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EVALUATION OF PARAMETERS IMPACTING THE PERMEABILITY OF A FRAGRANCE DELIVERY SYSTEM

By

Hojoon Lee

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ABSTRACT

EVALUATION OF PARAMETERS IMPACTING THE PERMEABILITY OF A FRAGRANCE DELIVERY SYSTEM

BY

Hojoon Lee

The permeation of selected fragrance volatiles through an ethylene-vinyl acetate copolymer (EVA) membrane based fragrance delivery system was studied by an isostatic procedure at 50°C and a constant air flow rate of 20 cc/min, to insure that the mass transport process is diffusion controlled. The permeation rates of the fragrance volatiles, linalool, phenethyl alcohol, benzyl acetate, and α-hexyl cinnamaldehyde, were determined as a function of time. Variables evaluated in a three level, three variable statistical design experiment included the vinyl acetate content of the EVA membrane the thickening agent and dispersing solvent contents of the fragrance formulations. Statistical analysis showed that the vinyl acetate content of the test membranes was a significant variable effecting the permeation rates of fragrance volatiles through the fragrance delivery system. Film A(vinyl acetate content 6.5%) was found to have significantly lower transmission rates for the respective probe compounds when compared to Film B(vinyl acetate content 9%) and Film C(vinyl acetate content 12%).

DEDICATION

This thesis is dedicated to my parents, brother and sister who encouraged and support my graduate education.

Without their endless patience and support, it is hardly possible to complete my graduate education. Special thanks to my father who gave me endless faith, patience and the idea that I can do.

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NOMENCLATURES

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C^*	-	Concentration of penetrant in purely amorphous polymer
c_s	-	Solubility of liquid in the polymer
D	-	Diffusion coefficient
D_o	-	Constant; Diffusivity at zero concentration of liquid
E_D	-	Activation energy for the diffusion
Hf	-	Heat of fusion
ΔH	-	Heat of solution
Mc	-	Average molecular weight of the amorphous chain segment in the presence of a penetrant
P	-	Permeability coefficient
q_A, q_B	-	Permeation rates of component A and B in binary mixture
Q^o	-	Total permeation rate of an ideal binary mixture
Q	-	Total permeation rate of a mixture
Q_A, Q_B	-	Permeation rates of pure components A and B
S	-	Solubility coefficient
Vs	-	Molar volume of penetrant
X_A, X_B	-	Weight fraction of A and B in the permeant
X_1	-	Flory-Huggins interaction parameter
ρa	-	Density of amorphous polymer
γ	-	Constant; a measure of the plasticizing action of the liquid on the membrane

α - Separation factor

θ - Permeation ratio

θ_A, θ_B - Permeation ratios of components A and B

INTRODUCTION

Packaging requirements often include a need to retain volatile contents within a package, or to prevent atmospheric vapors from entering a package. Such needs were usually easily handled by glass or metal containers. Because of a multitude of reasons, many economic, one would like to use lighter and disposable flexible packaging. Product vapors of concern are often organic and can include flavor ingredients in foods, as well as active ingredients in medical, household, and industrial products. Environmental vapors to be kept out of products include those of motor fuels, detergents, solvents, etc.

The selection of flexible packaging polymer films for the aforementioned applications requires more information than is normally available from resin and film suppliers. A quantitative knowledge of permeation rates, exposure conditions, and limits of acceptability allows one to optimize multilayer films and laminations, with respect to cost and performance.

The transport of non-interactive penetrant molecules such as fixed gases through polymeric materials has been studied in great detail (Chern et al., 1983; Crank and Park, 1968; Pasternak et al., 1970; Pye et al., 1976; Stannett et al., 1972). However, studies involving the permeation of organic vapors and liquids have been limited, and have focused primarily on single component organic vapor/polymer systems. Studies which have been published describing the permeation of organic vapors and liquids through barrier polymer include those by Rogers et al.,1960; Rogers,1964; Niebergall et al.,1978; Zobel,1982; Baner et

al.,1986; Hernandez et al.,1986; Liu et al.,1986; and Mohney et al.,1988. These studies were very important in providing a better understanding of the mechanism of the permeation process involving organic permeants. However, only a limited number of studies have been reported on the permeation of multi component mixtures of organic liquids and vapors through barrier membranes. The lack of data can be attributed to the complexities involved with organic vapors exposed to plastics.

In permeability studies reported by Michelson et al. (1985), it was found that for binary organic liquid mixtures of varying composition, three possible modes of interaction between the components of the mixture and the polymer could be described, namely :

1. The mixture may decrease the lag time or break through time of the individual components.
2. A component that does not permeate as a pure liquid may be transported through the membrane by another component, when present in the mixture.
3. The collective permeation rate for the mixture may be higher than the transmission rate of either pure component of the mixture.

The present study will focus specifically on determining the permeability of volatile compounds of a multi-component organic fragrance formulation through semi-permeable polymeric films, and the effect of formulation and barrier film composition on the transport process.

The objectives of this study are :

1. Carry out permeability studies with a multi-component organic fragrance formulation; Evaluate the following variables and the effect of membrane composition and formulation composition on the permeability of fragrance probe volatiles through the fragrance delivery system membrane.

2. Design and assembly of a test system to determine the permeability of the constituents of a multi-component organic fragrance mixture through a barrier film. The cell assembly will be designed to accommodate the fabricated fragrance delivery system, and will allow for measurement of the permeation rate as a function of time.

3. Carry out permeation studies with multi-component organic fragrance formulations and evaluate the effect of formulation variables and barrier film composition on the transport of the selective individual penetrants through the test polymer structure.

4. Perform statistical analysis on the permeability data to establish the significance of the respective test variables and the interaction terms associated with the permeability of volatiles through the fragrance delivery system.

. In terms of theoretical importance, a better understanding of the effect of penetrant/polymer interaction on the transport properties of individual components of a multi-component organic vapor mixture will be obtained.

LITERATURE REVIEW

PERMEATION OF ORGANIC VAPOR MIXTURES THROUGH POLYMER MEMBRANE

The barrier properties of different materials against various liquids, gases, and vapors are of paramount importance in packaging applications. The permeability of plastic films and other packaging materials to gases and vapors is of great practical interest.

In particular, knowledge of the permeability of organic vapors is needed for the successful design of packaging to prevent deterioration in product quality due to excessive loss or gain of such penetrants during storage. The transport of non-interactive penetrant molecules such as fixed gases through polymer materials has been studied thoroughly. However, studies involving the permeation of organic vapors and liquids have been limited, and have focused primarily on single component organic vapor/polymer systems. Studies which have been published describing the permeation of organic vapors and liquids through barrier polymers provide a better understanding of the mechanism of the permeation process involving organic permeants. However, only a limited number of studies have been reported on the permeation of multi-component mixtures of organic liquids and vapors through barrier membranes due to the complexities involved with organic vapors exposed to polymers membranes.

Studies involving the permeation of organic vapors have been limited, and have focused mainly on single component organic vapor/polymer systems.

Published studies describing the permeation of organic vapors through barrier polymer include those by Rogers et al., 1960; Gilbert et al., 1983; Niebergall et al., 1978; Zobel,1982; Rogers,1964; Baner et al., 1986; Liu et al., 1986 Hernandez et al., 1986; Hatzidimitriu et al., 1987, Mohney et al., 1988; Schaper, 1989, Rodney et al., 1992, and Johansson et al., 1994. These studies were valuable to provide a better understanding of the mechanism of the permeation process involving organic permeants. However, only a limited number of studies have been reported on the permeation of multi-component mixtures of organic vapors through barrier membranes (Li et al., 1965; Huang and Lin,1968; Tombalakian, et al., 1972, Fels, 1972, Weinberg, 1976; Michelson et al., 1985; Hensley et al., 1991, Theodorou, et al., 1992). Because of the complexities involved with organic vapors exposed to plastics, there are few data about the permeation of multi-component organic vapor. Hensley et al. (1991) reported on the concentration dependency of the permeability of organic vapor mixtures, and the effect of the relative concentration of individual components of the vapor mixtures on the transport of each particular penetrant comprising the mixture. Stannett and Yasuda (1963) have reported that with most organic vapors, the permeability increases rapidly with increasing vapor pressure. The permeability to liquid penetrants is considerably greater than with the corresponding saturated vapor. However, at lower vapor activity, the effect of vapor mixtures on the permeation and diffusion of the individual components of the vapor mixture is unpredictable.

Ghosh (1982) has studied the sorption characteristics of vapor of pure hydrocarbons and their binary mixtures in low density polyethylene, under various conditions of temperature and pressure. In order to compare the plasticizing effects of various hydrocarbons, Ghosh calculated the average molecular weigh of an amophorous chain segment in the presence of a penetrant within the polymer network (Mc) by using the method of Baddour et al. (1964). This relationship gives:

$$M_c = V_s \rho_a \left(\frac{1}{1+C^*}\right)^{1/3} \left\{ \ln\left(\frac{C^*}{1+C^*}\right) + \left(\frac{1}{1+C^*}\right) + X_1 \left(\frac{1}{1+C^*}\right)^2 \right\}^{-1} \qquad (1)$$

where C* is the concentration of penetrant in purely amorphous polymer, in cm^3/cm^3; Vs is the molar volume of the penetrant, cm^3/mole; ρ_a is the density of purely amophorous polymer in g/cm^3, and X_1 is the Flory-Huggins interaction parameter. Mc increases with vapor activity, i.e., increase in pressure and /or decrease in temperature.

The sorption in a semicrystalline polymer like low density polyethylene is dependent upon two factor: (a) temperature, which changes the amorphous content of the polymer and penetrant mobility; and (b) penetrant concentration, which brings about further changes within the amorphous polymer chain net work. The equilibrium sorption characteristics are very sensitive to temperature and pressure. The study showed that sorption increased with temperature and vapor activity. The increase being relatively slow at the initial stages and rapid subsequently, which is explained by Doolittle's theory of plasticization (Doolittle,

1954). The plasticization action in a noncrosslinked polymer like polyethylene mainly consists of reducing the number of pure mechanical entanglements of the amorphous chain segments between crystallites (Baddour et al., 1964; Ritchie, 1972).

Hensley et al (1991) studied the concentration dependency of the binary organic mixture,, limonene - ethyl acetate through biaxially oriented polypropylene film. The results showed that the collective permeation rate for the mixture was significantly higher than the transmission rates of the pure components, showing a synergistic effect. At lower activity levels, the presence of limonene vapor resulted in a dramatic increase in the transport properties of the co-permeant, ethyl acetate. At the highest vapor activity studied, ethyl acetate was found to significantly increase the transport properties of limonene, as compared to the permeability of pure limonene at similar activity levels.

DeLassus and Strandlburg (1991) studied the permeation of a mixture of organic vapors They observed both a slight decrease in the permeability of ethyl-2-methylbutyrate and a slight increase in the permeability of trans-2-hexenal and hexanal while an apple flavor compounds, when permeated as a mixture through low density polyethylene, at a very high concentration.

Theodorou et al. (1992) determined the permeability coefficients (P) of linalool, citral, ethyl butyrate, d-limonene and octanal through LDPE and ionomer film, when measured alone as individual permeant and as a component of a mixture at a temperature of 23°C and in saturated water vapor.

Generally, the permeability, diffusion and solubility coefficient (P, D, and S) values for permeants, measured in a mixture, were substantially less than the values obtained for the individual penetrants. Permeability behavior of these compounds, at low concentrations in the mixtures, was similar to that of permeant vapors. Reduction of the solubility coefficient for a permeation mixture was greater with penetrants with higher solubility coefficient values. Selected compounds in the mixture showed an increase in permeability coefficient values, which was attributed to high vapor concentration levels. However, a reduction in the permeability coefficient value with mixtures seem to indicate that plasticization or swelling of the polymer motion by the vapor mixture is not occurring at these low penetrant concentrations. The reduction in permeability is thought to be caused by the increase in competition for sorption and diffusion sites in the presence of other compound similar to the permeant gases. The reduction in permeability of a permeant gas in the presence of a second permeant gas such as CO_2 and CH_4 has been explained, based on competitive sorption and diffusion models (Story et al., 1989).

THEORY

LIQUID PERMEATION

Permeation normally occurs when a gas or organic vapor comes in contact with a polymer. Permeation is the flow of a vapor from one chemical potential to a lower level through a matrix. The rate of permeation through a polymer membrane depends on the penetrants solubility and diffusivity in the

polymer. The steady state permeation process may be simply described by Fick's law:

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

where Q is the permeation rate, D is the diffusion coefficient, and dc/dx is the concentration gradient across the membrane. The value of D depends strongly on the concentration of permeant liquid in the polymer membrane. An equation which is commonly used to relate D to the solubility of a liquid in the membrane and to a diffusivity D_o , obtained at zero concentration of liquid is:

$$D = D_o e^{\gamma c} \text{ (McCall,1957; Chandler and Henley, 1961)} \qquad (3)$$

where D_o and γ are constant at a given temperature. The constant γ, is a measure of the plasticizing action of a liquid on the polymer membrane; the concentration c of liquid in the polymer is the amount of sorption of liquid in the polymer, which is essentially determined by the solubility of the liquid in the polymer. Therefore, equation(3) shows that in the permeation process the diffusivity of a liquid is actually a function of its solubility in the polymer membrane.

Substituting eq.(3) in eq.(2), rearranging, and integrating with boundary condition gives:

$$Q \int_0^L dx = -Do \int_{c3}^{c2} e^{\gamma c} dc \qquad (4)$$

where L is the thickness of the membrane, c_1 and c_2 are the concentrations of permeant in the polymer at the upstream and downstream surfaces, respectively. At steady state, the permeation rate can be expressed as

$$Q = (D_o/\gamma L)\,(e^{\gamma c1} - e^{\gamma c2}) \qquad (5)$$

where c_1 can be determined by the equilibrium sorption of liquid in the polymer and c_2 is essentially zero, provided the downstream cell chamber is maintained at a low permeant partial pressure, and the rate of evaporation of permeate is not controlled by diffusion.

Equation (5) can then be simplified to

$$Q = (Do / \gamma L)\,(e^{\gamma cs} - 1) \qquad (6)$$

where c_s is the solubility of the liquid in the polymer membrane. This equation shows that the permeation rate of a liquid through a polymer membrane depends not only on its diffusivity, but also on its solubility in the membrane (Huang and Lin, 1968)

BINARY LIQUID PERMEATION

The membrane selectivity of a binary system consisting of two liquids A and B can be expressed in terms of a separation factor α, defined as the concentration ratio B/A of the permeants in the downstream, divided by the concentration ratio B/A of the permeants in the upstream.

$$\alpha_{B/A} = (Y_B / Y_A) / (X_B / X_A) \qquad (7)$$

where X_A and X_B are the weight fractions of downstream A and B in the permeant upstream mixture, while Y_A and Y_B are the weight fractions of A and B in the permeate.

The total permeation rate (Q) of a mixture through a polymer membrane is:

$$Q = q_A + q_B \quad (8)$$

where q_A and q_B indicate the permeation rates of components A and B in the binary mixture.

If the permeation process is ideal, the transmission rate of the mixture can be expressed in terms of the pure component permeation rates as:

$$q^o_A = X_A q_A \quad (9)$$

$$q^o_B = X_B q_B \quad (10)$$

where Q is the permeation rate of the individual components and the superscript zero refers to the ideal permeation rate. The total ideal permeation rate Q^o is given by

$$Q^o = X_A Q_A + (1 - X_A) Q_B \quad (11)$$

and the selectivity for a system which exhibits ideal behavior is simply the ratio of the pure component permeation rates. (Huang and Lin, 1968)

$$\alpha^o_{B/A} = Q_B / Q_A \quad (12)$$

Stannett (1962) and Rogers (1965) found that permeant gas and mixtures exhibit such ideal behavior. Non-ideal behavior results when on component of the permeating mixture plasticizes the membrane to a greater extent than the other. Organic vapors or liquids do not exhibit ideal permeation behavior because the permeants swell the membrane to different degrees. The measure of the non-ideal behavior of the permeation of liquid mixtures can be expressed by a permeation ratio θ, defined as the ratio of the actual permeation rate Q and its ideal permeation rate Q^o.

$$\theta = Q / Q^o \quad (13)$$

The permeation ratios for the individual components can be expressed as

$$\theta_A = q_A / Q_A \quad (14)$$

and

$$\theta_B = q_B / Q_B \quad (15)$$

where θ_A and θ_B are the permeation ratios of components A and B, q_A and q_B are the permeation rates of components A and B in the binary mixtures and Q_A and Q_B are the permeation rates of pure components A and B respectively.

Thus the permeation ratio should be equal to unity when a system exhibits ideal permeation behavior. The value of the permeation ratio may be higher or lower than unity for non-ideal permeation. If the permeation ratio of a system is higher than unity, the system can be said to exhibit a permeation enhancement effect, while a value lower than unity indicates a permeation depression effect.

FACTORS AFFECTING PERMEATION

Some of the principal factors affecting the rates of permeation are:

- Temperature
- The nature of the permeant, including molecular size, shape
- The nature of the polymer, including morphology and molecular motion of the polymer
- The penetrant concentration (Rogers et al., 1962)

TEMPERATURE

For the mass transfer process described by Fick's first and second Laws of diffusion, permeation is the flow of a vapor from one chemical potential to a lower level through a matrix. The process involves several steps, the slowest of which is usually movement through the non-crystalline regions of the polymer. The permeant molecules are able to diffuse through the polymer matrix by "jumping" from one sorption site to the next, under a pressure gradient. The amorphous sections of the polymer, or the free volume, create the "holes or microvoids" required to accommodate a permeant molecule, and enough holes must be present to create a channel or pathway to allow for successful diffusional jumps. In general, the temperature dependence of P, D, and S are given by the Arrehenius relationships:

$$D = D_o \exp(-E_D/RT) \quad (16)$$

$$S = S_o \exp(-\Delta H/RT) \quad (17)$$

$$P = P_o \exp(-E_P/RT) \quad (18)$$

where D is the diffusion coefficient, S is the solubility coefficient, and P is the permeability constant. ΔH is the heat of solution, E_D and E_p are the activation energies for the diffusion and permeation processes, and $P_o = D_o S_o$.
For easily condensable vapors, ΔH is usually negative due to the contribution of the heat of condensation, and thus S decreases with increasing temperature (Stannett et al, 1962).

Generally, an increase in temperature causes an increase in the rate of permeation of binary mixture and a decrease in selectivity. The decrease in

selectivity can be explained by the increase in agitational energy or motions of the polymer chains at higher temperatures. According to Eyring's hole theory, the formation of "holes or voids " in the polymer microstructure requires enough energy to break down a number of secondary valence bonds. At low temperature there are more smaller holes than larger holes within the amorphous regions. At higher temperatures, larger holes or voids are produced as a result of the higher agitational energy of the polymer chains (Huang and Lin, 1968).

THE NATURE OF PEMEANT

Since the first two steps of the permeation process are (1) dissolution of molecules into the polymer membrane, and (2) the diffusion of the molecules though it. Differences in either the solubility or the diffusivity can result in separation. The solubility difference depends primarily on the difference in the chemical nature of the permeating species. On the other hand, the diffusivity difference is determined largely by the size and shape of these molecules and by the degree of aggregation among the diffusing species within the polymer. For molecules with similar shape and chemical nature, the permeation rate was found to decrease with increasing molecular length (Huang and Lin, 1968). Organic penetrants solubilize, swell and plasticize the polymer. The quantitative measure of the swelling ability can be obtained by examining the solubility parameters of the liquids and polymer. In general, solvent with the solubility parameter (δ) close to that of the polymer membrane sorbs to a greater extent

than a solvent which has a value of (δ) which is far from that of the polymeric substance (Huang and Lin, 1968). Fels (1972) explained the variability of the permeation and separation factors with composition (other than ideal behavior) quantitatively in the following way : "if there is a difference in swelling ability of the two liquids towards the polymer, then one liquid will see a different polymer structure because of the swelling effect of the other liquid. If the interactions of the two liquids were the same, a constant separation factor would result, and the permeability would follow ideal behavior. This qualitative explanation has been incorporated into the quantitative expression for the permeability of the individual components in a mixture".

From the study of the permeation characteristics and the separation behavior of 25 combinations of binary liquid mixtures through low density polyethylene membrane, Huang and Lin (1968) found that when molecules of similar chemical nature were compared, the permeation rate increased with decreasing V/L, the diffusional cross section of the molecule, where V is the molecular volume and L the maximum molecular length. From the experimental results, they observed three general trends:

(1) For single component permeation, when comparing members of a given homologous series of compounds, those with lower molecular weight permeate faster than the higher molecular weight members. In binary permeation, for a given binary mixture containing two members of a homologous series,, the lower molecular weight member permeates preferentially.

(2) For single component permeation, molecules with a smaller cross section permeate faster, when comparing molecules of similar molecular weight and chemical nature. For binary liquid permeation, molecules with smaller cross sections will permeate at a faster rate than the other.

(3) In liquid permeation, shape and size effects predominate for molecules with small differences in chemical nature. However, molecules with large differences in chemical nature are not as affected by their shape and size, but depend more on parameters such as solubility, which are related to the chemical nature of the molecule.

DeLassus and Strandburg (1991) studied the effects of some parameters for selected flavor molecules. They investigated the diffusion coefficient for two families of permeants at 10 to 18 Pa partial pressure, in a vinylidene chloride copolymer film. For both the linear esters and the n-alkanes evaluated, the diffusion coefficient decreases smoothly, as the size of the permeant increases. For linear molecules, the diffusion coefficient changes slowly as the permeant changes size. For more spherical molecules, the diffusion coefficient is expected to change more rapidly (Berens and Hopfenberg, 1982). The solubility coefficient has been observed to be strongly related to the boiling point within a family of permeants. As the boiling point increases, the solubility increase. The act of solubilization from the vapor phase into a polymer may be analyzed as condensation followed by mixing. Within a family of permeants, the heat of condensation varies more than the heat of mixing, hence the solubility coefficient follows the boiling point closely.

NATURE OF POLYMER

During the permeation process, permeant molecules pass through temporary voids or "holes" in the amorphous polymer regions. These voids are the result of the temperature dependent segmental motion of the polymer chains. The magnitude of the diffusion rate depends both on the permeant and the polymer. Factors which improve barrier properties of a polymer relate to the tightness of molecular packing and forces which restrict the segmental movement of the polymer. The regularity of branching and the number and length of branches in polymer are recognized as important to the barrier properties (Murray, 1985).

