14, $\bar{P}$ vs.Time) together.

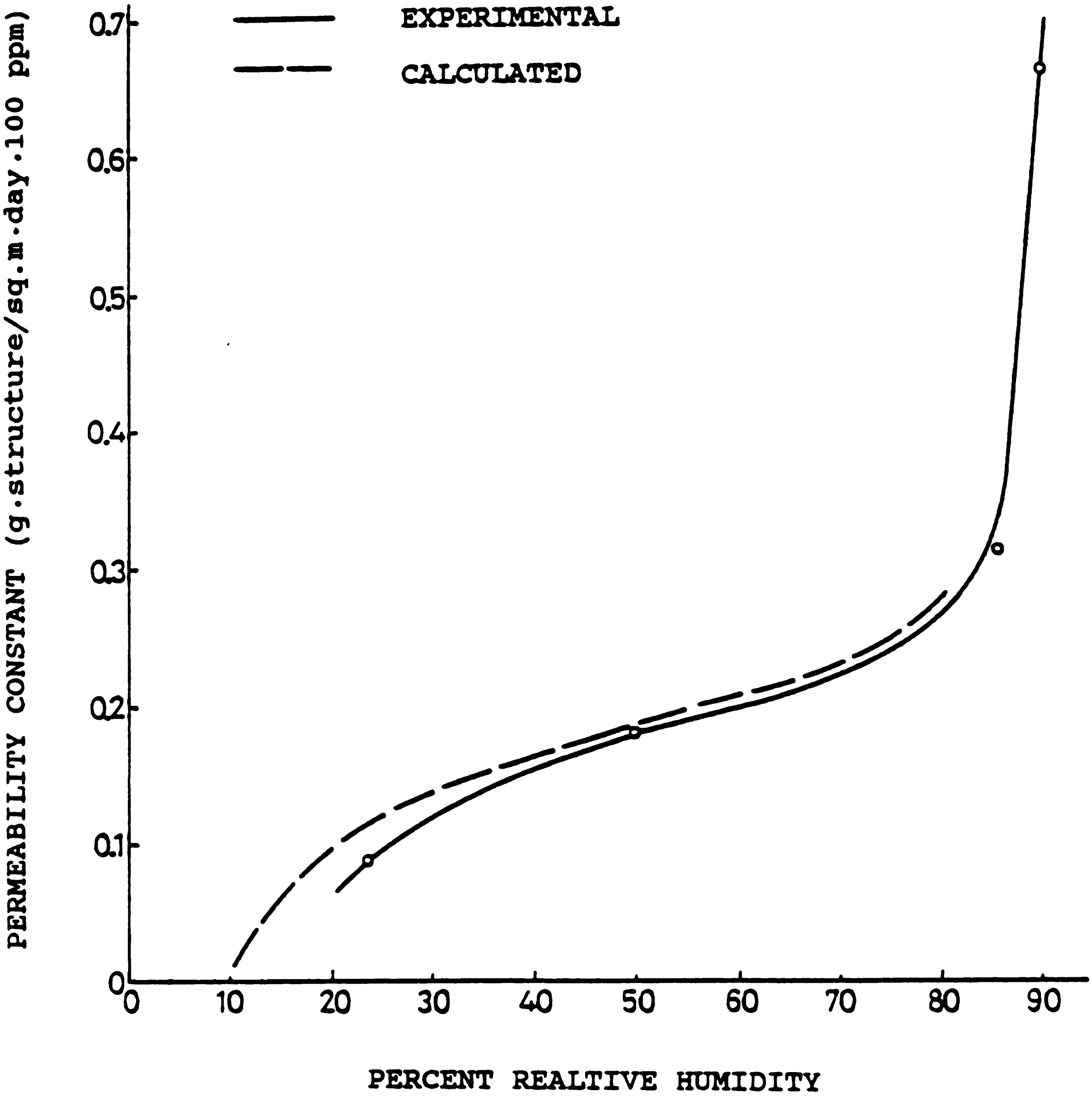
A polynomial equation for Figure 17 (calculated data) is then given by:

$$Y = -0.37X^4 + 3.04X^3 - 3.38X^2 + 1.63X - 0.12 \qquad (12)$$

When compared to the experimental data from Figure 10 ($\bar{P}$ vs. RH%), good agreement was obtained between experimental and calculated values. From Equation 12, the $\bar{P}$ for toluene vapor through the test film can be predicted over the entire range of relative humidities.