The existence of crystalline regions in the polymer have at least three effects on the sorption and diffusion process :

(1) The crystalline region is essentially impermeable to permeant molecules i.e. sorption and diffusion occur almost exclusively through the amorphous component. Hence, less polymeric material is available to the diffusing species.

(2) The diffusing molecule must take a more tortuous pathway through the semi-crystalline polymer in order to avoid the impermeable crystalline domains.

(3) The crystalline domains, acting like giant cross-linking regions, impose strong constraints on the amorphous phase and give rise to considerable

decrease in the mobility of the amorphous chain segment. Thus, the amorphous phase in a semi-crystalline polymer is usually less permeable than in a fully amorphous sample (Mark et al., 1985).

Any factor which tends to make the polymer - chain segments less mobile, or pack more closely, will decrease the permeation rate. The permeation rate can be expected to decrease as the symmetry and cohesive energy density of the polymer increases.

The interaction of polymer and permeant is a major consideration when the two materials form solutions or the permeant swells or plasticizes the polymer, creating enhanced segmental motion and larger voids. The presence of a plasticzing component such as water in the binary permeating mixture should result in permeation enhancement, i.e. θ greater than unity. However, Huang and Jarvis (1970) observed depression of permeation rates below the ideal rates in a plasticized system. This was shown to be due to other phenomena masking the initial plasticizing action of water. Several workers have postulated that the permeation of water through polymer membrane can be hindered by the formation of water clusters. The significant permeation depression observed for water-alcohol solutions through cellophane is explained by the clustering of water molecules. The clustering of water molecules dominates the effect of plasticization, resulting in a depression of the permeation rate from the ideal rate.

Liu et al. (1988) found an increase in the diffusion of toluene vapor through laminates containing a water - sensitive barrier layer as a function of solid water. DeLassus et al. (1988) showed that moisture had considerable plasticizing effect on EVOH (ethylene vinyl alcohol copolymer), resulting in increased permeability and diffusion of an aldehyde (i.e. trans-2-hexanal). Landois-Garza and Hotchkiss (1988) reported that the permeability and diffusion of an ester (i.e. ethyl propionate) in PVOH (poly vinyl alcohol copolymer) decrease when the relative humidity increased. Harzidimitriu et al. (1987) showed that for some organic vapors, permeability through various mutilayered films increased when relative humidity increased.

Johansson and Leufven (1994) investigated the influence of humidity on the sorption, diffusion and permeation of alcohols and aldehydes in three common packaging polymers (linear low density polyethylene, LLDPE; high density polyethylene, HDPE; and ethylene vinyl alcohol copolymer, EVAL). Higher humidity decreased diffusion of alcohol, and increased diffusion of aldehyde. This might be explained by the combination of the plasticizing effect of water with the interaction between aroma and water vapors. Relative humidity had a great influence on barrier properties of polyethylene film with lower crystallinity (i.e. LLDPE) than on more crystalline film (i.e. HDPE). The effect of water was more pronounced with the polar EVAL films.

CONCENTRATION

The concentration (or partial pressure) of organic vapor in equilibrium with a plastic can affect the vapors permeability constant. For permeants with relatively high solubility in polymers, such as organics, the concentration dependence of D becomes important, since the organic penetrants are capable of plasticizing the polymer chain segments, resulting in a rapid increase of D with increasing permeant concentration.

Studies by Zobel (1985) on permeation of limonene in polyethylene at 25°C indicated that at permeant pressure less than about 10%of the saturated vapor pressure, the permeability was not affected. However, at permeant pressure above about 15 to 20% of the saturation vapor pressure, he found that the permeability increased sharply with increasing permeant pressure. Landois-Garza and Hotchkiss(1988) found that the permeability of ethyl propionate through dry polyvinyl alcohol was independent of concentration below about 30% of the saturation vapor pressure. Above this concentration, the permeation rate increased sharply.

PERMEANTION MEASUREMENT

ORGANIC VAPOR PERMEATION:

For permeation studies, quasi-isostatic and isostatic methods are commonly employed for determining the diffusion of organic vapors through barrier films using gas chromatographic analysis for quantification (Stannett et al,

1972; Zobel, 1982; Baner et al., 1986; Hernandez et al.,1986; DeLassus, 1985). The partial pressure difference of the test vapor provides the driving force for permeation, with the total pressure on both sides of the film being one atmosphere.

In the quasi-isostatic method, the permeated gas of vapor is accumulated in the lower concentration chamber of the permeability cell, and monitored as a function of time. The total quantity of penetrant to have transmitted through the film is plotted as a function of time.

The isostatic method allows for the continuous collection of permeation data of an organic vapor or gas through a polymer membrane from the initial time zero to steady state conditions, as a function of temperature and permeant concentration. A constant concentration of permeant vapor is continually flowed through the high concentration cell chamber. At the same time a constant flow of carrier gas is passed through the lower cell chamber, removing permeant vapor at a constant rate and conveying it to the detector apparatus. At pre - selected time intervals the concentration of penetrant in the carrier system flowing through the low concentration cell chamber is determined, and the transmission rate is monitored continually until steady state conditions are attained.

MATERIALS AND METHODS

BLISTER TRAYS AND FILM SAMPLES

Blister trays (L X W X D - 2.75" X 1.5" X 0.25" and flange width of 1/4") as shown in Figure 1, were thermoformed from a Barex-polyethylene coextrusion and film samples of three different ethylene-vinyl acetate copolymers (film A-5.5 mil, 93.5% ethylene/ 6.5% vinyl acetate) (film B-5 mil, 91% ethylene/ 9% vinyl acetate) (film C-5 mil, 88% ethylene/ 12% vinyl acetate) were provided by the Dial Corp.(Scottsdale, AZ), and were used in all studies. Barex is a copolymer of 74% acrylonitrile and 26% methyl acrylate modified with a butadiene rubber graft. The film samples serve as the membrane lid for the fragrance delivery system and were heat sealed to the tray.

FRAGRANCE FORMULATIONS

The fragrance formulations evaluated in the study were provided by the Dial Corp, and were a floral type. The nine different formulations evaluated were formulated with 3 different levels of Cabosil and 3 Isopar content levels, as indicated below: Cabosil was used as a thickening agent, and Isopar served as the dispersing solvent. The make up of the respective test formulations are summarized in Table 1.

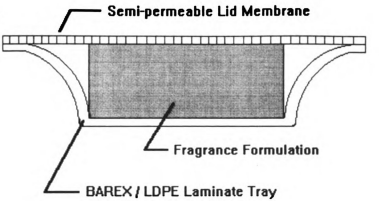


Figure 1. Fragrance delivery system

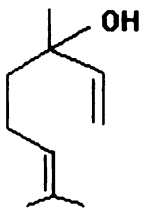
Table 1. Fragrance formulations

Fragrance Formulation	Isopar Content (wt %)	Cabosil Content (wt %)
1	2	4
2	2	6
3	2	8
4	5	4
5	5	6
6	5	8
7	8	4
8	8	6
9	8	8

PROBE COMPOUNDS

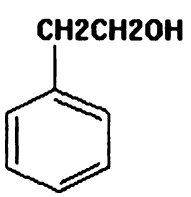
To provide a relative evaluation of the aroma barrier properties of the polymer film, four probe compounds, characteristic of the fragrance profile, were selected. The probe compounds were selected based on their relative concentration in the aroma profile, contribution to the aroma, low sensory threshold, and ease of analysis. The probe compounds selected included linalool, phenethyl alcohol, benzyl acetate, andα-hexyl cinnamaldehyde and were obtained from Aldrich Chemicals (Milwaukee, WI).

Linalool



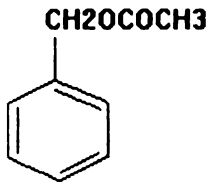
Molecular weight	154.25
Boiling point	194-197°/720 mm
Refractive index	1.462
Density	0.87

phenethyl alcohol



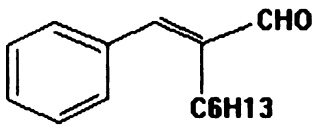
Molecular weight	122.17
Boiling point	219-221°/750 mm
Melting point	-27°
Refractive index	1.532
Density	1.023

benzyl acetate



Molecular weight	150.18
Boiling point	206°
Melting point	-51°
Refractive index	1.502
Density	1.04

α-hexyl cinnamaldehyde



Molecular weight	216.33
Boiling point	174-176°/15 mm
Refractive index	1.55
Density	0.95

METHANOL ABSOLUTE (Baker analyzed - J.T. Baker Inc., philipsburg, NJ)

Molecular weight 32.04

Methanol was used as the solvent for preparing standard solutions of the probe compounds for calibration, and to quantify the levels of the respective probe compounds in the fragrance formulations.

NITROGEN - CARRIER GAS

High purity dry nitrogen (99.98%) provided by the AGA Gas Inc (Cleveland, OH) was used as the carrier gas.

ANDEX LABORATORY BLISTER SEALER

The blister trays were mounted on a wooden mold, and filled with 3 ml of test fragrance formulation. A sample of the ethylene-vinyl acetate (EVA) copolymer film was cut to the size of the blister, placed over the blister, covered with Teflon film and heat sealed. An effective heat seal was obtained at a temperature 280°F and dwell time of 15 sec for film A and 285°F and dwell time of 10 sec for film B and film C. The heat seal obtained was examined visually and tested manually for peel resistance. The sealing conditions were based on the endotherm profiles of the three films by differential scanning calorimetry (DSC) analysis At this seal temperature, the film samples exhibiting the lowest onset temperature and melting point required the shortest dwell time to obtain an effective heat seal.

ANALYTICAL

A Hewlett Packard Model 5890A gas chromatography (GC), equipped with 30m X 0.32mm ID SPB-5 nonpolar capillary column having a 25μm film of 5%diphenyl, 94%dimethyl, and 1% vinyl polysiloxane phases obtained from Supelco (Bellefonte, PA), and flame ionization detector was used for all analyses. The GC was interfaced to a HP 3392A integrator to record all data. The GC was operated in the splitless mode with the following conditions.

Initial temperature - 60°C, Initial time - 1.00 min, Final temperature - 260°C, Final time - 10.00 min, Rate - 4°C/min, Purge off - 1.00 min, Range - 4, Attenuation - 2, Total run time - 61 min, Inlet temperature - 220°C, Detector temperature - 220°C.

The four probe compounds were eluted at the following retention times: linalool - 10.72 min, phenethyl alcohol - 11.06 min, benzyl acetate - 12.82 min, α-hexyl cinnamaldehyde - 31.51 min.

Standard calibration curves of area response versus mass of probe compound, were constructed for each probe compound, from standard solutions of known concentration. Standard solutions were prepared by dissolution of known quantities of linalool, phenethyl alcohol, benzyl acetate, and α-hexyl cinnamaldehyde in methanol, respectively. The concentration of the probe compounds in each study was determined by reference to the calibration curves.

PERMEATION MEASUREMENTS

Permeability experiments were carried out at 50°C for a period of thirty days at a flow rate of 20 cc/min. The permeability cells used in this study are described by Hernandez et al. (1986). The test apparatus is of our own design, and was used to monitor the transport of volatile fragrance compounds through the filled delivery tray system by the isostatic method of measurement. The cells are comprised of two aluminum disc shaped plates and a center ring, that when clamped together to form the complete cell which was comprised of an upper chamber, a lower chamber, and a middle chamber. Each cell chamber contains and inlet and outlet port for the continuous flow of a carrier gas stream. Analysis of penetrant concentration was based on a chromatographic procedure, with flame ionization detection (FID).

A schematic diagram of the system utilized is presented in Figure 2. All permeation cells and cell parts were rinsed with acetone and baked at 120°C for a period of at least 72 hours to remove any residual sorbed permeant from the previous experiment. The "O" rings in the permeation cells were replaced before each run. Hermetic isolation of the cell chamber from the environment is achieved by the compression of a Viton "O" ring between the lower chamber and the center ring. Viton™ is a fluorocarbon elastomer compound which is resistant to attack and swelling by most organic vapors.

A Blue M electric Stabil-therm Mechanical convection oven with Protronics II control (Fisher Scientific Co., USA) was used in the study to provide a constant temperature environment for mass transport studies. Protronics II control

consists of a main temperature control and over temperature alarm (OTA) control. When the main control set point was 50°C, the OTA set point was 60°C, 10°C above the desired operating temperature of the oven, as verified with a thermometer.

For each permeation test cell, a sealed fragrance delivery tray was placed in the lower chamber, and the upper cell chamber was covered with aluminum foil to reduce the cell volume. Carrier gas was then flowed through the middle chamber. The inlet an outlet ports of the lower and upper cell chambers were closed. In operation, the assembled cells (two) were placed horizontally on the top rack of the oven and were connected to the sampling cells. The sampling cell also has three chambers with the center one being isolated from the top and bottom cell chamber by aluminum foil. The center chamber contains a sampling port from which aliquots are taken for quantification of permeant concentration. Rotameters were used to provide a fixed and constant gas flow through the test and sampling cells. The carrier gas flow to the rotameter were regulated by Nupro "M" series needle valves. Electronic mass flow meters manufactured by Sierra Instruments (Monterey,CA), Top Trak 820 model, 9-20 SCCM with an accuracy of 2% of full scale and 0.5% repeatability were incorporated between the rotameter and the testing cell to provide a continuous indication that a constant rate of flow of carrier

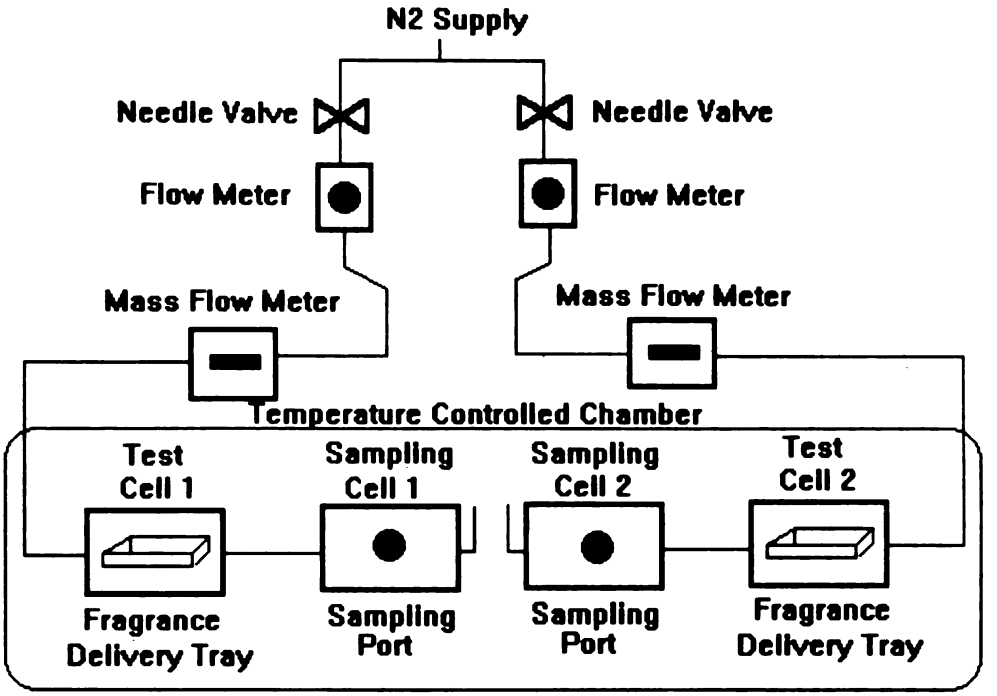


Figure 2. Schematic of fragrance delivery system permeation test apparatus.

gas was maintained. The mass flow meter reading was also verified using a bubble flow meter. All connections were made with copper refrigeration tubing 1/8" OD and 1.65 mm ID. All fittings and tubing connections used were Swagelok fittings. Before each run, the test cell and sampling cells were flushed with nitrogen and an aliquot was taken from the sampling cell and injected directly into the GC to determine the presence of residual organic vapors.

At predetermined time intervals (every 72 hours) a 50 microliter sample was removed from the middle chamber of the sampling cell with a gas tight syringe(1750SN, 500μl, Hamilton) and injected directly into the gas chromatograph. Replicated samples were analyzed and the average values reported.

The transmission rate or flux of the probe compounds through the fragrance delivery system was calculated by substitution into the following equation:

$$\text{Flux}\left(\frac{g}{day}\right) = AU \times CF \times \left(\frac{1}{V\,inj}\right) \times \text{flow rate} \times 1440\left(\frac{min}{day}\right) \qquad (19)$$

where AU = average area units from gas chromatogram

CF = calibration factor (g/AU)

Vinj = sample injection volume (0.05 cc)

Flow rate = cell flow rate (20 cc/min)

The sensitivity of the GC was determined with a calibration standard, prior to all sample analysis.

MASS BALANCE STUDIES

The concentration of probe compounds in the formulation was determined by chromatographic analysis prior to and following termination of the permeation experiments, and a mass balance determination was made for each probe compound. The blister trays were also weighed before and after the permeability experiment to determined global loss , where global loss is defined as the total level of volatiles lost.

$$\text{Global loss (\%)} = \frac{\text{initial wt - final wt}}{\text{initial wt}} \times 100 \qquad (20)$$

The initial concentration of the probe compounds in the fragrance formulation was determined before each run by dissolving 0.1 ml of the fragrance formulation in methanol, in a 200 ml volumetric flask. 0.5μL aliquot of this sample was injected into the GC for analysis. All analyses was done in duplicate and the average area response used to calculate the initial concentration of the probes in the fragrance formulation. After the permeation experiments were completed, a known amount (<0.05 g) of the fragrance formulation remaining, was weighed into a 100 ml volumetric flask partially filled with solvent. The solution is swirled to dissolve the fragrance formulation and made-up to volume with methanol. A 0.5μL aliquot of this sample was analyzed by GC to determine the final concentration of probes. From the difference between the quantity of probe compounds before and after completion of the permeability experiments, the percent loss of individual probes was determined.

$$\% \text{ probe loss} = \frac{\text{initial quantitty - final quantity}}{\text{initial quantity}} \text{ X } 100 \qquad (21)$$

Table 2. DESIGN OF THE STUDY

	RUN NUMBER								
VARIABLE NUMBER	1	2	3	4	5	6	7	8	9
Vinyl acetate content	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Isopar content	2	2	2	5	5	5	8	8	8
Cabosil content	4	6	8	4	6	8	4	6	8
VARIABLE NUMBER	10	11	12	13	14	15	16	17	18
Vinyl acetate content	9	9	9	9	9	9	9	9	9
Isopar content	2	2	2	5	5	5	8	8	8
Cabosil content	4	6	8	4	6	8	4	6	8
VARIABLE NUMBER	19	20	21	22	23	24	25	26	27
Vinyl acetate content	12	12	12	12	12	12	12	12	12
Isopar content	2	2	2	5	5	5	8	8	8
Cabosil content	4	6	8	4	6	8	4	6	8

STATISTICAL ANALYSIS

The statistical design, as shown in Table 2 was based on a three(3) level, three (3) variable factorial design and considered three variables including: ethylene-vinyl acetate copolymer composition, isopar content, and cabosil content. For each variable, three concentration levels were selected in order to create a linear level of concentration that could be easily extrapolated after experimental analysis.

For statistical analysis, the slopes obtained from transmission profile curves of each probe compound were utilized. The slope of the transmission profile curves were used as an indication of the barrier characteristics of each system considered.

The analysis of variance (ANOVA) statistical technique was then used to examine the variability of the individual observations within each group, as well as the variability between group means. This analysis allowed determination of the variables which had the most significant effect on the permeability of fragrance volatiles from the fragrance delivery system. A Simple Factorial and a One-way ANOVA in SPSS for Windows was used to perform this statistical analysis.

The following assumptions were made when performing the analysis of variance:

- sample data/observation is an independent random sample from a normal population.
- homogeneous within group variance across all groups.

The statistical procedure for comparing two or more treatment means, involves testing of the null hypothesis of no effect. If the analysis leads to the conclusion that we could expect such mean differences quite frequently by chance, we do not reject the null hypothesis and conclude that we have no good evidence of a real treatment effect. If the analysis indicates that the observed differences would rarely occur in random samples drawn from populations with equal means and variances, we reject the null hypothesis and conclude that at least one treatment had a real effect. At least one of the means is said to be significantly different from the others. If the probability of the statistical analysis is less than 5% of the variation among means, the null hypothesis is rejected and we can say that the means are significantly different.

The Simple Factorial ANOVA procedure considers the probability of the null hypothesis, that the data are a sample from a population in which the mean of a test variable is equal in several groups of cases defined by factor variables. It differs from One-way ANOVA in handling several grouping variables simultaneously.

RESULT AND DISCUSSION

VAPOR PRESSURE AND VAPOR ACTIVITY OF THE FRAGRANCE FORMULATION:

The saturation vapor pressure, vapor pressure and vapor activity of the individual probe compounds in the test fragrance formulations are summarized in Tables 3-5, respectively. The vapor pressure and vapor activity values of the probe compounds in the fragrance formulations were found to be higher with an increase in Isopar content. The saturation vapor pressure of hexyl cinnamaldehyde was lower than the other probe compounds, which could be explained by its very high boiling point (174°C). The vapor pressure of hexyl cinnamaldehyde in the fragrance formulations was not detected.

The concentration of the respective probe compounds in the test fragrance formulations are tabulated in Table 6. The tabulated data shows linalool to be present at the highest concentration in all the fragrance formulations, as compared to the other selected fragrance volatiles. This in part, also explains the higher vapor pressure levels of linalool in the fragrance formulations.

Table 3. SATURATION VAPOR PRESSURE OF PROBE COMPOUNDS AT 50^0C (mmHg)

Linalool	Phenethyl Alcohol	Benzyl Acetate	α-Hexyl Cinnamaldehyde
0.6905	0.1128	0.3359	0.0014

Table 4. VAPOR PRESSURE OF PROBES IN THE FRAGRANCE FORMULATIONS AT 50^0C (mmHg)

Fragrance Formulations	Linalool	Phenethyl Alcohol	Benzyl Acetate	α-Hexyl Cinnamaldehyde
1	0.1983	0.0685	0.0823	0
2	0.1841	0.0666	0.0815	0
3	0.1409	0.0508	0.0625	0
4	0.2160	0.0776	0.0821	0
5	0.2519	0.0881	0.1019	0
6	0.2184	0.0850	0.0916	0
7	0.2595	0.0967	0.0865	0
8	0.2840	0.1097	0.1051	0
9	0.2582	0.0951	0.0839	0

Table 5. VAPOR ACTIVITY OF PROBES IN FRAGRACNE FORMULATIONS

Fragrance Formulations	Linalool	Phenethyl Alcohol	Benzyl Acetate	α-Hexyl Cinnamaldehyde
1	0.2871	0.6071	0.2451	0
2	0.2667	0.5903	0.2427	0
3	0.2040	0.4507	0.1861	0
4	0.3129	0.6884	0.2444	0
5	0.3648	0.7812	0.3034	0
6	0.3162	0.7534	0.2727	0
7	0.3758	0.8575	0.2574	0
8	0.4114	0.9729	0.3128	0
9	0.3739	0.8432	0.2498	0

Table 6. THE CONCENTRATION OF THE PROBE COMPOUNDS(g/ml) IN THE FRAGRANCE FORMULATIONS

Fragrance Formulations	Linalool	Phenethyl Alcohol	Benzyl Acetate	α-Hexyl Cinnamaldehyde
1	0.1968	0.1471	0.0736	0.0007
2	0.1983	0.1456	0.0753	0.0007
3	0.2204	0.1597	0.0821	0.0009
4	0.2344	0.1753	0.0888	0.0005
5	0.2042	0.1521	0.0787	0.0004
6	0.2044	0.1521	0.0785	0.0005
7	0.2375	0.1656	0.0877	0.0006
8	0.2084	0.1512	0.0800	0.0007
9	0.1949	0.1407	0.0740	0.0009

THE PERMEATION STUDIES OF FRAGRANCE VOLATILES

The permeability studies were carried out at 50°C at a cell flow rate of 20cc/min for all fragrance formulations. Studies were terminated after 30 days of continuously monitoring the transmission rate of each probe compound through the fragrance delivery system membrane. The obtained mass flow values were assumed to be diffusion controlled, which simulated the conditions for the loss of fragrance volatiles for the fragrance delivery system under end-use applications. At the actual end-use application, the external membrane of the fragrance delivery system is exposed to an infinite volume into which the fragrance volatiles would diffuse.

Three distinct steps are involved in the transport of organic compounds through a polymeric film ;

(1) absorption of permeant molecules at the polymer film surface

(2) diffusion of the permeant molecules through the polymer bulk phase

(3) removal of the permeant molecules from the low concentration film surface by evaporation.

The total or global loss and the percent loss of the four probe compounds through film A, film B, and film C, on a weight percent basis, are summarized in Tables 7-10 respectively. As shown, after 4 weeks of test, nearly quantitative losses of linalool, phenethyl alcohol, and benzy acetate were found, while about 50% loss of α-hexyl cinnamaldehyde was observed at the test conditions of 50°C and a carrier gas velocity of 20cc/min.

Table 7. GLOBAL LOSS OR THE TOTAL VOLATILES LOSS FROM FRAGRACNE FORMULATIONS THROUGH FILM A, FILM B, AND FILM C

Fragrance Formulations	Percent Loss		
	Film A	Film B	Film C
1	45.43	43.34	44.85
2	43.77	46.05	44.62
3	43.26	45.07	41.04
4	47.18	43.87	44.33
5	42.72	43.82	45.19
6	39.91	43.86	45.27
7	45.69	50.23	46.61
8	46.07	45.44	46.07
9	44.33	43.88	44.69

Table 8. PERCENT LOSS OF SPECIFIC PROBE COMPOUNDS FROM FRAGRANCE FORMULATION THROUGH FILM A.

Fragrance formulation	Percent loss (wt/wt %)			
	Linalool	Phenethyl alcohol	Benzyl acetate	α-hexyl cinnamaldehyde
1	96.95	83.55	92.34	57.51
2	97.36	82.68	99.40	38.30
3	98.86	84.06	99.69	70.66
4	98.72	86.68	99.56	44.81
5	97.46	80.31	98.83	30.41
6	96.88	77.00	98.75	N/A
7	97.24	84.93	98.93	64.85
8	97.65	84.38	99.15	75.28
9	97.61	83.12	98.82	72.34

N/A denotes not available

Table 9. PERCENT LOSS OF SPECIFIC PROBE COMPOUNDS FROM FRAGRANCE FORMULATION THROUGH FILM B.

Fragrance formulation	Percent loss (wt/wt %)			
	Linalool	Phenethyl alcohol	Benzyl acetate	α-hexyl cinnamaldehyde
1	97.52	77.74	98.27	35.30
2	98.68	80.51	99.41	43.76
3	99.25	83.43	99.32	59.12
4	98.06	78.44	98.98	26.54
5	97.99	75.64	99.13	N/A
6	98.06	80.05	99.54	N/A
7	99.27	93.06	100	63.83
8	98.05	85.24	99.53	54.89
9	97.52	83.09	99.37	64.88

N/A denotes not available

Ta

FF

Table 10. PERCENT LOSS OF SPECIFIC PROBE COMPOUNDS FROM FRAGRANCE FORMULATION THROUGH FILM C.

Fragrance formulation	Percent loss (wt/wt %)			
	Linalool	Phenethyl alcohol	Benzyl acetate	α-hexyl cinnamaldehyde
1	99.46	87.77	99.74	64.37
2	99.62	87.65	100	42.90
3	99.45	85.74	100	56.11
4	99.56	90.71	100	57.76
5	99.56	87.33	100	N/A
6	100	89.94	100	32.54
7	99.68	92.71	100	68.90
8	99.59	90.99	100	75.81
9	99.49	90.04	100	33.76

N/A denotes not available

The respective transmission profile curves for linalool, phenethyl alcohol and benzyl acetate, from fragrance formulations 1-9, through film A, film B. and film C are presented in Figures 3-83, where the flux of the specific permeating fragrance volatiles (g/day) is plotted as a function of run time. The level of α-hexyl cinnamaldehyde was below the limit of detectability by chromatography analysis. Therefore, no permeation behavior for this probe volatile was obtained. The reported data are the average of duplicate values. The flux data or transmission rate values through film A, film B, and film C for the respective probe compounds, at 50°C and flow rate of 20cc/min, are summarized in Tables 15-41, and are presented in Appendix C.

From the transmission profile data, linalool shows the highest transmission rate when compared to phenethyl alcohol, benzyl acetate, and α-hexyl cinnamaldehyde. Linalool is present in the highest concentration in the fragrance formulation and has the highest vapor pressure value, which explains the observed higher transmission rate of linalool. Also, α-hexyl cinnamaldehyde was not detected in the permeated vapor stream in the present studies, which can be attributed to its low concentration in the fragrance formulation and high boiling point (i.e. low vapor pressure).

If a polymer film is placed in contact with an infinite concentration of diffusant, the transmission curve would follow Fickian behavior and show an initial induction period followed by a non-steady state transmission rate of diffusion, which precedes a steady state rate. However, for the fragrance

delivery system studied, there is a limited concentration of fragrance volatiles in the system, so there will be a continuous decrease in fragrance volatiles concentration, as well as a continuous decrease in the partial pressure gradient with time, as a result of fragrance volatiles diffusion. These dynamic factors and the limited fragrance volatile concentration levels present in the delivery system trays will result in the transmission rate profile curves observed for the respective penetrant/delivery system membranes investigated.

As shown in transmission profile curves (see Figures 7 to 87) , the permeability behavior of the respective penetrant/barrier membrane systems studied, typically followed a Gaussian type plot, where there was an initial rapid rate of increase in the penetrant flux to a maximum level, which was then followed by a linear decrease in the rate of diffusion with time. The finite concentration of fragrance volatile in the fragrance formulations and the dynamic nature of the system, which resulted in a continuous change in both the penetrant driving force concentration and composition of the fragrance copolymer, are both contributing factors to the Gaussian-like transmission rate profile curves obtained. While the transmission rate profile curves obtained for linalool and benzyl acetate followed Gaussian-like behavior, the plotted flux data obtained for phenethyl alcohol showed a significant degree of data scattering (for example see Figures 4, 7, 10 and 31). Although the permeability behavior of phenethyl alcohol showed considerable data scattering, it was assumed that a smooth curve fit of the flux data would follow the expected rapid increase in the penetrant flux to maximum, preceded by a steady decline in the flux with time. The observed scatter of the

data about a smooth fit curve can result from errors arising from the gas chromatographic analysis of phenethyl alcohol level in the carrier gas stream. Since the mass transfer rates are determined by substitution into Equation (22),

$$\text{Flux} = \text{A.U} \times \text{C.F} \times \frac{1}{Vinj} \times \text{flow rate} \times 1440\left(\frac{\min}{day}\right) \qquad (22)$$

it follows that an inaccurate value of detector response (AU) would result in either an overestimation or an underestimation of the flux rate of phenethyl alcohol. In this regard, it is important to note that gas chromatographic analysis is valid only in a negative sense in that a response from the detector, under specified conditions, is recorded. Since it is possible for different compounds to have identical, or very similar retention times, poor peak resolution of a co-permeant can result in a detector response value (A.U) for phenethyl alcohol, which would overestimate its actual concentration level and its concomitant flux rate.

The permeation process involves dissolution of molecules into the polymer membrane and diffusion of the molecules through the membrane. Differences in either the solubility or diffusivity can effect the transmission characteristics of the fragrance volatiles. The solubility difference depends on the difference in the chemical nature of the permeating species. However, the difference in diffusivity is primarily determined by the size and shape of the molecules, and by the degree of aggregation among the diffusing species in the polymer. In general, polar compounds permeate polar membranes faster than non-polar compounds. Therefore, linalool and phenethyl alcohol, which are more polar, as compared to benzyl acetate and α-hexyl cinnamaldehyde, would

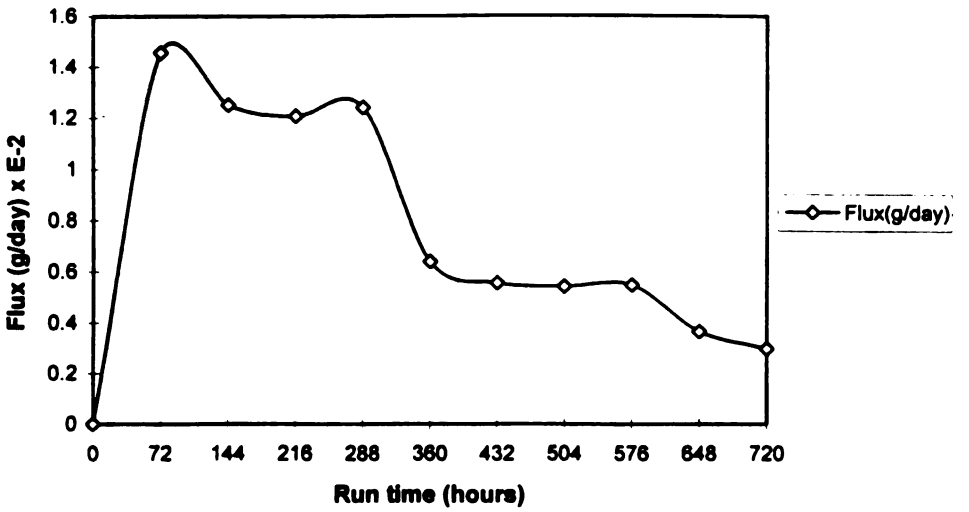


Figure 3. Transmission profile of linalool through a film A from fragrance formulation #1 at 50°C and flow rate of 20cc/min

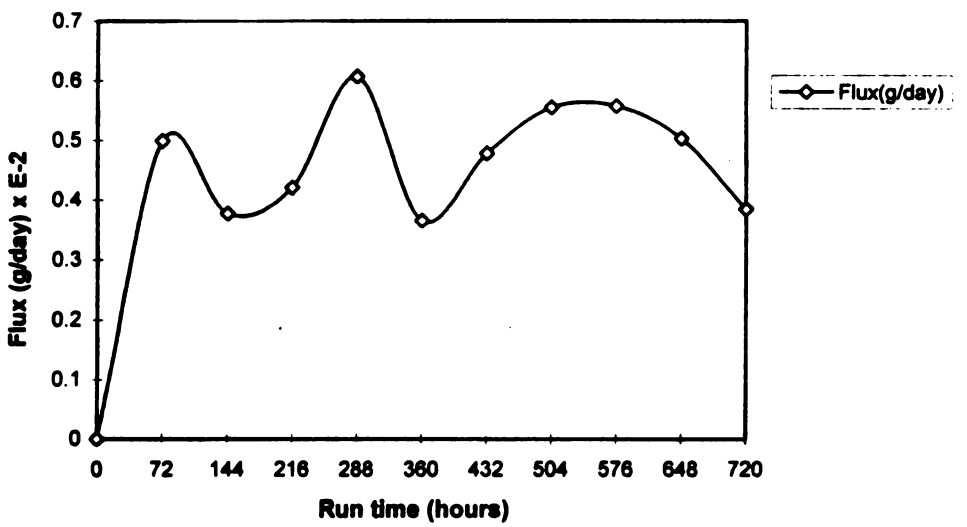


Figure 4. Transmission profile of phenethyl alcohol through a film A from fragrance formulation #1 at 50°C and flow rate of 20cc/min

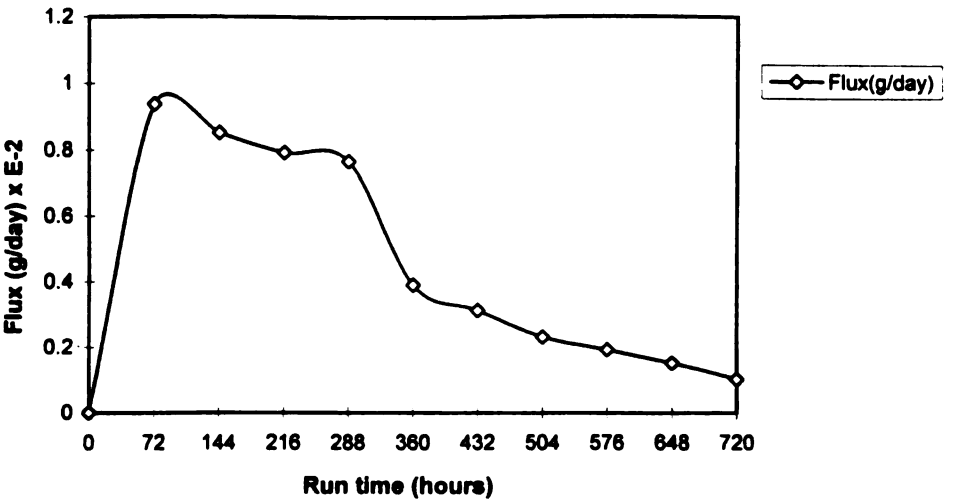


Figure 5. Transmission profile of benzyl acetate through a film A from fragrance formulation #1 at 50°C and flow rate of 20cc/min

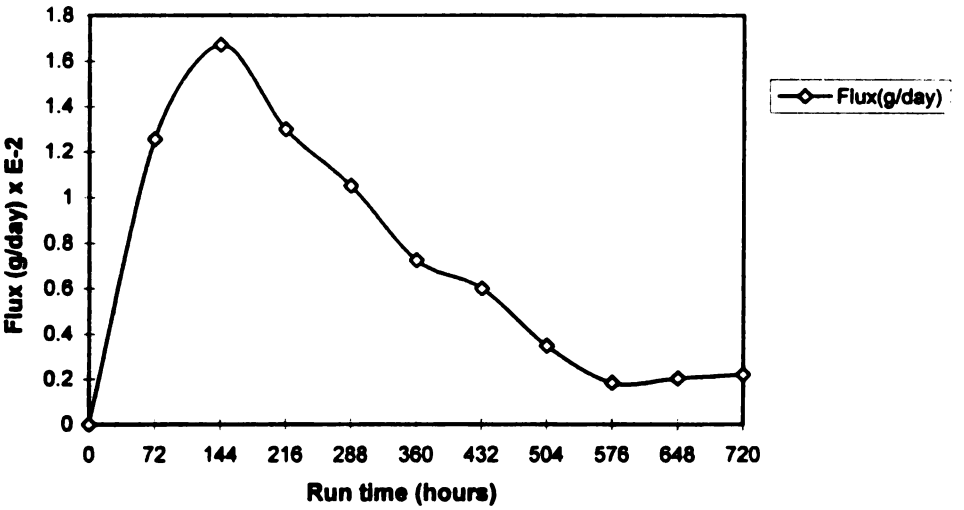


Figure 6. Transmission profile of linalool through a film A from fragrance formulation #2 at 50°C and flow rate of 20cc/min

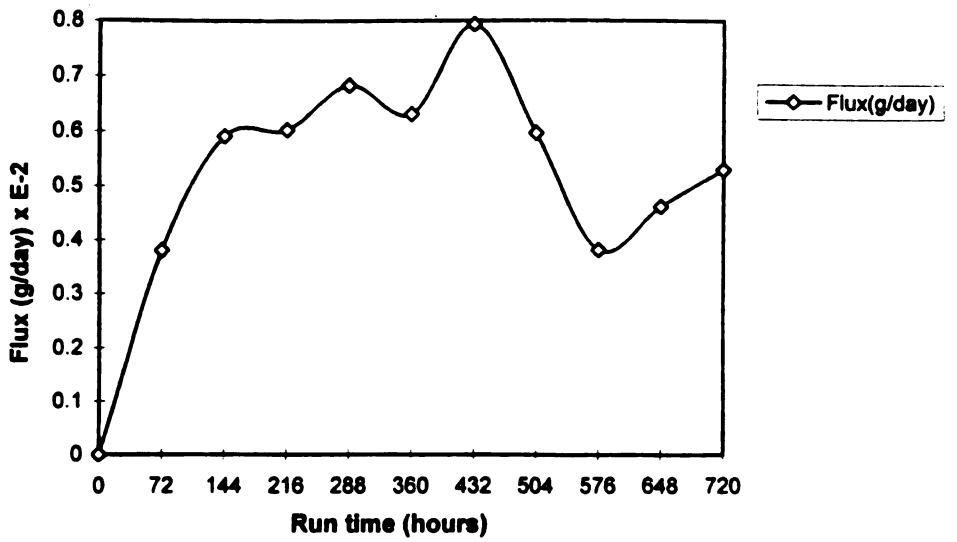


Figure 7.Transmission profile of phenethyl alcohol through a film A from fragrance formulation #2 at 50°C and flow rate of 20cc/min

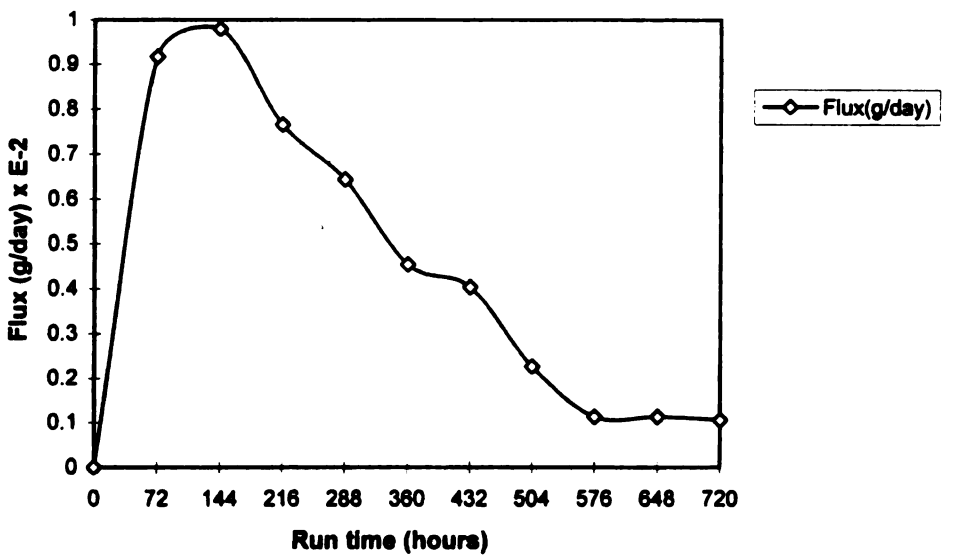


Figure 8. Transmission profile of benzyl acetate through a film A from fragrance formulation #2 at 50°C and flow rate of 20cc/min

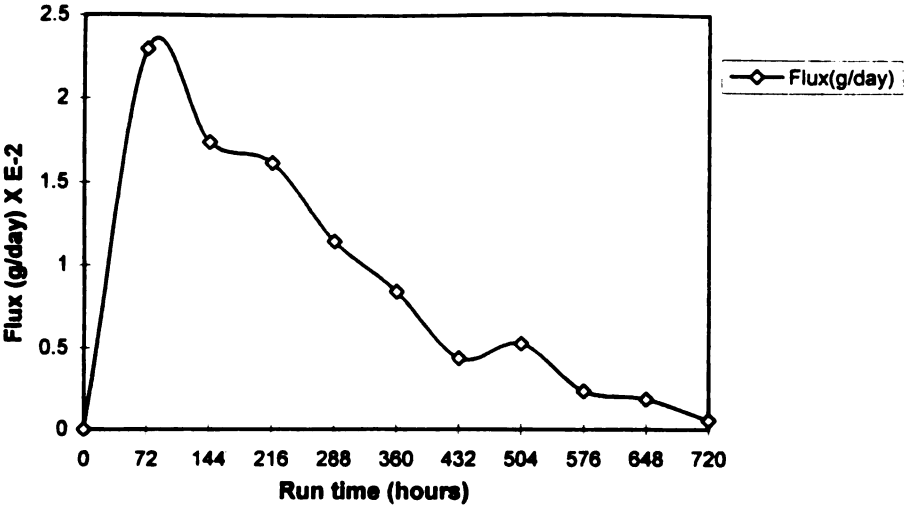


Figure 9. Transmission profile of linalool through a film A from fragrance formulation #3 at 50°C and flow rate of 20cc/min

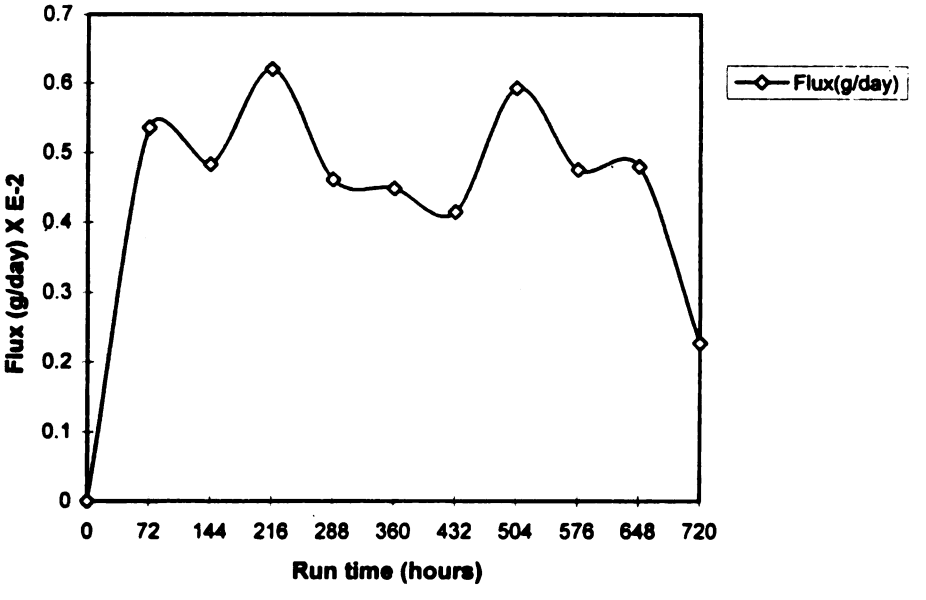


Figure 10. Transmission profile of phenethyl alcohol through a film A from fragrance formulation #2 at 50°C and flow rate of 20cc/min