Similarly, the relationship between the permeability constant ($\bar{P}$) of toluene vapor through the test films and water vapor absorbed by the test films can also be obtained simply from equation 10 (Figure 13, Time vs.%Meq) and equation 11 (Figure 14, Time vs. $\bar{P}$) or from equation 8

(Figure 10, %RH vs. $\overline{P}$) and equation 9 (Figure 12, RH% vs. Meq%). Figure 18 showed the plot of the permeability constant ($\overline{P}$) of toluene vapor through the films as a function of moisture content gained (Meq%) by the film sample.



Fogure 17 PERMEABILITY CONSTANT OF CRYOVAC FDX 1570 FILM VERSUS RELATIVE HUMIDITY AT 81 PPM, 72 °F.

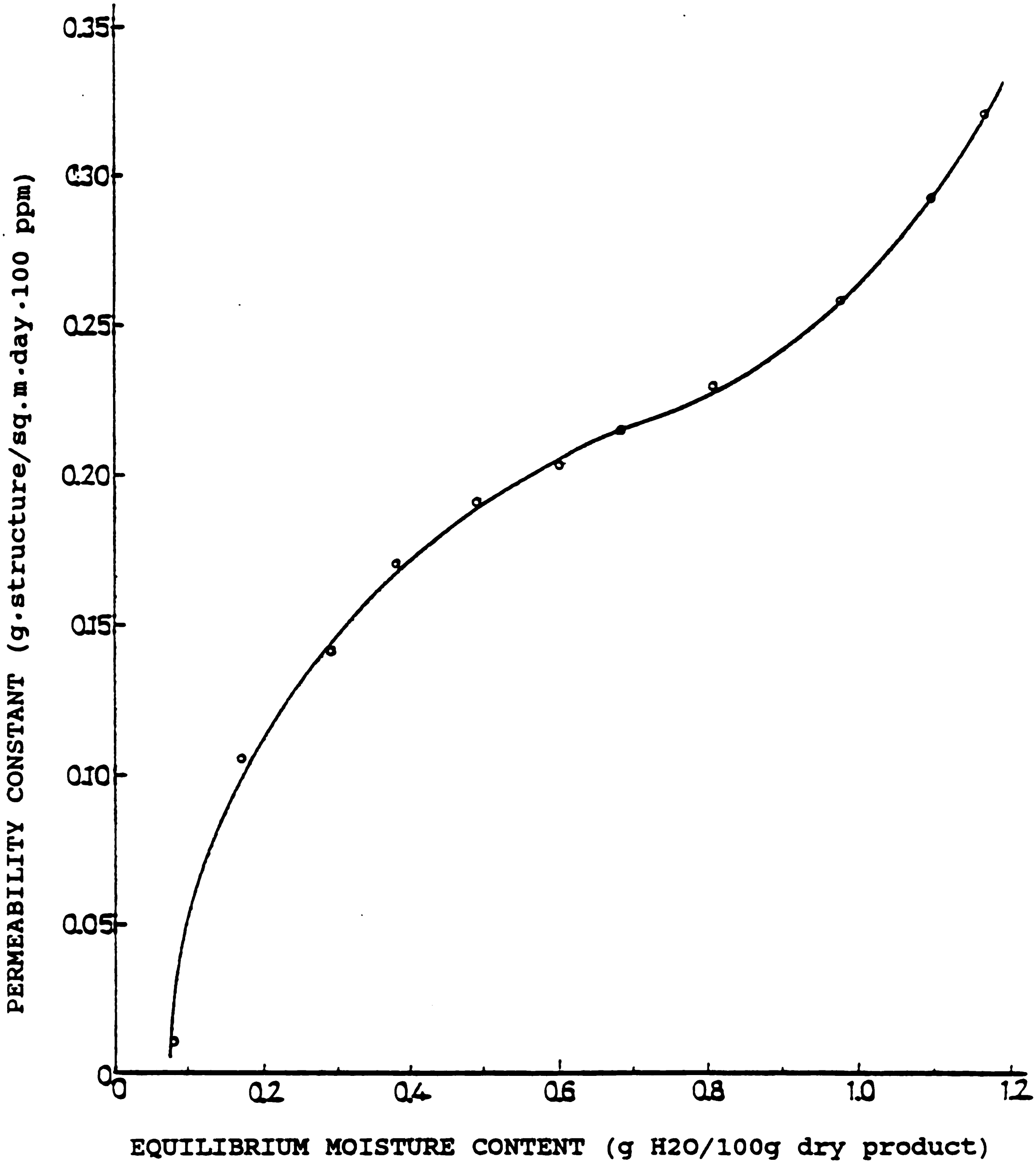


Figure 18 PERMEABILITY CONSTANT VERSUS EQUILIBRIUM MOISTURE CONTENT OF CRYOVAC FDX 1570 FILM AT 81 PPM, 72°F.

CONCLUSION

These studies were designed to develop a better understanding of the mechanism of diffusion of organic vapors through polymer membranes and to evaluate the effect of relative humidity on the diffusion of organic vapor molecules through multi-layer coextrusion structures . It was found that water vapor exhibits strong interactive effects with the hydrophilic (moisture sensitive) polymer layers of the coextrusion which resulted in an increase in the diffusion of toluene vapor through the barrier structure.

In terms of practical importance, the studies allow for a comparison of barrier properties of polymer membranes to organic vapors over a broad range of water vapor activities (RH%) and vapor concentrations. In addition, the studies provide a means of determining the relationship between the permeability constant ($\overline{P}$) of toluene vapor through the barrier film and the equilibrium moisture content (Meq%) of the polymer films.