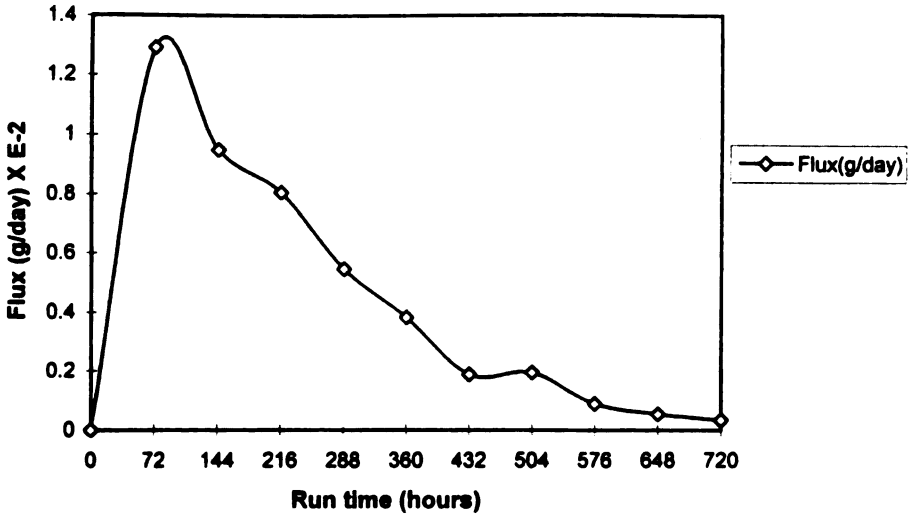


Figure 11. Transmission profile of benzyl acetate through a film A from fragrance formulation #3 at 50°C and flow rate of 20cc/min

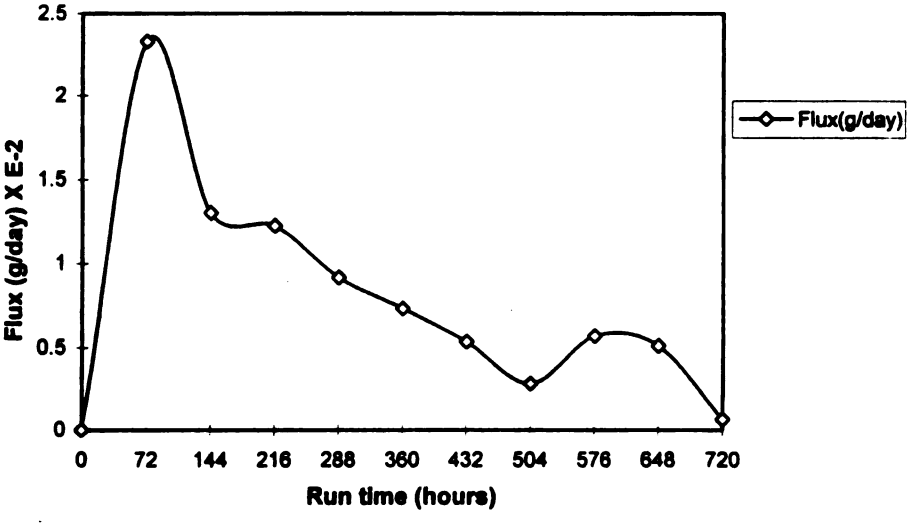


Figure 12. Transmission profile of linalool through a film A from fragrance formulation #4 at 50°C and flow rate of 20cc/min

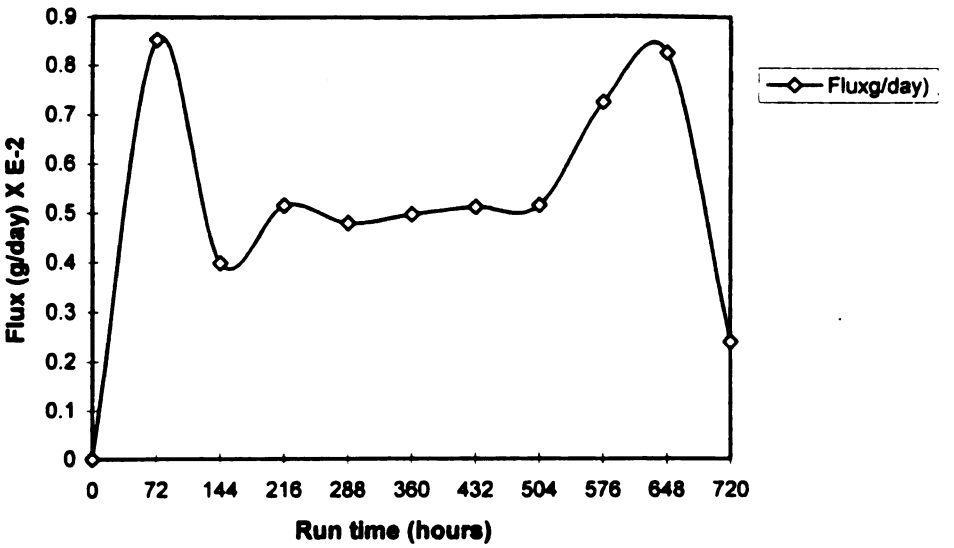


Figure 13. Transmission profile of phenethyl alcohol through a film A from fragrance formulation #4 at 50°C and flow rate of 20cc/min

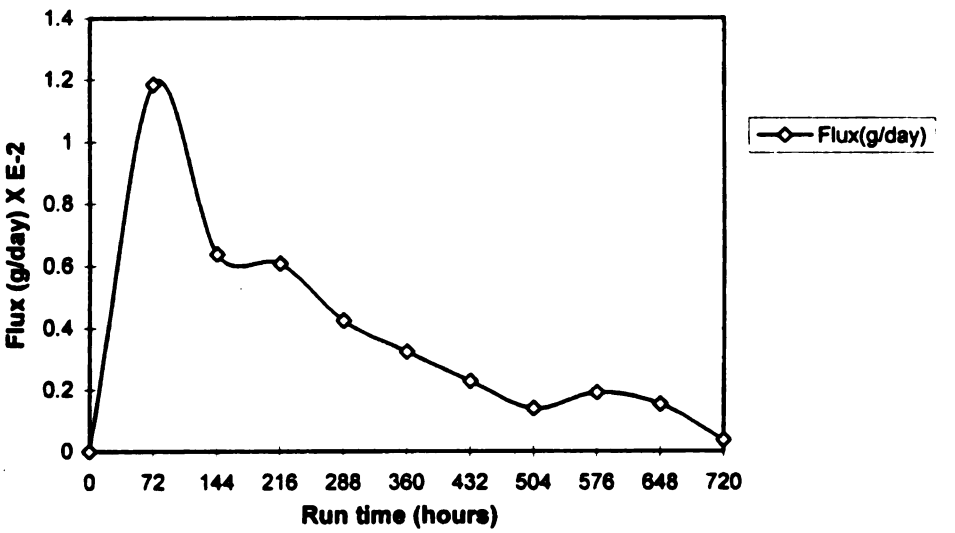


Figure 14. Transmission profile of benzyl acetate through a film A from fragrance formulation #4 at 50°C and flow rate of 20cc/min

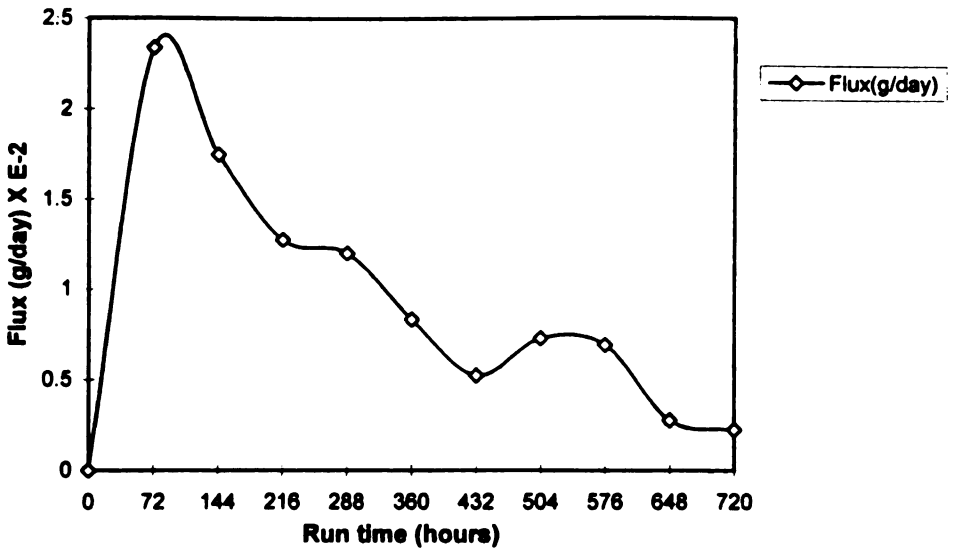


Figure 15. Transmission profile of linalool through a film A from fragrance formulation #5 at 50°C and flow rate of 20cc/min

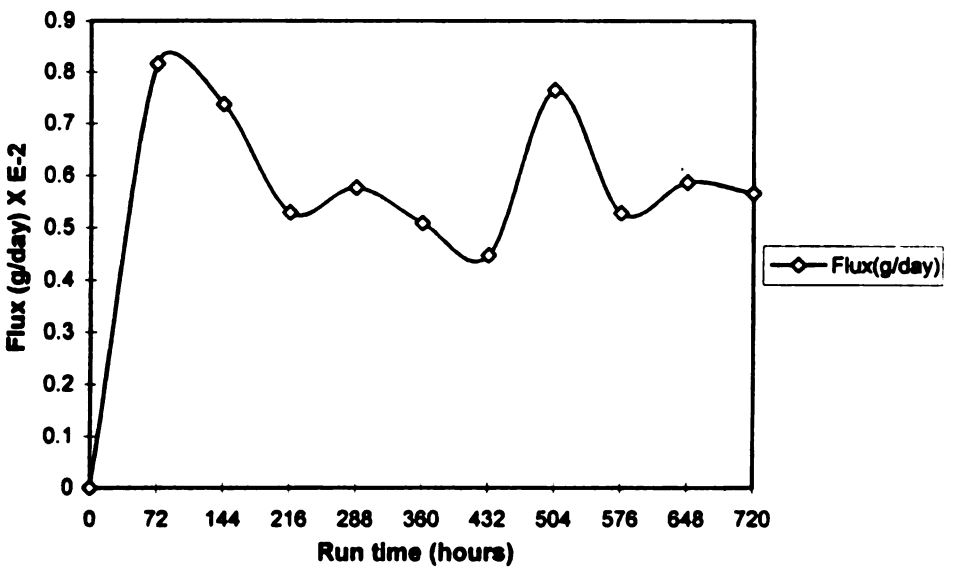


Figure 16. Transmission profile of phenethyl alcohol through a film A from fragrance formulation #5 at 50°C and flow rate of 20cc/min

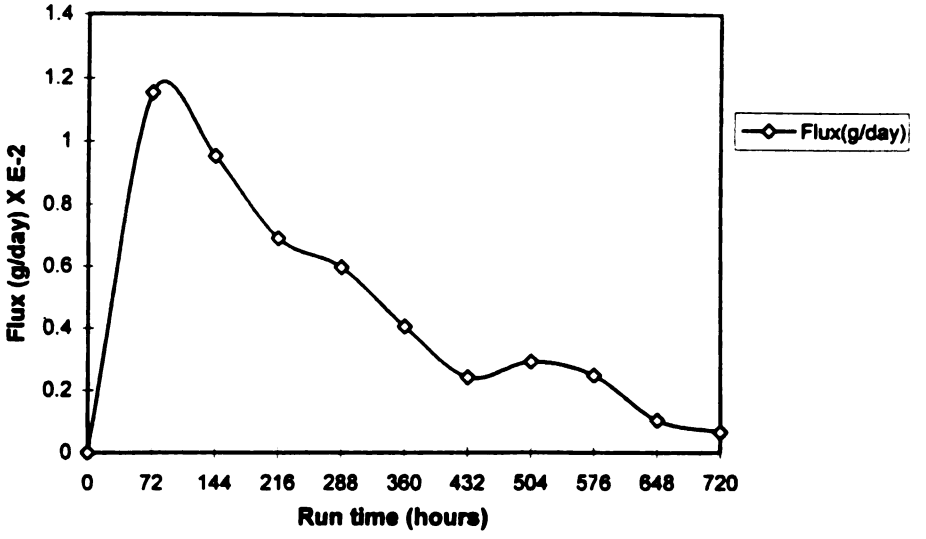


Figure 17. Transmission profile of benzyl acetate through a film A from fragrance formulation #5 at 50°C and flow rate of 20cc/min

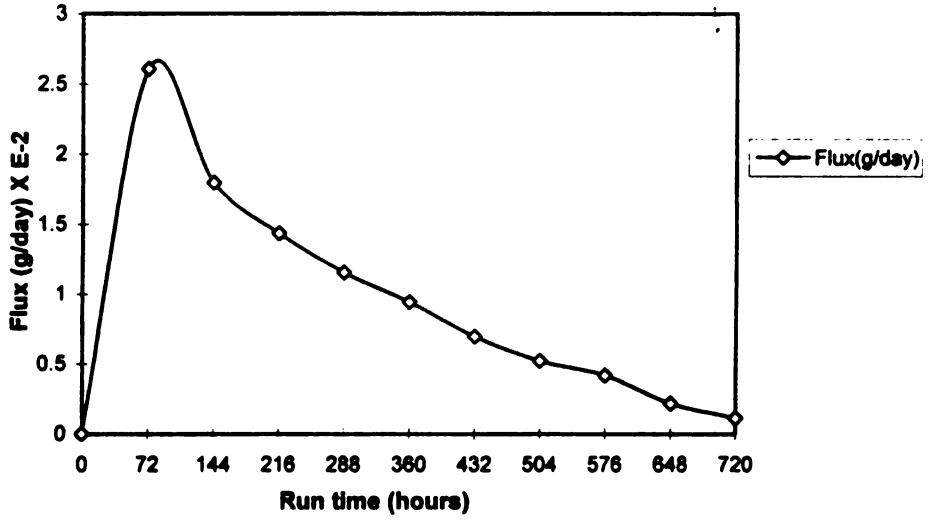


Figure 18. Transmission profile of linalool through a film A from fragrance formulation #6 at 50°C and flow rate of 20cc/min

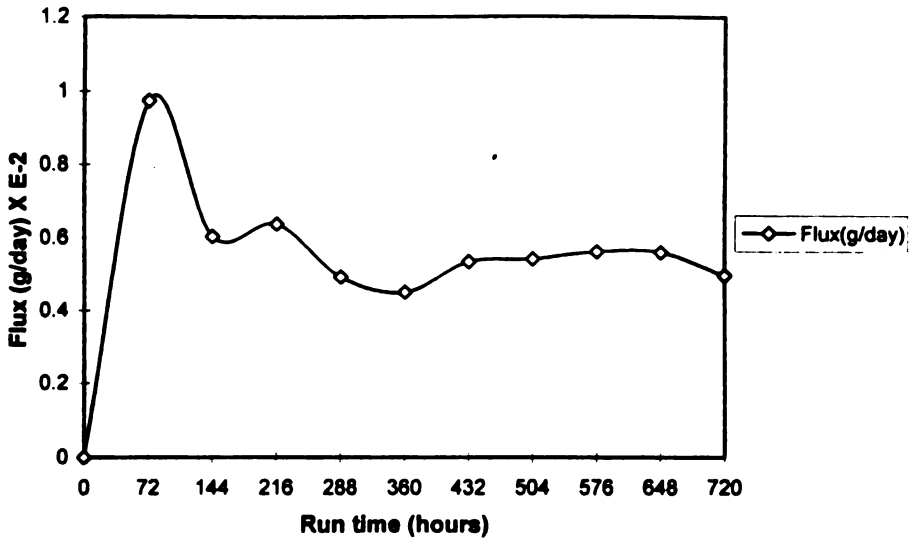


Figure 19.Transmission profile of phenethyl alcohol through a film A from fragrance formulation #6 at 50°C and flow rate of 20cc/min

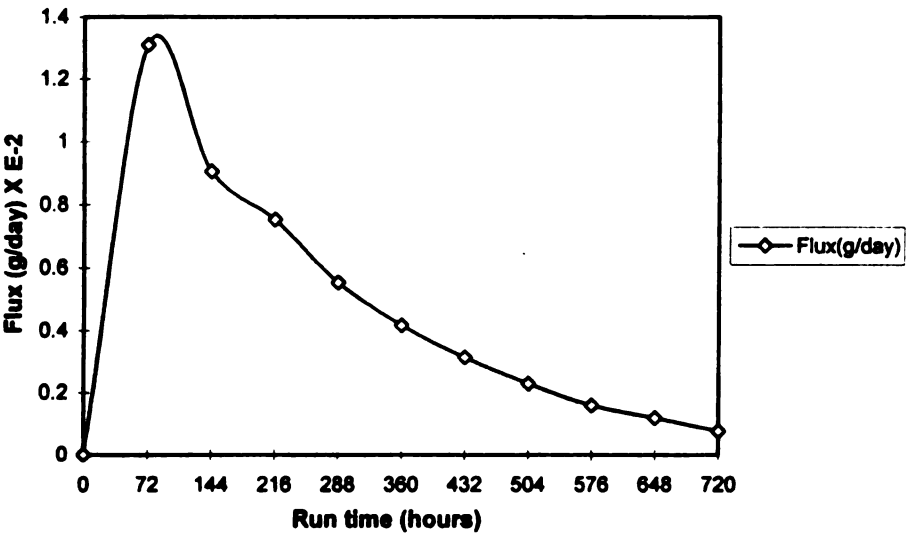


Figure 20.Transmission profile of benzyl acetate through a film A from fragrance formulation #6 at 50°C and flow rate of 20cc/min

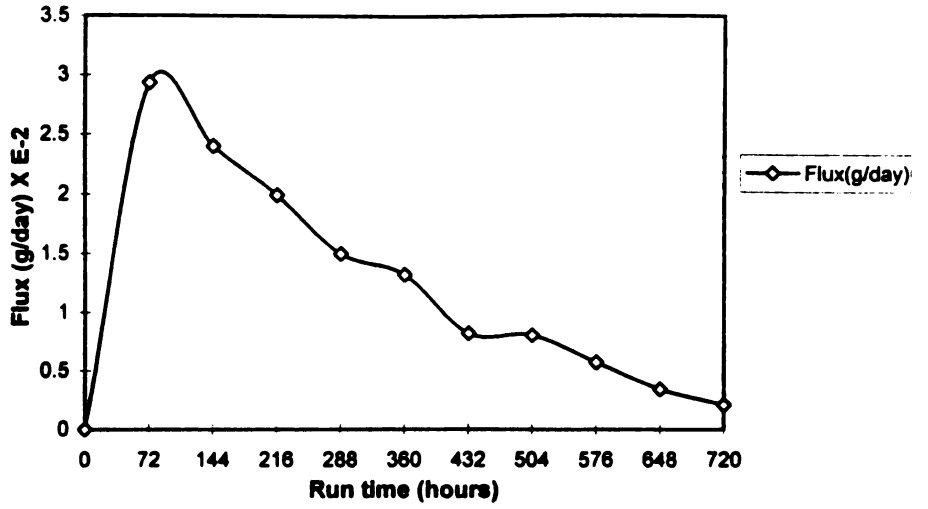


Figure 21.Transmission profile of linalool through a film A
from fragrance formulation #7 at 50°C and flow rate of 20cc/min

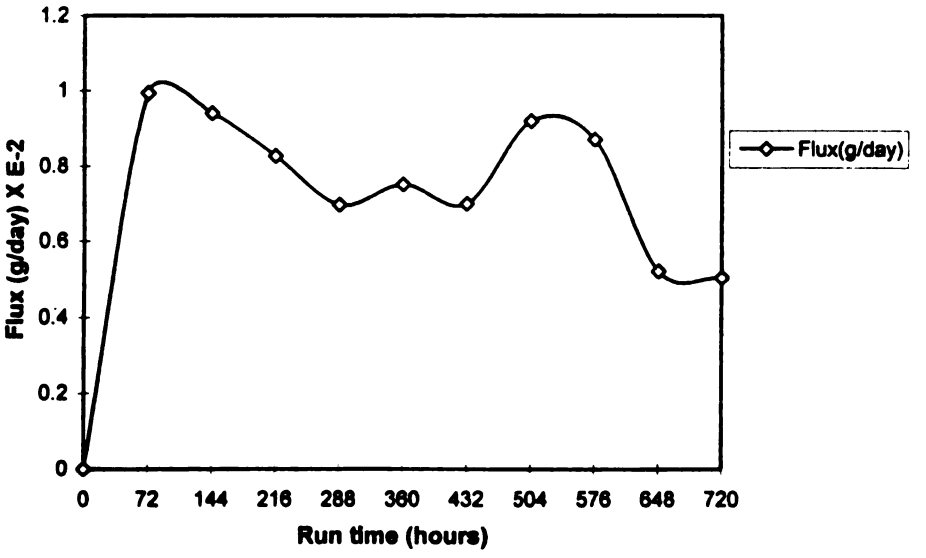


Figure 22.Transmission profile of phenethyl alcohol through a film A
from fragrance formulation #7 at 50°C and flow rate of 20cc/min

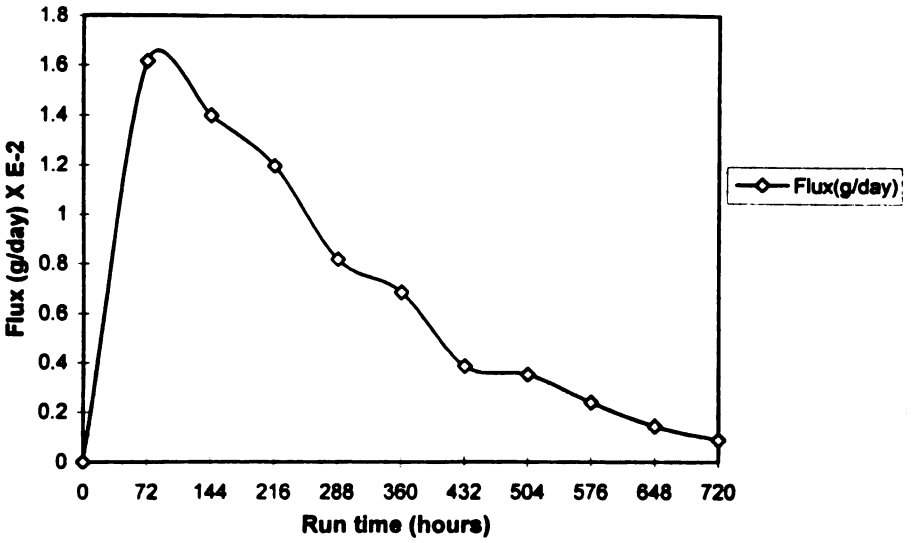


Figure 23.Transmission profile of benzyl acetate through a film A from fragrance formulation #7 at 50°C and flow rate of 20cc/min

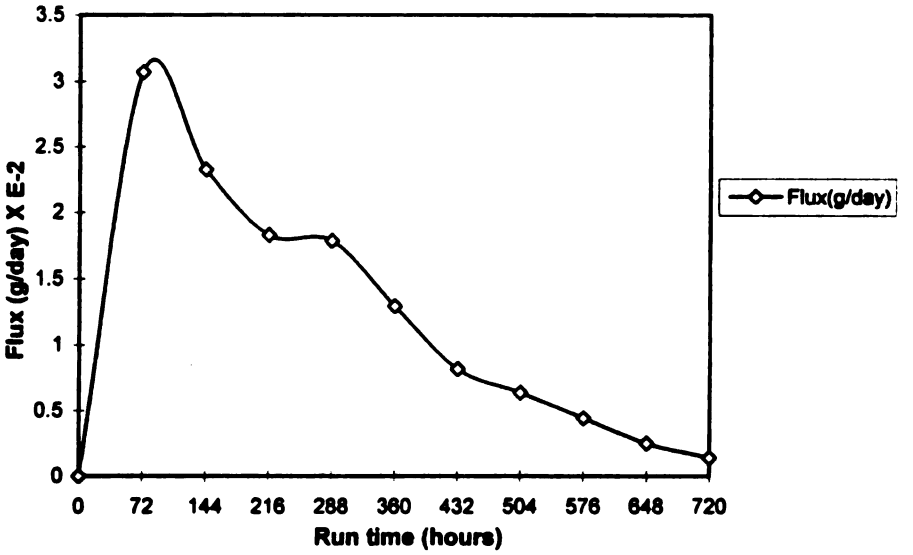


Figure 24.Transmission profile of linalool through a film A from fragrance formulation #8 at 50°C and flow rate of 20cc/min

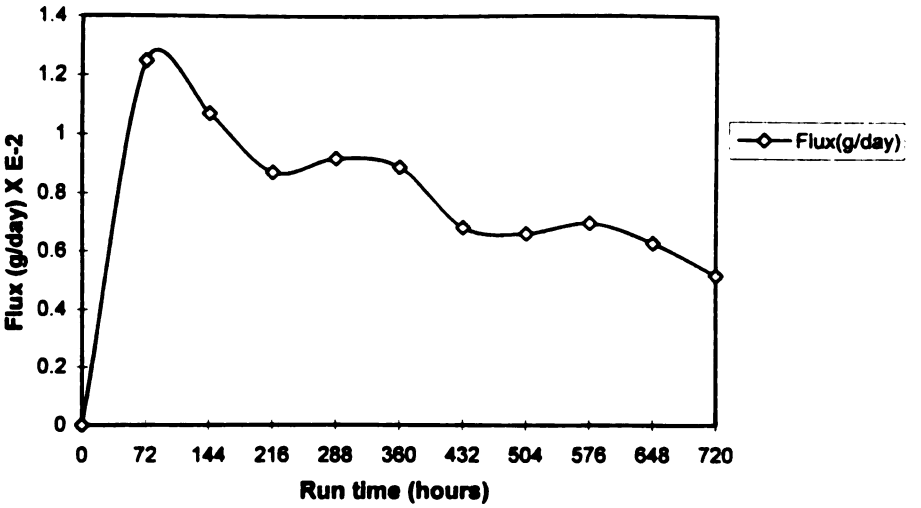


Figure 25. Transmission profile of phenethyl alcohol through a film A from fragrance formulation #8 at 50°C and flow rate of 20cc/min

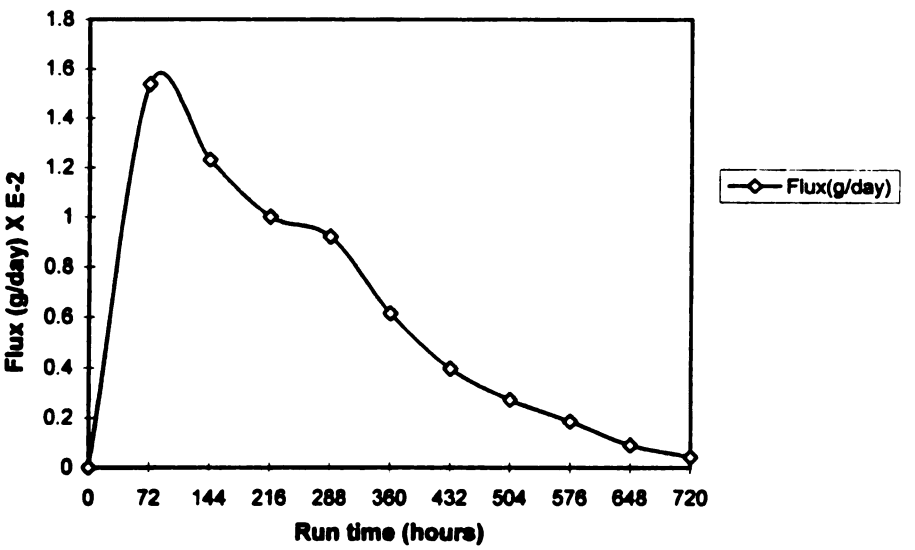


Figure 26.Transmission profile of benayl acetate through a film A from fragrance formulation #8 at 50°C and flow rate of 20cc/min

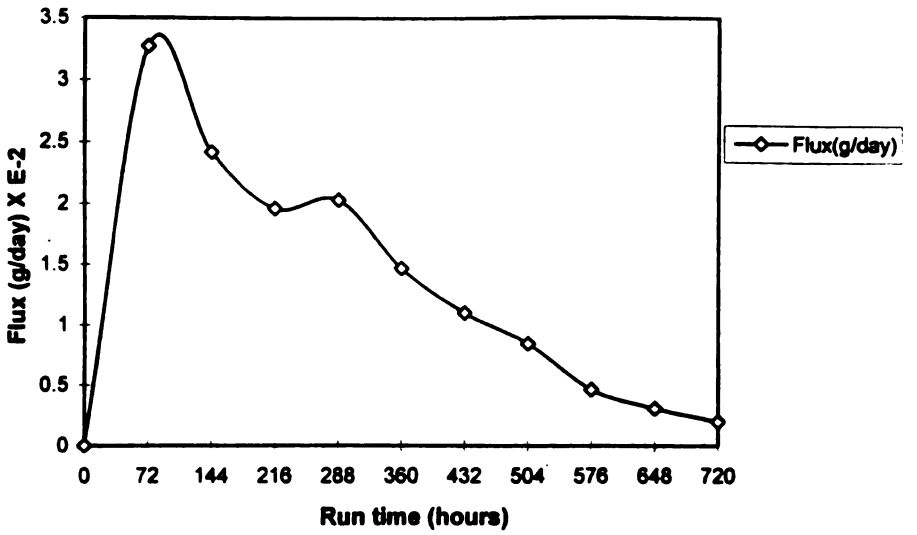


Figure 27.Transmission profile of linalool through a film A
from fragrance formulation #9 at 50°C and flow rate of 20cc/min

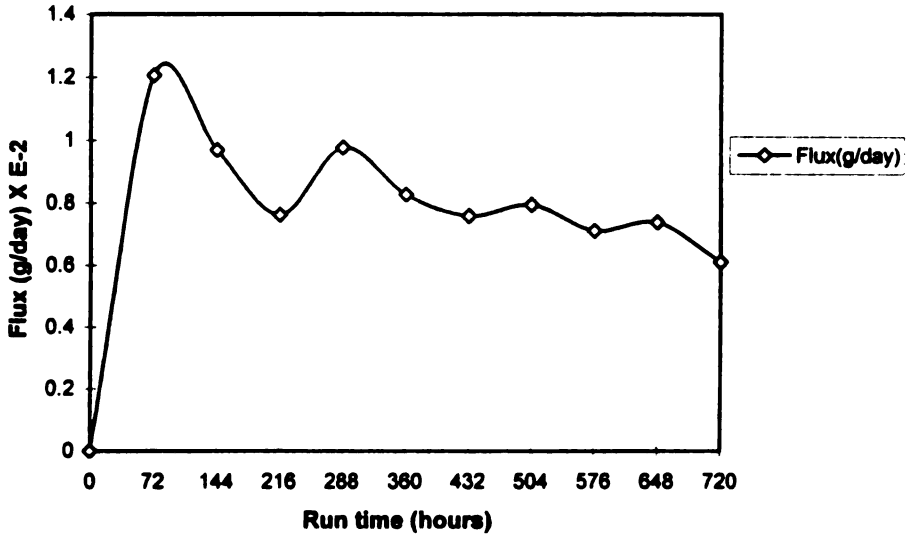


Figure 28.Transmission profile of phhenethyl alcohol through a film A
from fragrance formulation #9 at 50°C and flow rate of 20cc/min

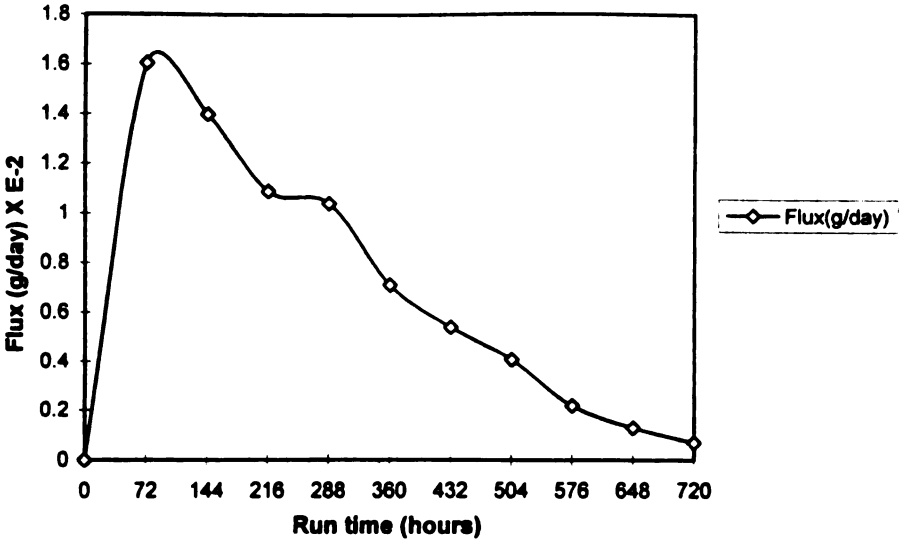


Figure 29.Transmission profile of benzyl acetate through a film A from fragrance formulation #9 at 50°C and flow rate of 20cc/min

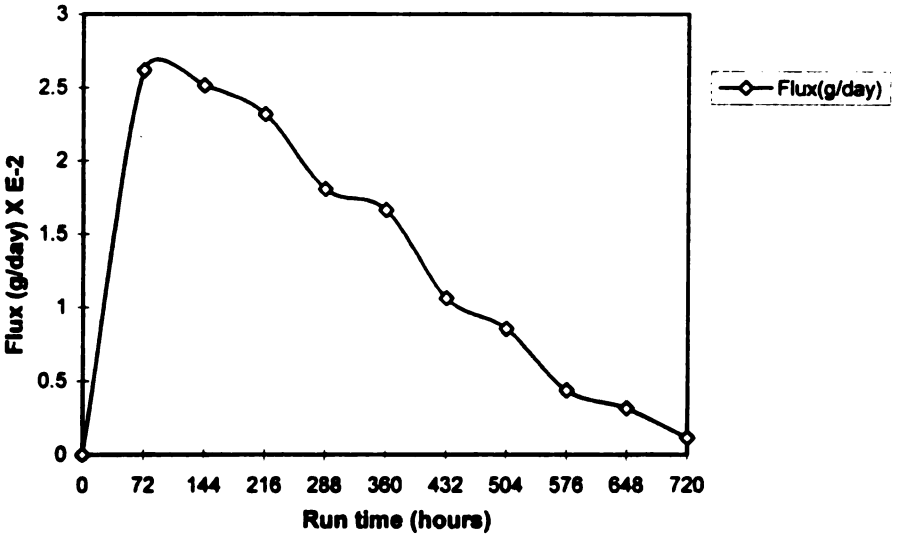


Figure 30.Transmission profile of linalool through a film B from fragrance formulation #1 at 50°C and flow rate of 20cc/min

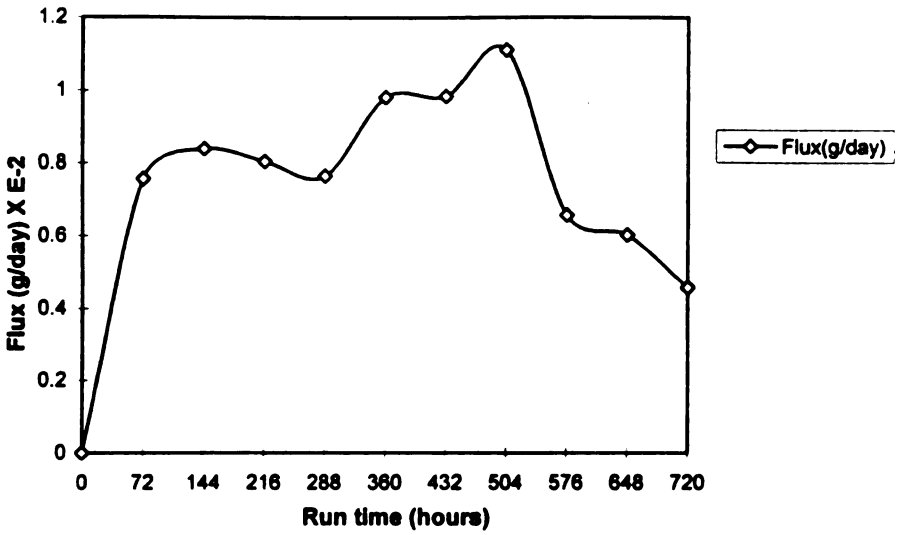


Figure 31.Transmission profile of phenethyl alcohol through a film B from fragrance formulation #1 at 50°C and flow rate of 20cc/min

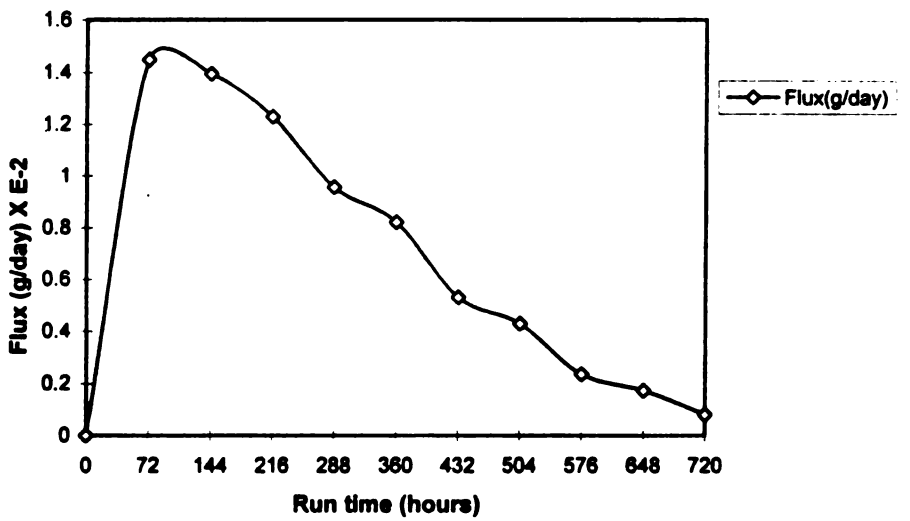


Figure 32.Transmission profile of benzyl acetate through a film B from fragrance formulation #1 at 50°C and flow rate of 20cc/min

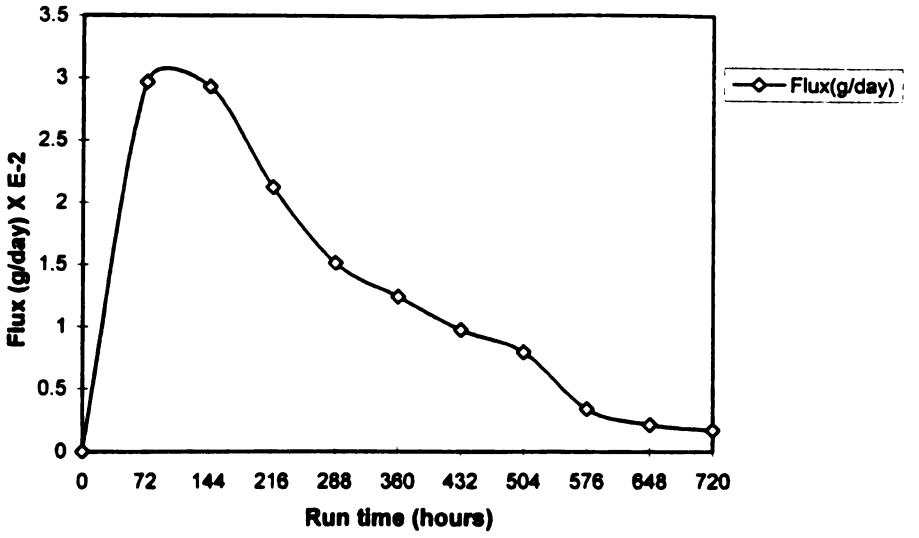


Figure 33.Transmission profile of linalool through a film B
from fragrance formulation #2 at 50°C and flow rate of 20cc/min

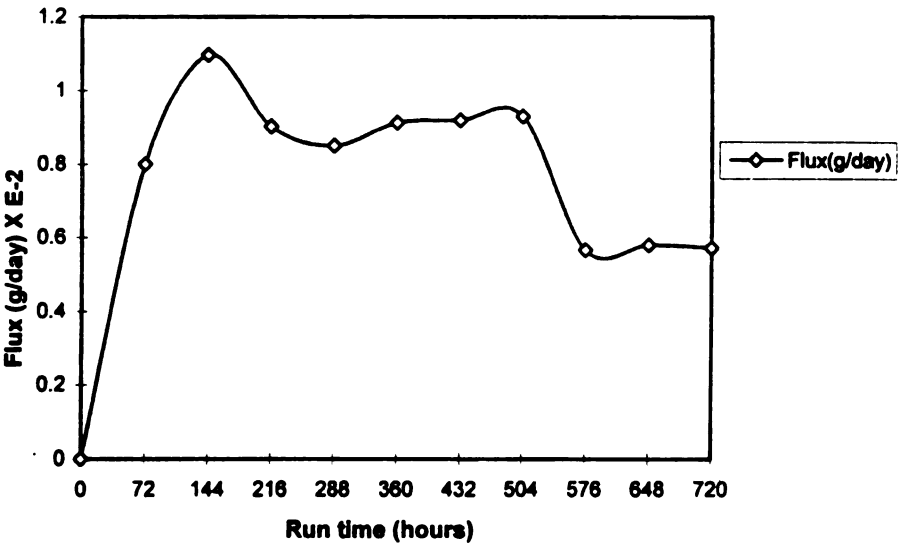


Figure 34.Transmission profile of phenethyl alcohol through a film B
from fragrance formulation #2 at 50°C and flow rate of 20cc/min

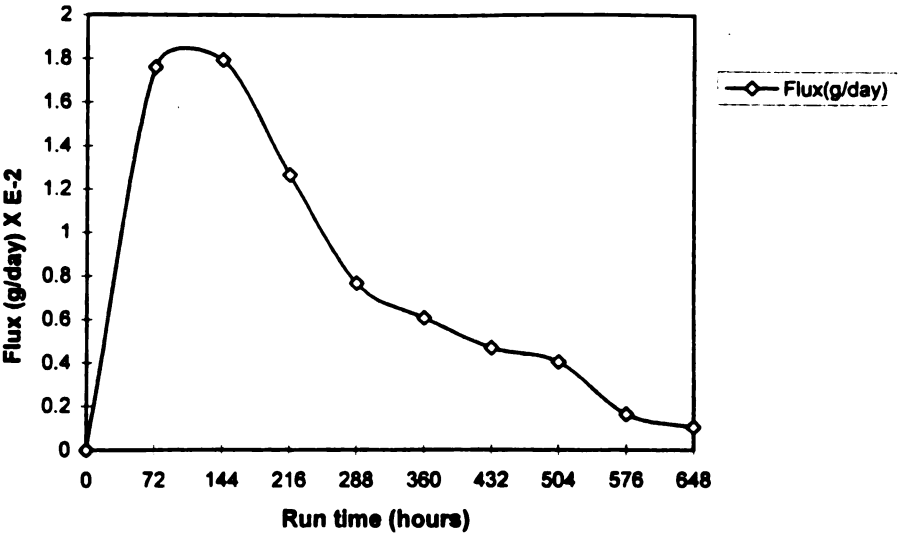


Figure 35.Transmission profile of benzyl acetate through a film B from fragrance formulation #2 at 50°C and flow rate of 20cc/min