In terms of theoretical importance, the investigation described was viewed as a method of studying the phenomenon of diffusion of organic vapors through polymer membranes. It is believed that water vapor can serve to plasticize the hydrophilic components of the multi-layer coextrusion, thus enhancing the transport of the organic vapor through a polymer coextrusion containing moisture sensitive layers such as nylon and EVAL. This suggests that the extent to which the EVAL and nylon are hydrogen bonded is reduced when moisture is present. Thus, the strong thermodynamic interactions between water vapor and polymers were anticipated.

RECOMMENDATIONS

The data obtained in these studies on the diffusion of toluene vapor (81 ppm) through test films as a function of relative humidity showed a marked increase in the permeability constant with an increase in relative humidity in the range of 50-89% RH. More experiments are proposed within this range of relative humidity in order to determine whether the effect of RH on toluene permeability is as predicted in Figure 10, and at what relative humidity the onset of an exponential increase in $\overline{P}$ with an increase in RH is observed.

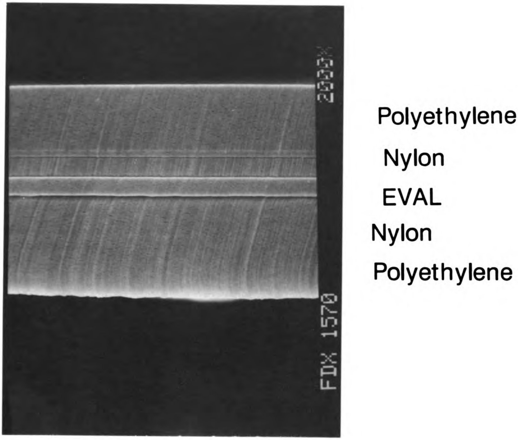
In addition, further experiments are of theoretical and practical interest to obtain a "threshold" relative humidity for the diffusion of toluene vapor through this coextrusion barrier structure.