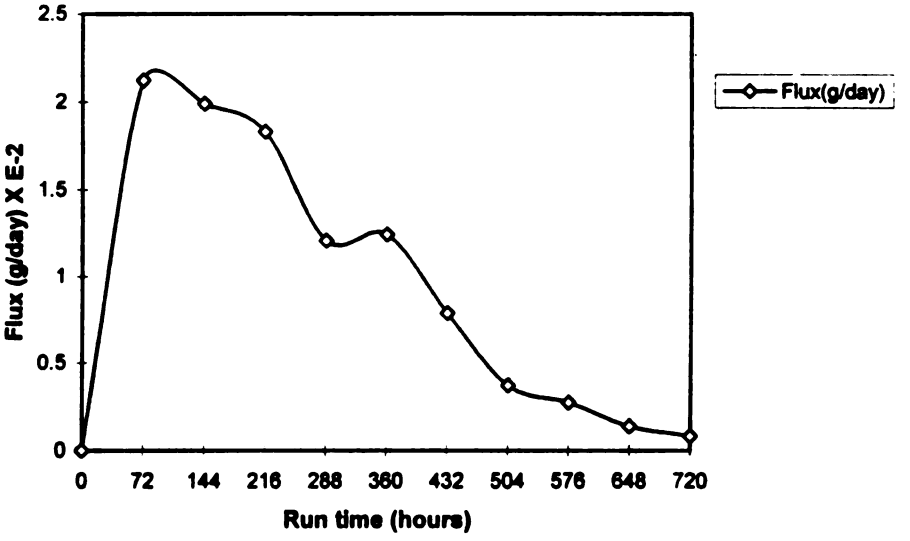


Figure 36.Transmission profile of linalool through a film B from fragrance formulation #3 at 50°C and flow rate of 20cc/min

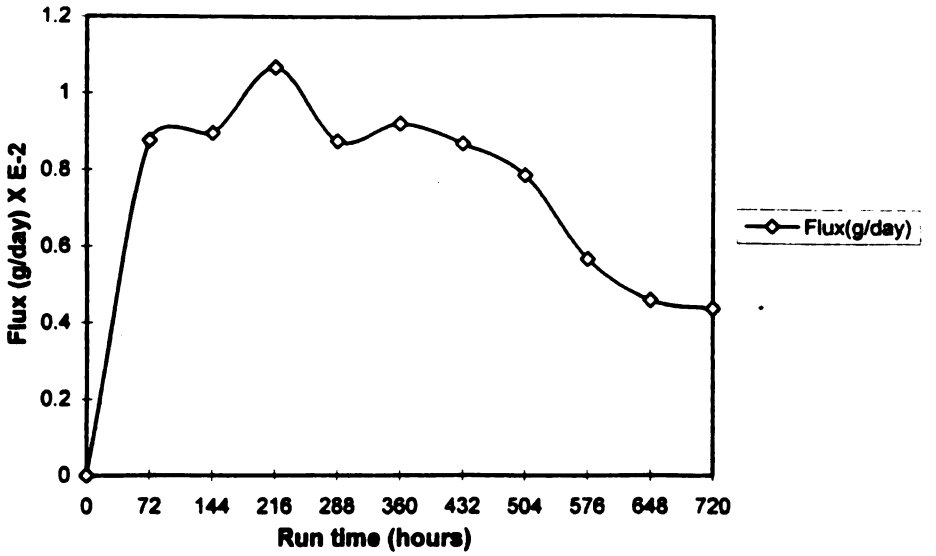


Figure 37.Transmission profile of phenethyl alcohol through a film B from fragrance formulation #3 at 50°C and flow rate of 20cc/min

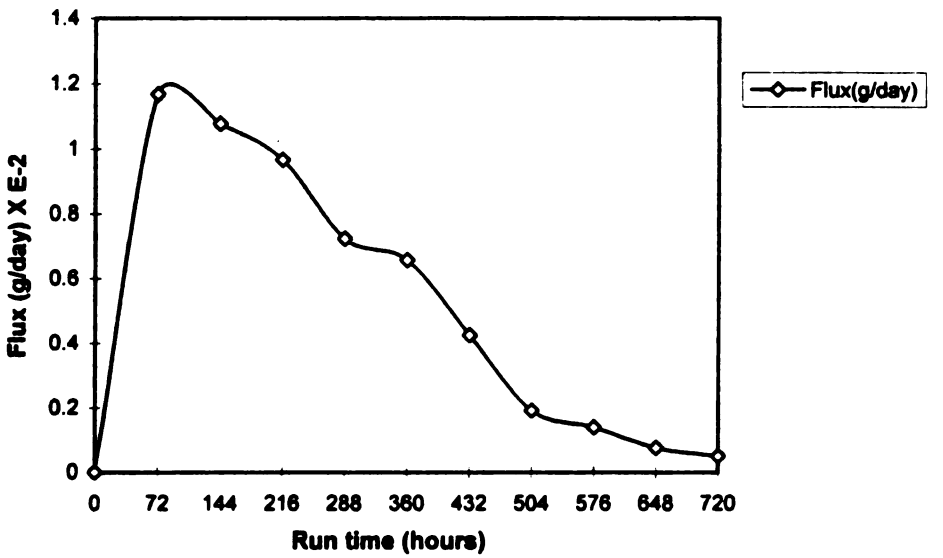


Figure 38.Transmission profile of benzyl acetat through a film B from fragrance formulation #3 at 50°C and flow rate of 20cc/min

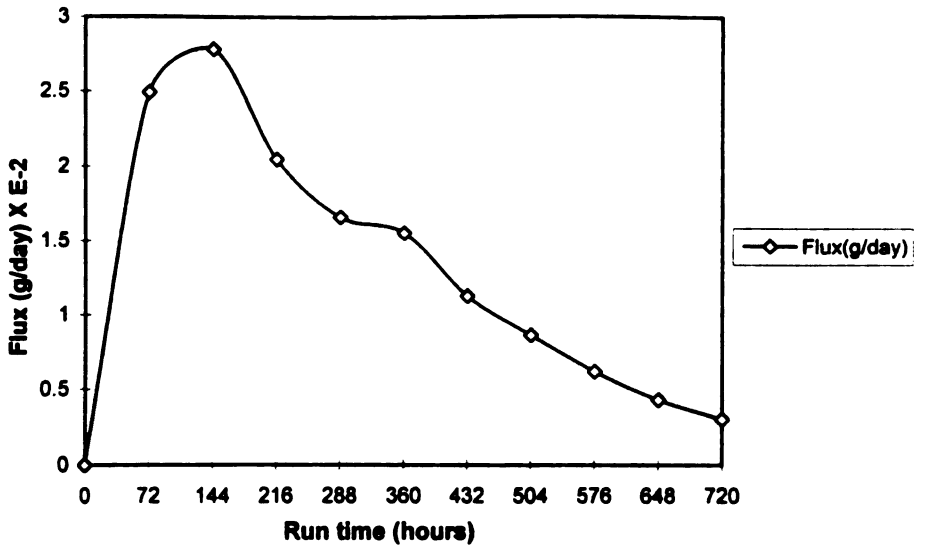


Figure 39.Transmission profile of linalool through a film B
from fragrance formulation #4 at 50°C and flow rate of 20cc/min

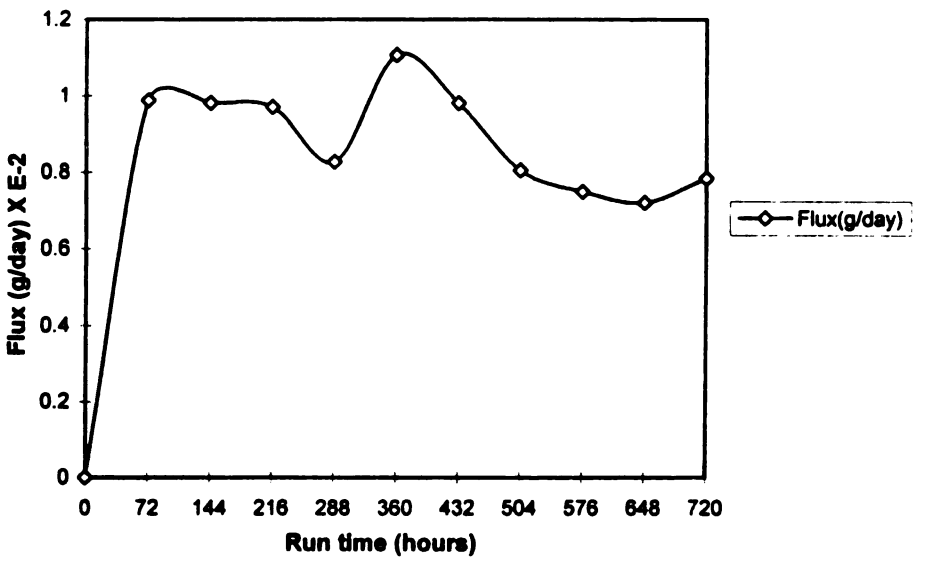


Figure 40.Transmission profile of phenethyl alcohol through a film B
from fragrance formulation #4 at 50°C and flow rate of 20cc/min

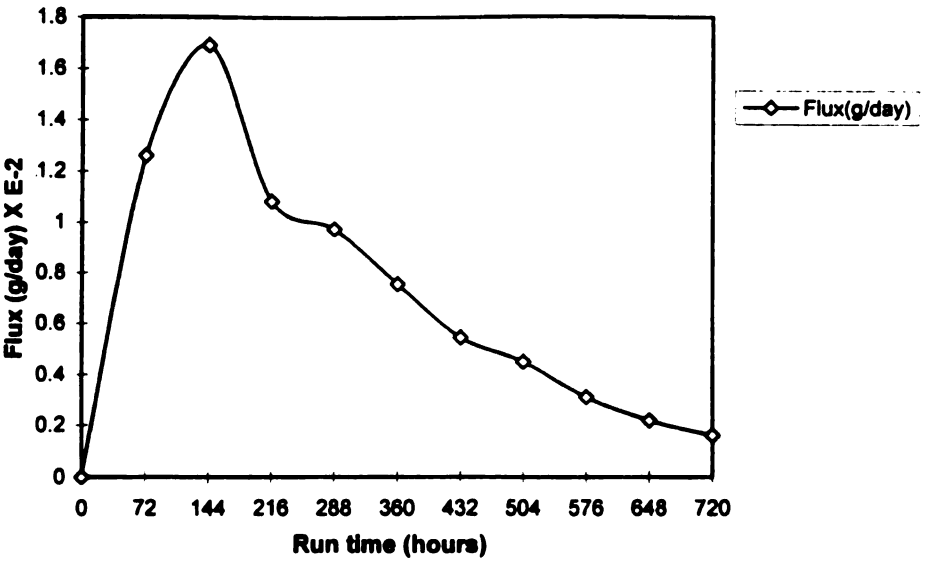


Figure 41.Transmission profile of benzyl acetate through a film B from fragrance formulation #4 at 50°C and flow rate of 20cc/min

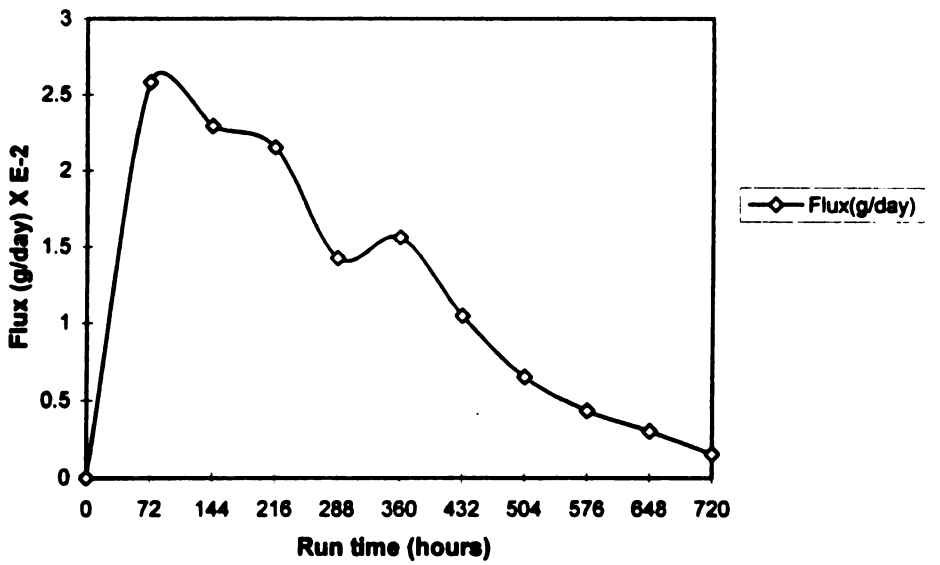


Figure 42.Transmission profile of linalool through a film B from fragrance formulation #5 at 50°C and flow rate of 20cc/min

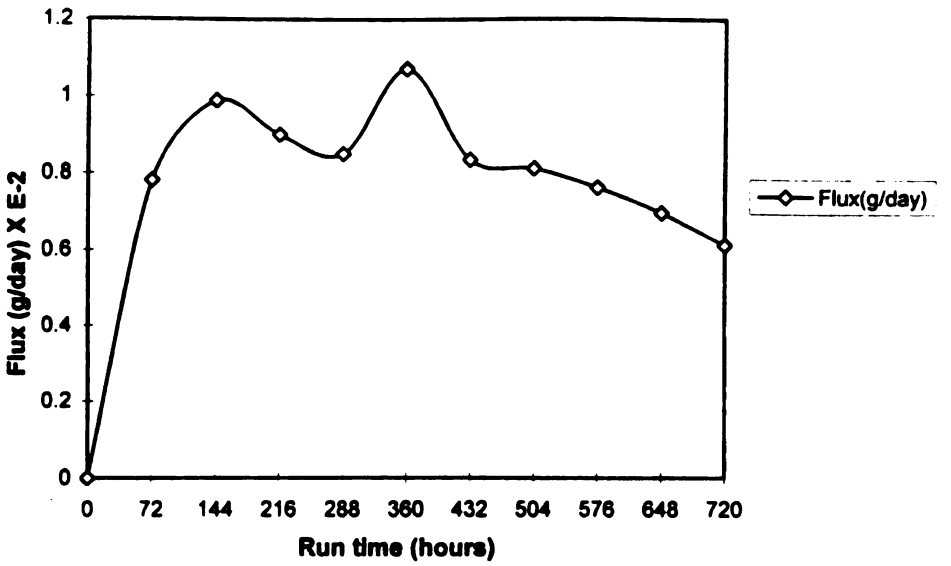


Figure 43.Transmission profile of phenethyl alcohol through a film B from fragrance formulation #5 at 50°C and flow rate of 20cc/min

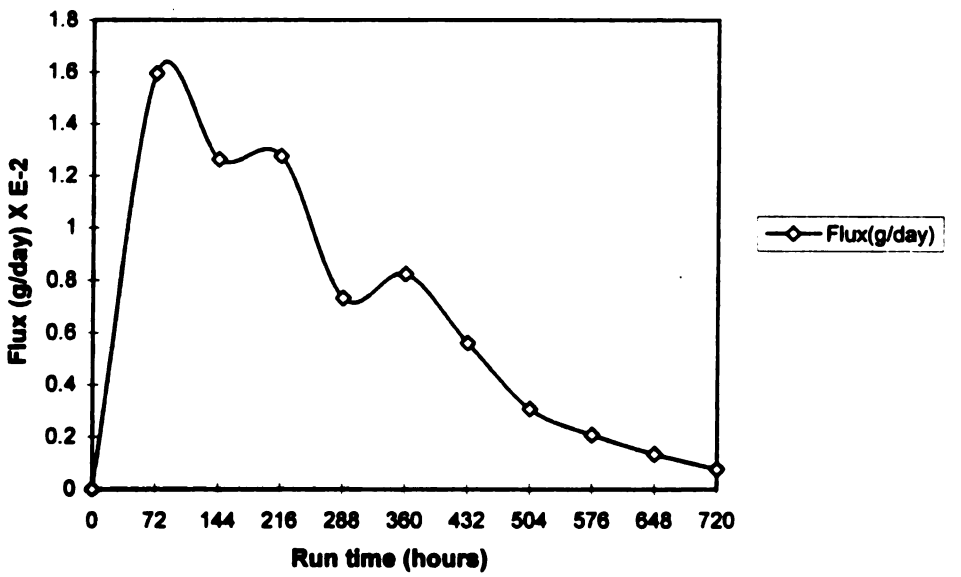


Figure 44.Transmission profile of benzyl acetate through a film B from fragrance formulation #5 at 50°C and flow rate of 20cc/min

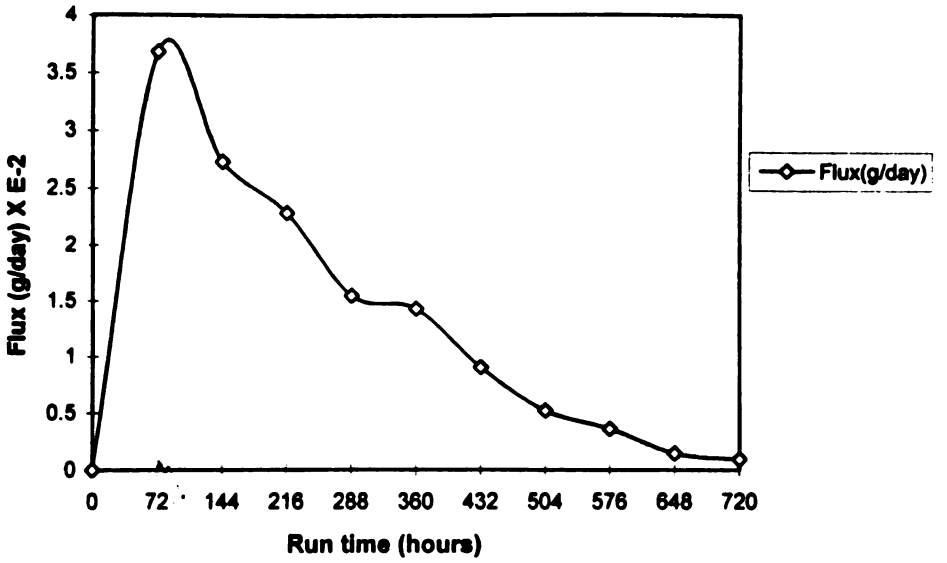


Figure 45.Transmission profile of linalool through a film B from fragrance formulation #6 at 50°C and flow rate of 20cc/min

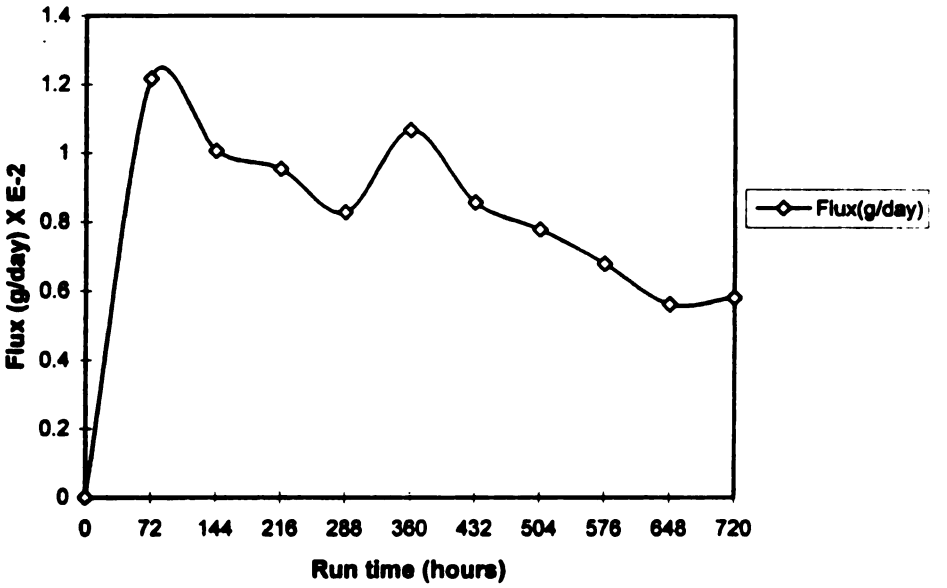


Figure 46.Transmission profile of phenethyl alcohol through a film B from fragrance formulation #6 at 50°C and flow rate of 20cc/min

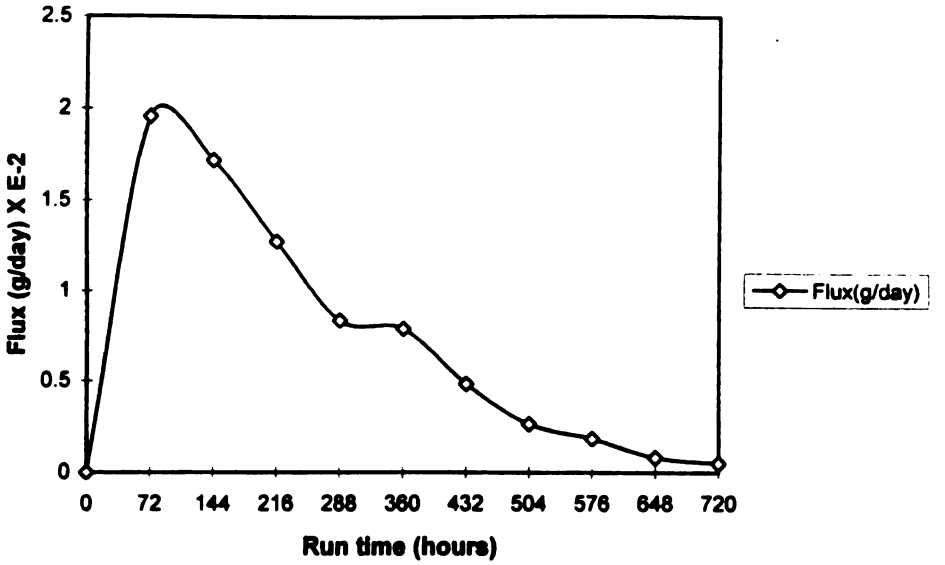


Figure 47.Transmission profile of benzyl acetate through a film B from fragrance formulation #6 at 50°C and flow rate of 20cc/min