The film sample tested in these studies contained two hydrophilic layers (i.e. nylon and EVAL) both of which can affect the permeability constant of the coextrusion to organic vapor when moisture is present. Additional studies are proposed involving coextrusions containing only nylon or EVAL as the barrier layer to determine whether the effect of relative humidity upon the diffusion of toluene vapor through the Cryovac FDX 1570 film structure is dominated by either nylon or EVAL barrier layers. A mathematical model may then be developed based on these further experimental profiles for a specific organic vapor (i.e. toluene). These studies should lead to a better understanding of the effect of relative humidity on the aroma barrier properties of hydrophilic polymer film structures.

In addition, similar studies should be carried out with other organic vapor penetrants, representing a range of polarities and molecular size, to compare their relative behavior with respect to the effect of relative humidity and concentration dependency of the diffusion process.

APPENDICES

APPENDIX A


2000X
FDX 1570
Polyethylene
Nylon
EVAL
Nylon
Polyethylene

APPENDIX B

Outlined below is the method used to estimate the lower limit of detectability by the gas chromatography.

The lowest area response for detecting toluene with good precision and accuracy was assumed to be 1000 area units (AU). Based on the calibration curve an area response of 1000 AU is equivalent to 3.60 x 10-7 grams toluene injected. Based on a 0.5 ml aliquot removed from the permeation cell and considering the cell chamber of 50 cc :

(3.60 x 10-7 grams) x 50 cc / 0.5 cc

= 3.6 x 10-5 grams

= minimum total number of grams of toluene
vapor which would have to permeate to
get a measurable response from the gas
chromatograph.

Assuming this minimum quantity of toluene to have permeated in a period of 336 hours (i.e. 14 days) and disregarding lag time, a linear relationship can be established between 0 hour and 336 hours. The slope of this plot represents the estimated permeation rate.

BIBLIOGRAPHY

ASTM DESIGNATION E104-51 Standard Method of Test for Saturated Salt Solutions.

ASTM DESIGNATION E96-80. Standard Method of Test for Water Vapor Transmission of Material in Sheet Form.

BANER, A. L., " Diffusion and Solubility of Toluene in Polymeric Films ", IAPRI Annual Award, 13th Annual IAPRI Symposium, Oslo, Norway (1985)

BARRER, R. M., " Permeation, Diffusion and Solution of Gases in Organic Polymer ", Trans. Faraday Soc. 35:628 (1939)

BARRER, R. M., J. BARRER, J. SLATER, " Sorption and Diffusion in Ethyl Cellulose, Part I, History - Dependence Sorption Isotherms and Permeation Rates ", J. of Polymer Science. 23:315 (1958)

BARRIE, J. A., "Water in Polymers",Diffusion in Polymers,Edited by J. Crank and G. S. Park. Academic Press, New York, N.Y. (1968)

CRANK, J., The Mathematics of Diffusion , 2nd Edition, Clarendon Press, Oxford, (1975)

CRANK, J., G.S. PARK., Diffusion in Polymers, Academic Press, New York, N.Y. (1968)

HILTON, B. W., S. Y. NEE., " Permeability of Organic Vapor through Packaging Films ", Ind. Eng Chem. Prod. Res. Dev. 17(1):80 (1979)

ITO, Y., " Effect of Water Vapor on Permeation of Gases through Hydrophilic Polymers ", Chem. High. Polym. (Japan) 18:158 (1961)

JABAR S. A., AND F. A. LOFGREN, " Effect of Water Absorption on Physical Properties of High Nitrile Barrier Polymers ", Polym. Eng. Sci. 26(6):405 (1986)

KAMIYA, Y., F. TAKAHASHI., " Effect of Water on Permeation, Diffusion and Solution of Gas in Cellophane ", J. Appl. Polym. Sci. 21:1945. (1977)