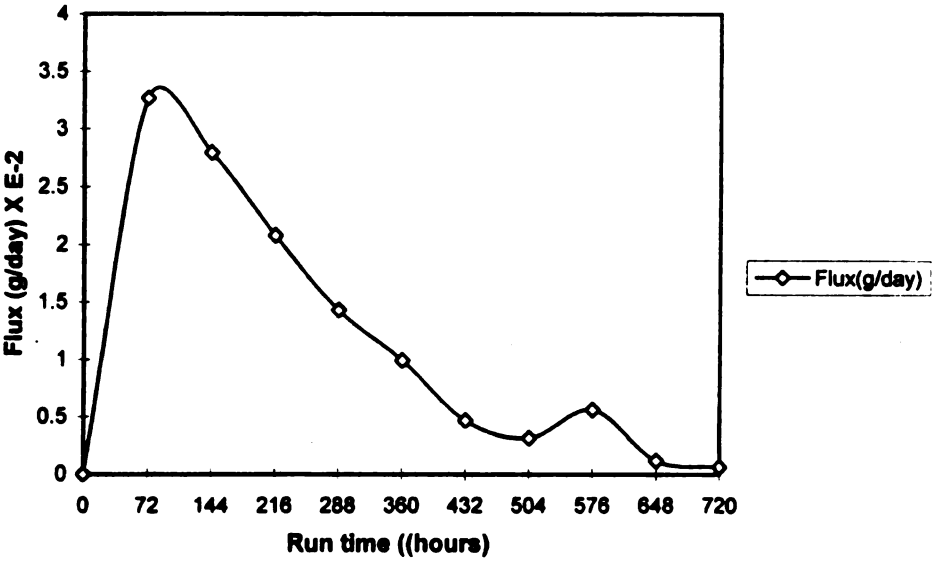


Figure 48.Transmission profile of linalool through a film B from fragrance formulation #7 at 50°C and flow rate of 20cc/min

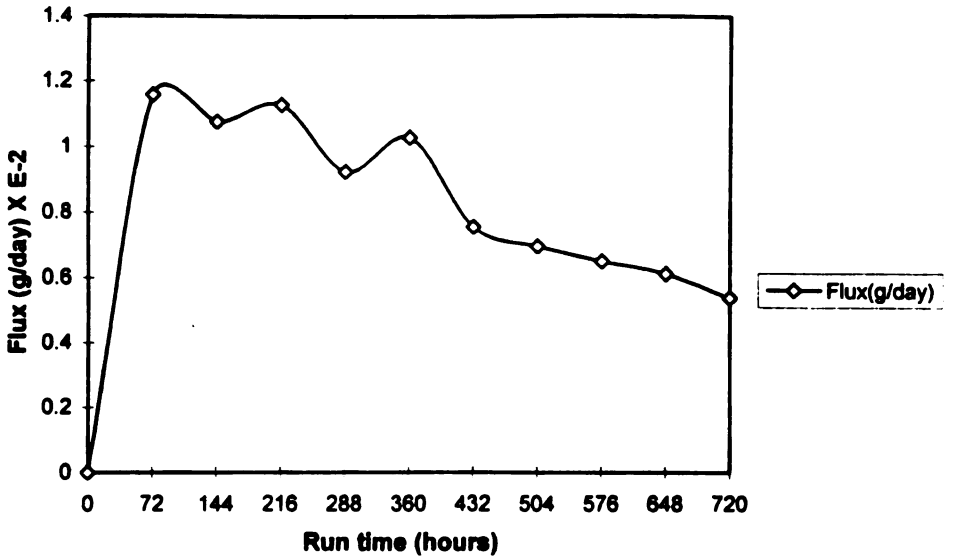


Figure 49.Transmission profile of phenethyl alcohol through a film B from fragrance formulation #7 at 50°C and flow rate of 20cc/min

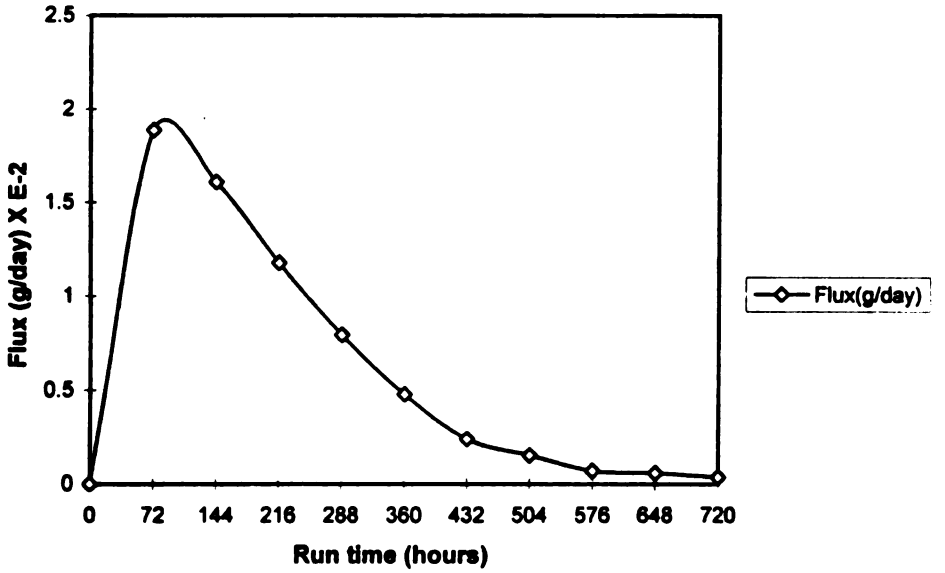


Figure 50.Transmission profile of benzyl acetate through a film B from fragrance formulation #7 at 50°C and flow rate of 20cc/min

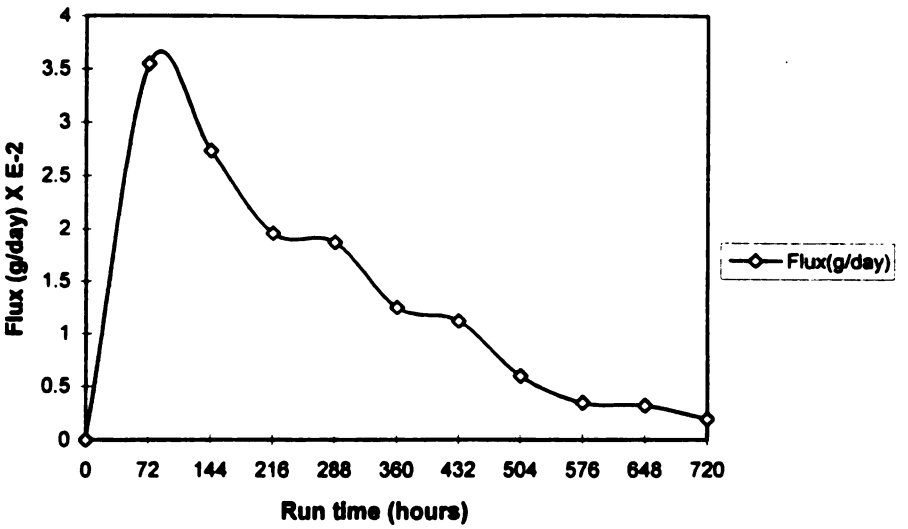


Figure 51.Transmission profile of linalool through a film B
from fragrance formulation #8 at 50°C and flow rate of 20cc/min

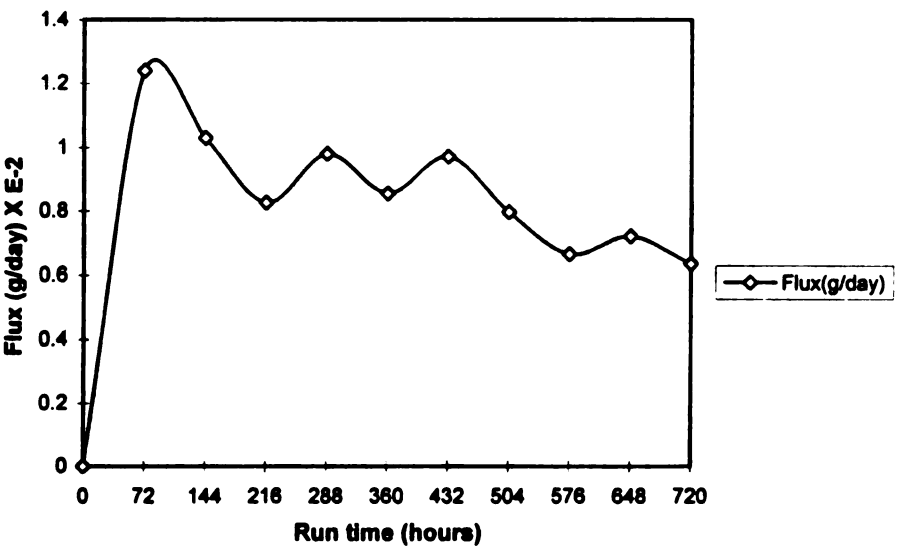


Figure 52.Transmission profile of phenethyl alcohol through a film B
from fragrance formulation #8 at 50°C and flow rate of 20cc/min

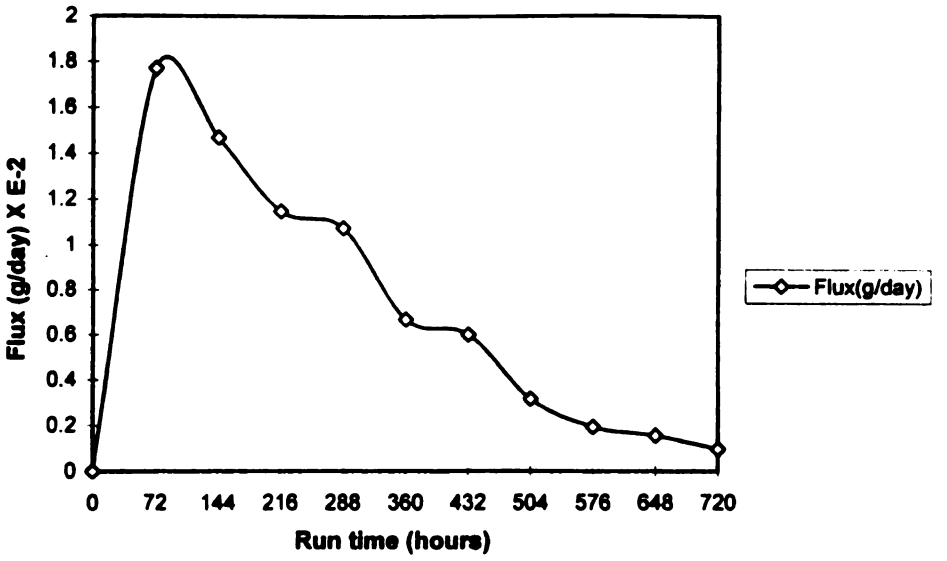


Figure 53.Transmission profile of benzyl acetate through a film B from fragrance formulation #8 at 50°C and flow rate of 20cc/min

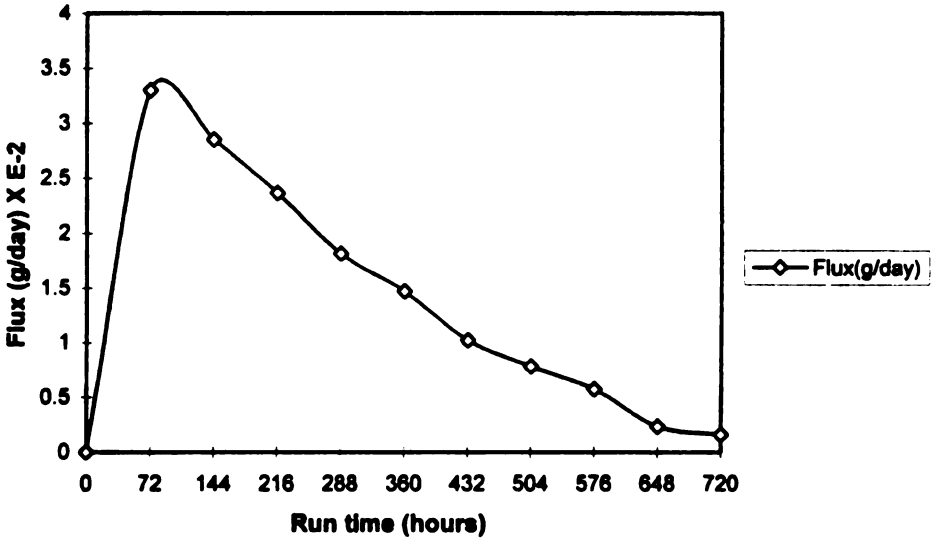


Figure 54.Transmission profile of linalool through a film B from fragrance formulation #9 at 50°C and flow rate of 20cc/min

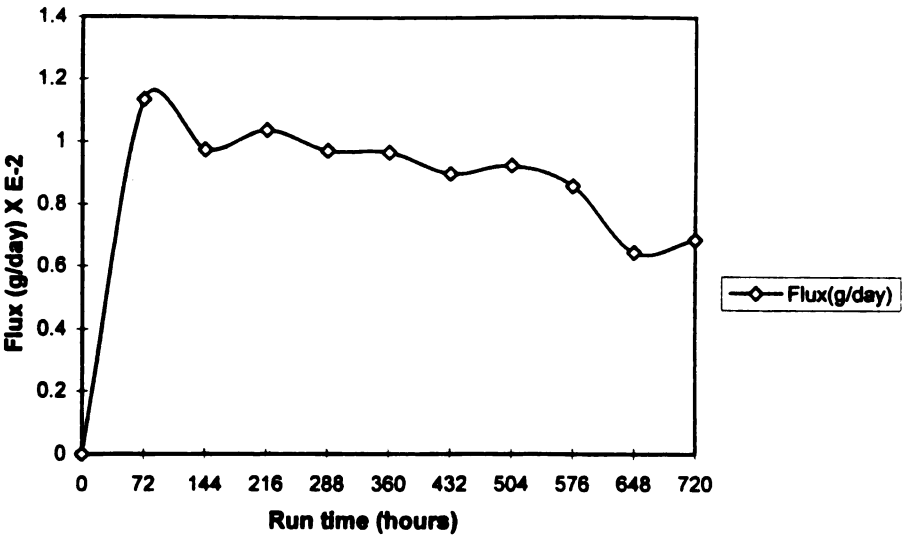


Figure 55.Transmission profile of phenethyl alcohol through a film B from fragrance formulation #9 at 50°C and flow rate of 20cc/min

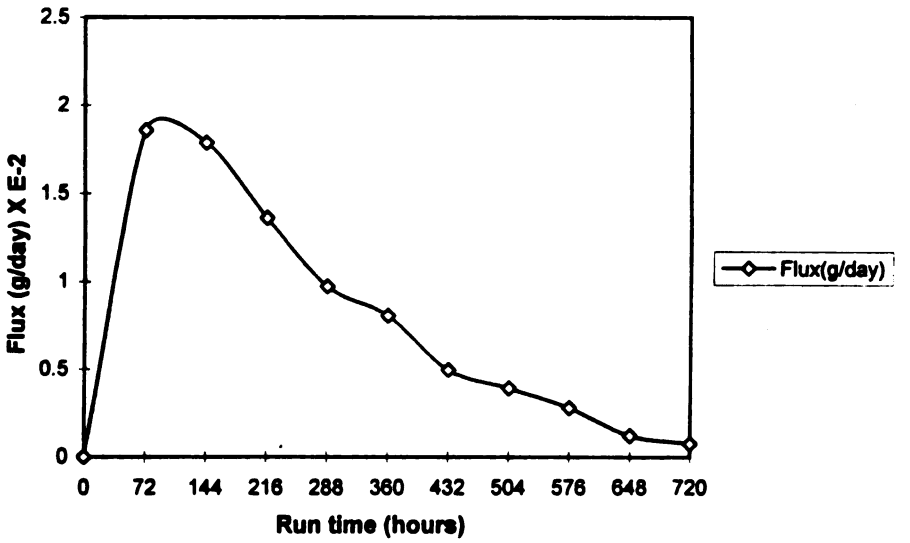


Figure 56.Transmission profile of benzyl acetate through a film B from fragrance formulation #9 at 50°C and flow rate of 20cc/min

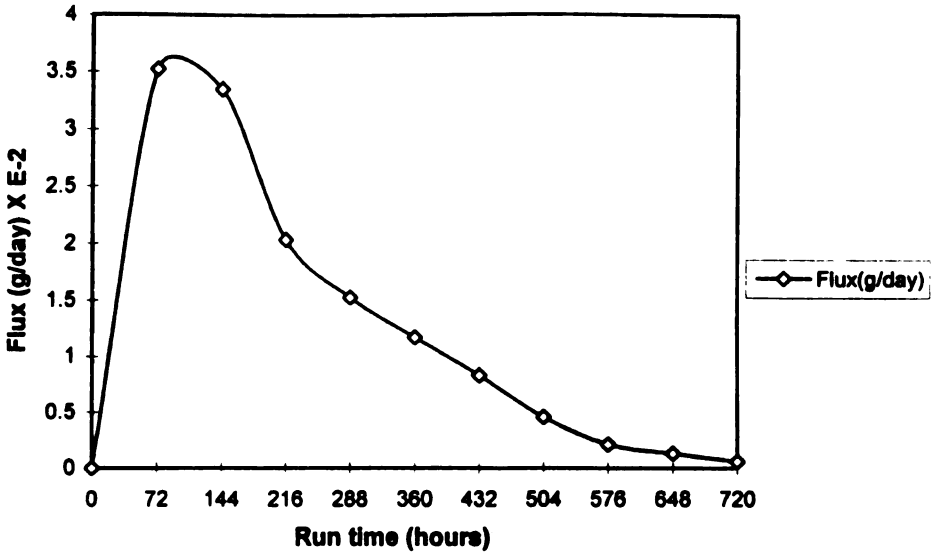


Figure 57.Transmission profile of linalool through a film C
from fragrance formulation #1 at 50°C and flow rate of 20cc/min

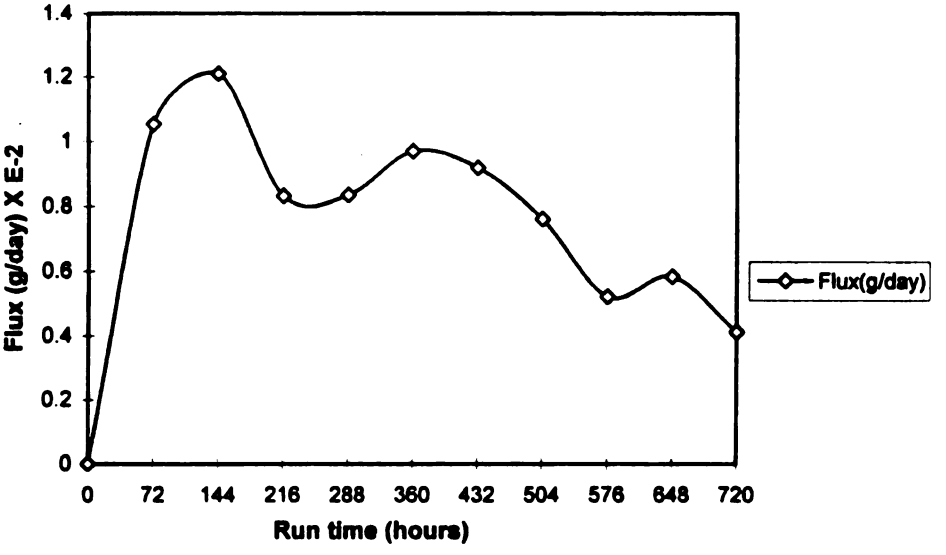


Figure 58.Transmission profile of phenethyl alcohol through a film C
from fragrance formulation #1 at 50°C and flow rate of 20cc/min

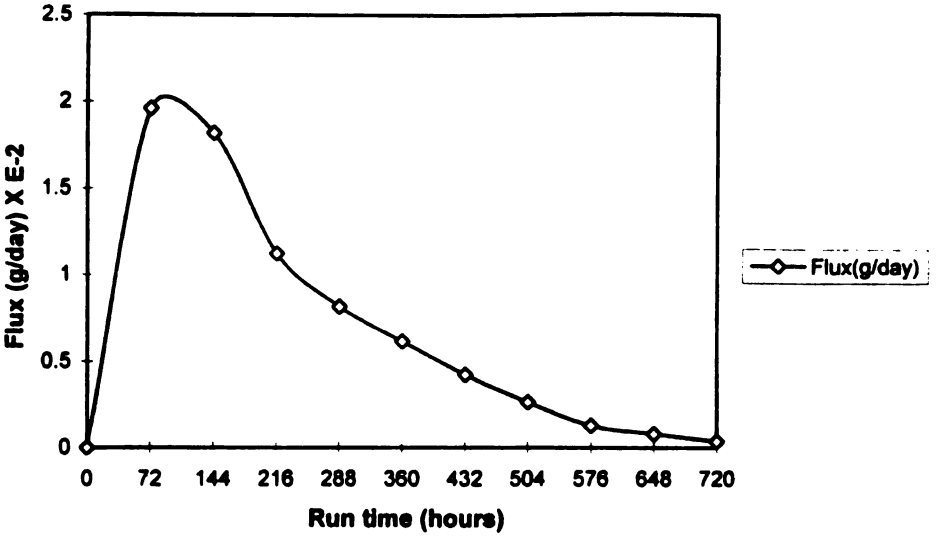


Figure 59.Transmission profile of benzyl acetate through a film C from fragrance formulation #1 at 50°C and flow rate of 20cc/min

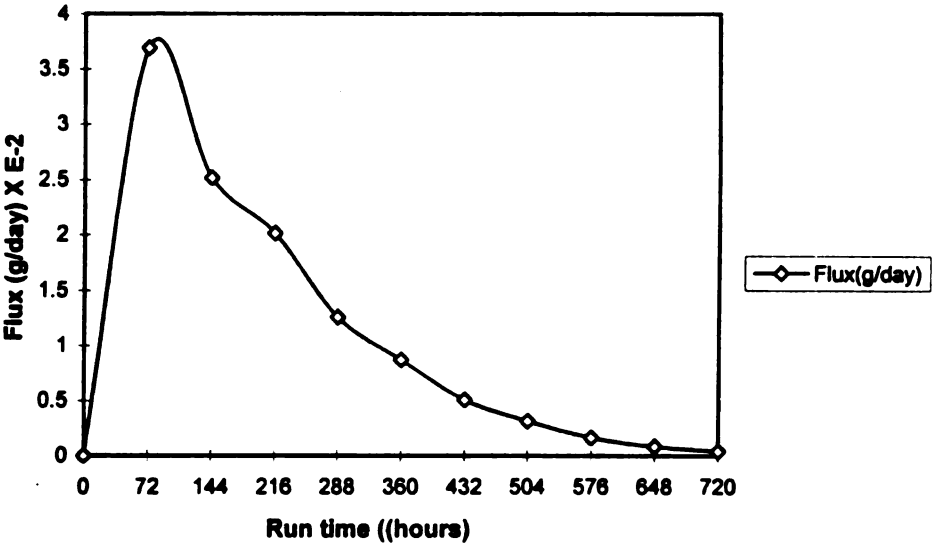


Figure 60.Transmission profile of linalool through a film C from fragrance formulation #2 at 50°C and flow rate of 20cc/min