KUNZ, W. B., R. T. K. CORNWELL., " Oxygen Permeability of Cellophane ", TAPPI 45(7):583 (1962)

LONG, F. A., L. J. THOMPSON., " 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)

MEARES, P., " The Diffusion of Gases through Polyvinyl Acetate ", J. Am. Chem. Soc. 76:3415. (1954)

MEARES, P., " Diffusion of Allyl Chloride in Polyvinyl Acetate ", J. Polym. Sci. 27:391. (1958)

MEARES, P., " Transient Permeation of Organic Vapors through Polymer Membranes ", J. Appl. Polym. Sci. 46:684. (1965)

MEYER, J. A., C. ROGERS., V. STANNETT, AND M. SZWARC., "Studies in the Gas and Vapor Permeability of Plastic Films and Coated Papers Part III The Permeation of Mixed Gases and Vapors ", TAPPI 40(3):142 (1957)

NOTLEY, N. T. "Permeability of Oxygen of Cellophane Laminates", J. App. Chem. (London), 13:107 (1963)

NEWNS, A. C., " The Methods of Determining the Water Vapor Permeability of Lamina, a Review of the Literature ", J. Textile Institute. 41:T269 (1950)

PACE, R. J., A. DATYNER., "Statistical Mechanical Model of Diffusion of Complex Penetrants in Polymers I : Theory ", J. Polym. Sci., Polym. Phys. Edition. 17:1675 (1979)

PANDE, A., <u>Handbook of Moisture Determination and Control</u>, Vol. 1, Marcel Dekker Inc. N.Y. (1974)

PETRAK K., E. PITTS., " 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., F. A. LONG., " Diffusion of Hydrocarbons in Polyisobutylene ", J. Am. Chem. Soc. 73:4072. (1951)

PYE, D. G., H. H. HOEHN, AND M. PANAR, " Measurement of Gas Permeability of Polymers II Apparatus for Permeabilities of Mixed Gases and Vapors ", J. Appl. Polym. Sci., 20:287. (1976)

REITINGER, R. M. " Diffusion of Gases through Plastics ", J. Gen. Chem., 14:420 (1944)

ROGERS, C. E., J. A. MEYER, V. T. STANNETT, AND M. SZWARC, " Studies in the Gas and Vapor Permeability of Plastic Films and Coated Papers Part I ", TAPPI, 39:737. (1956a)

ROGERS, C. E., J. A. MEYER, V. T. STANNETT, AND M. SZWARC, " Studies in the Gas and Vapor Permeability of Plastic Films and Coated Papers Part II ", TAPPI, 39:741. (1956b)

SIMRIL, V. L., S. E. SMITH., " Sorption of Water by Cellophane ", Ind. Eng. Chem., 34:226. (1942)

SIMRIL, V. L., A. HERSHBERGER., " Permeability of Polymeric Films to Gases", Mod. Plast., 22(11):155. (1944)

STANNETT, V., H. YASUDA., " The Measurement of Gas and Vapor Permeation and Diffusion in Polymer ", Testing of Polymers, Vol. 1, John Wiley and Sons, Inc. Chap. 13, 393, (1965)

TAN, S., "Effect of Relative Humidity on The Permeability of Organic Vapor", Thesis for Master of Science, Department of Chemical Engineering, Michigan State University. (1986)

WACHTEL, J. A., B. C. TSAI, C. J. FARREL., "Retorted EVOH Multilayer Cans with Excellent Oxygen Barrier Properties", Second International Ryder Conference on Packaging Innovation. (1984)

WATT, I. C., "Determination of Diffusion Rate in Swelling Systems", J. Appl. Polym. Sci., 8:2835. (1964)

ZOBEL, M. G. R.," Measurement of Odour Permeability of Polypropylene Packaging Films at Low Odourant Levels ", Polymer Testing, 3:133 (1982)