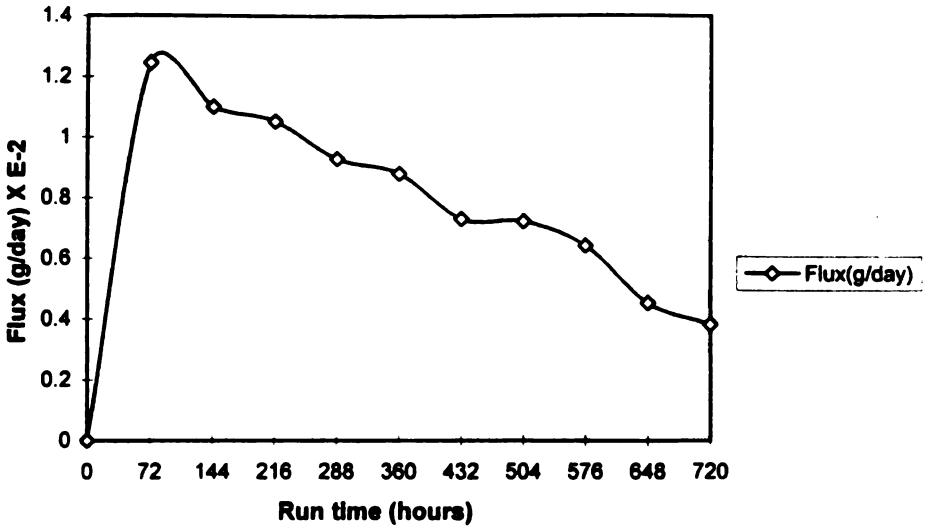


Figure 61.Transmission profile of phenethyl alcohol through a film C from fragrance formulation #2 at 50°C and flow rate of 20cc/min

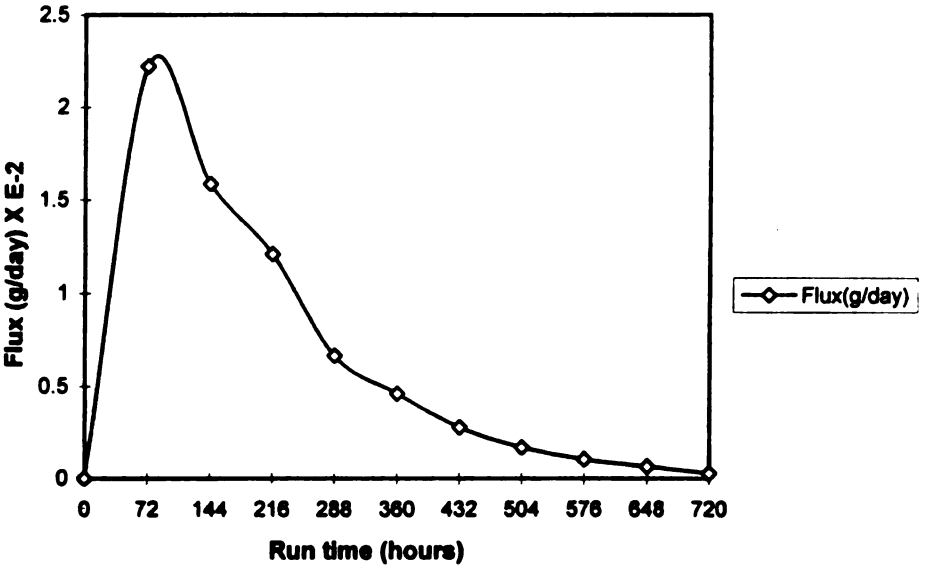


Figure 62.Transmission profile of benzyl acetate through a film C from fragrance formulation #2 at 50°C and flow rate of 20cc/min

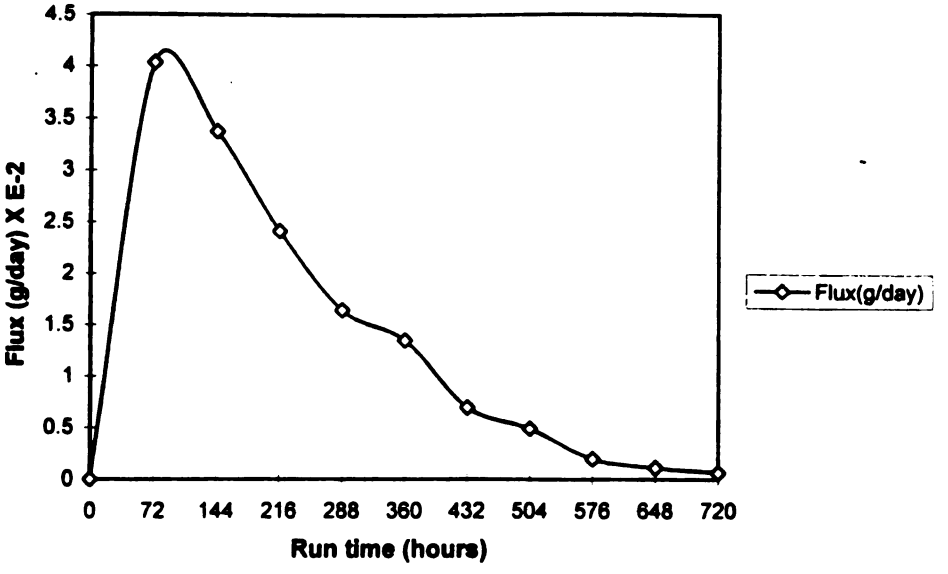


Figure 63.Transmission profile of linalool through a film C
from fragrance formulation #3 at 50°C and flow rate of 20cc/min

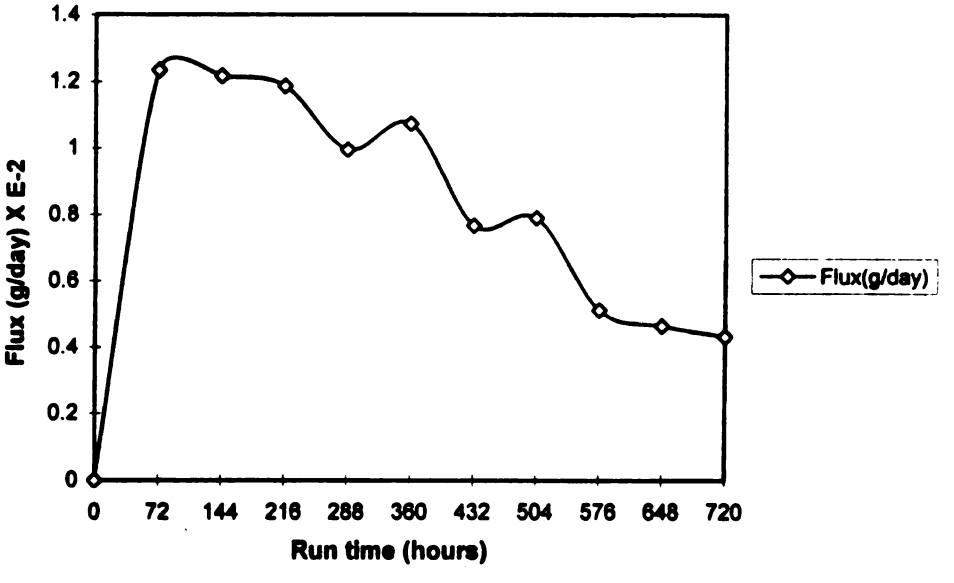


Figure 64.Transmission profile of phenethyl acohol through a film C
from fragrance formulation #3 at 50°C and flow rate of 20cc/min

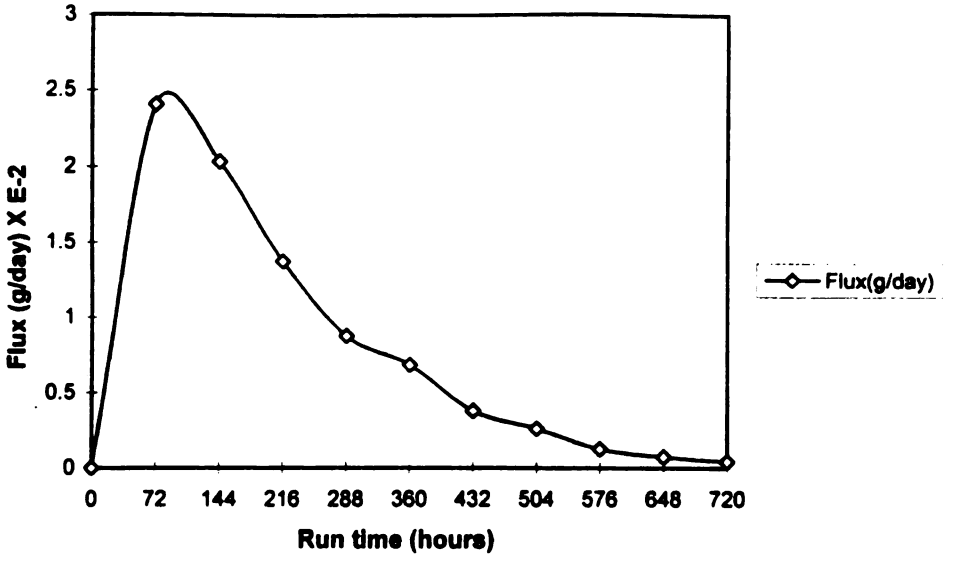


Figure 65.Transmission profile of benzyl acetate through a film C from fragrance formulation #3 at 50°C and flow rate of 20cc/min

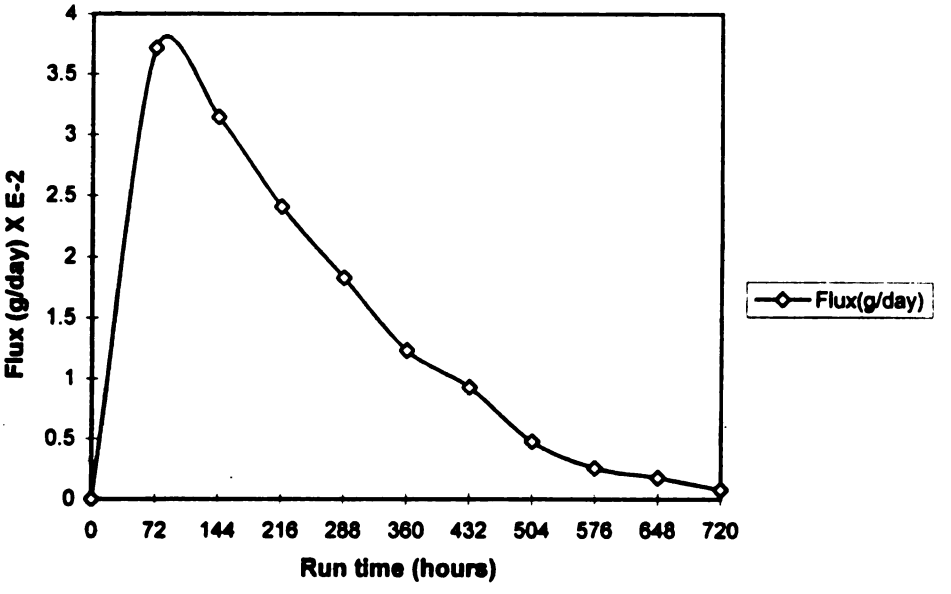


Figure 66.Transmission profile of linalool through a film C from fragrance formulation #4 at 50°C and flow rate of 20cc/min

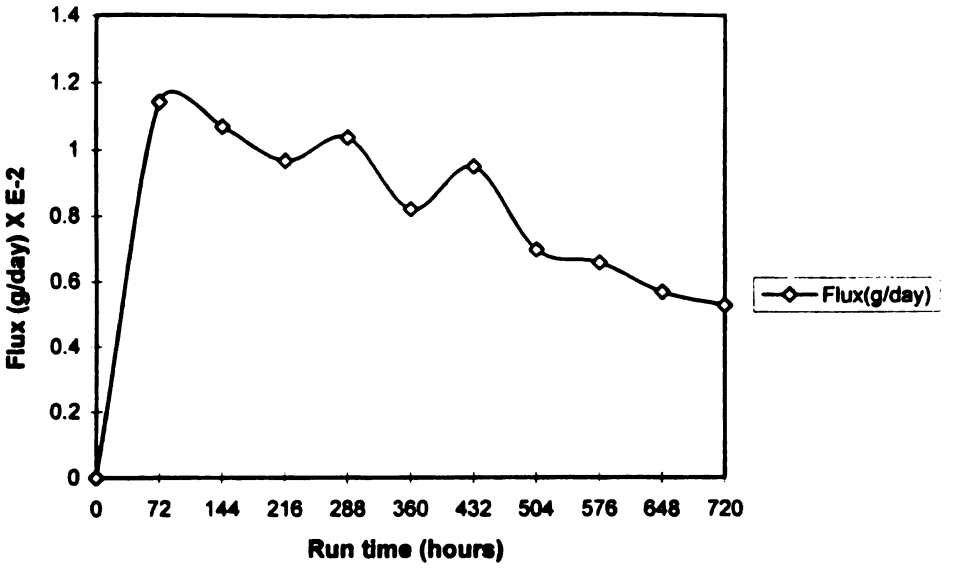


Figure 67.Transmission profile of phenethyl alcohol through a film C from fragrance formulation #4 at 50°C and flow rate of 20cc/min

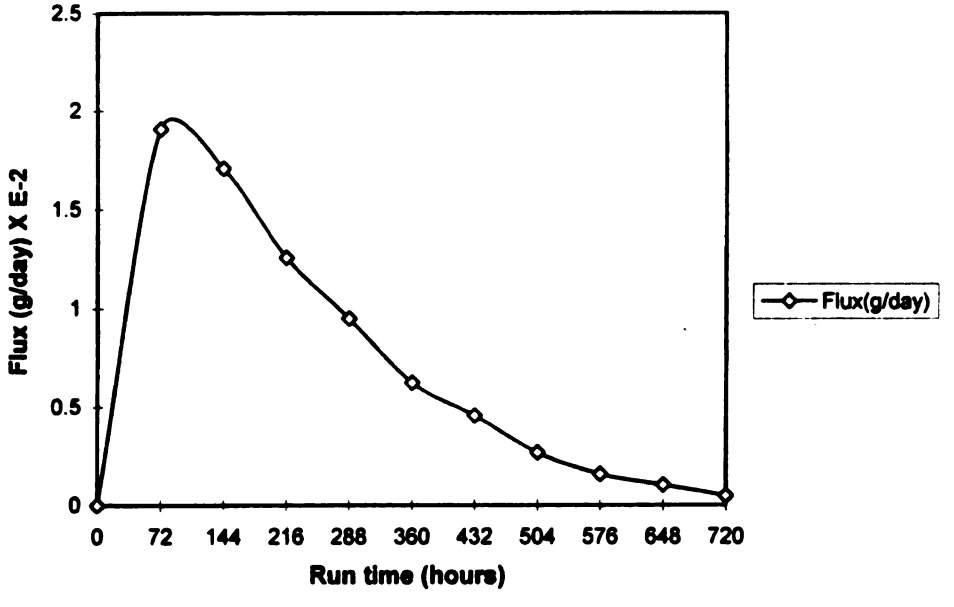


Figure 68.Transmission profile of benzyl acetate through a film C from fragrance formulation #4 at 50°C and flow rate of 20cc/min

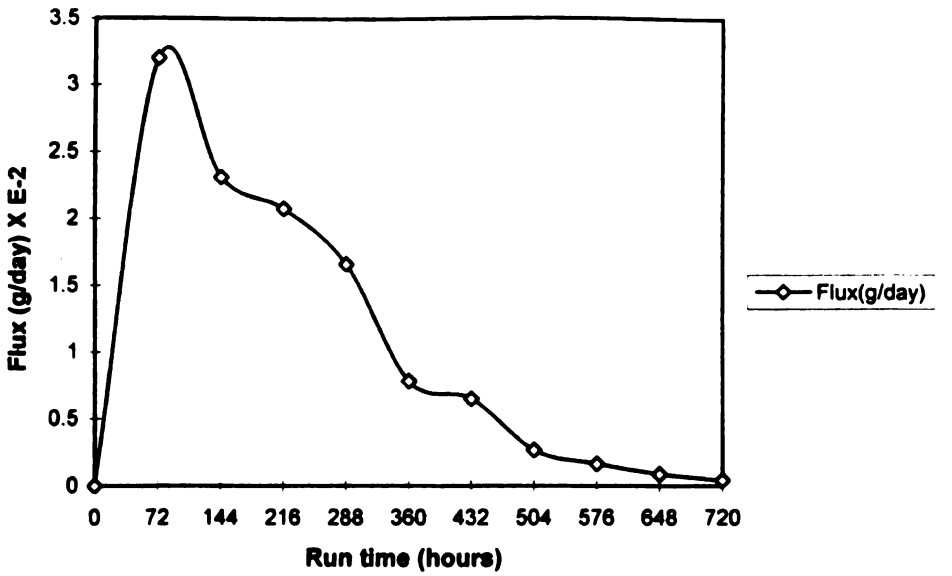


Figure 69.Transmission profile of linalool through a film C
from fragrance formulation #5 at 50°C and flow rate of 20cc/min

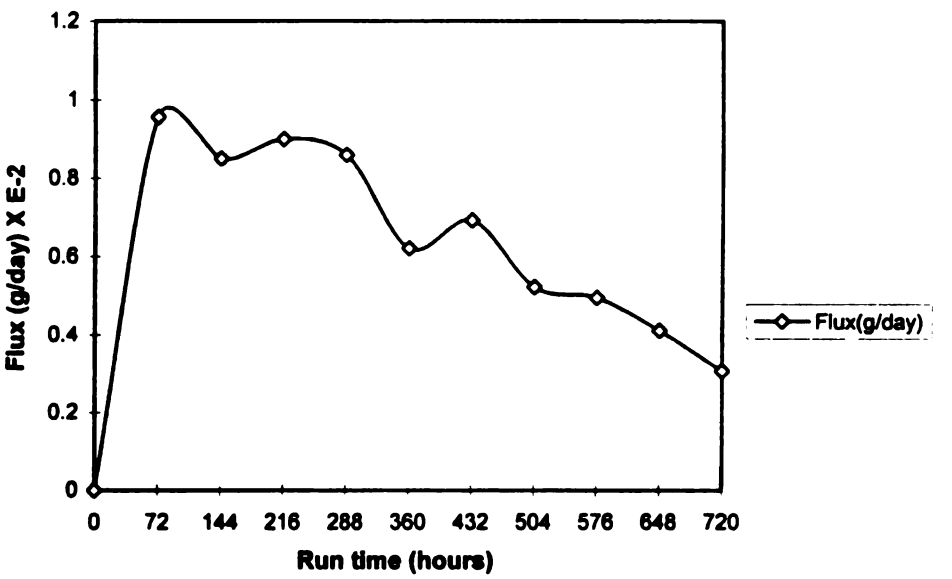


Figure 70.Transmission profile of phenethyl alcohol through a film C
from fragrance formulation #5 at 50°C and flow rate of 20cc/min

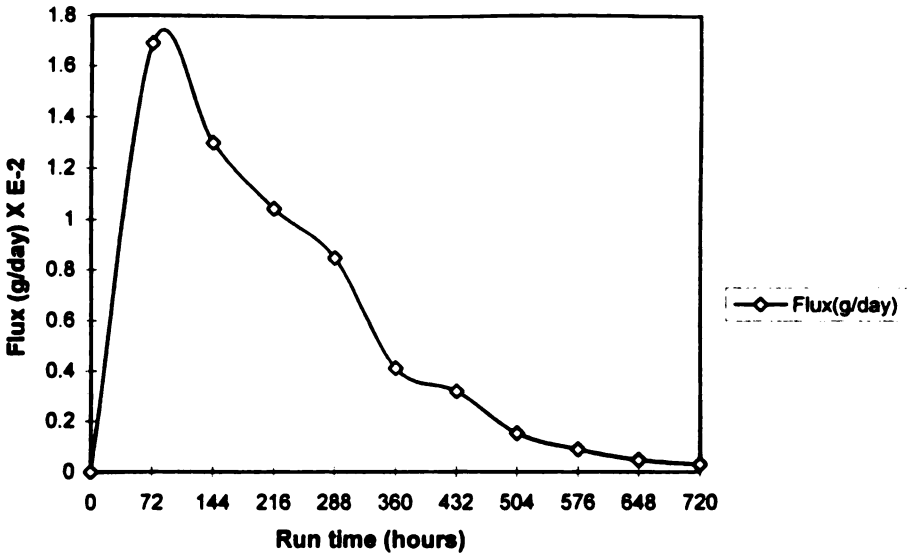


Figure 71.Transmission profile of benzyl acetate through a film C from fragrance formulation #5 at 50°C and flow rate of 20cc/min

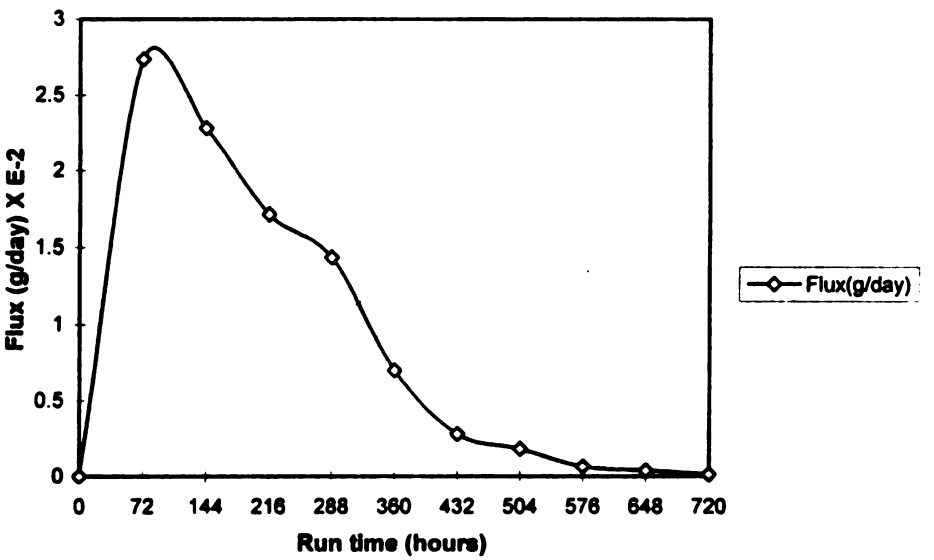


Figure 72.Transmission profile of linalool through a film C from fragrance formulation #6 at 50°C and flow rate of 20cc/min

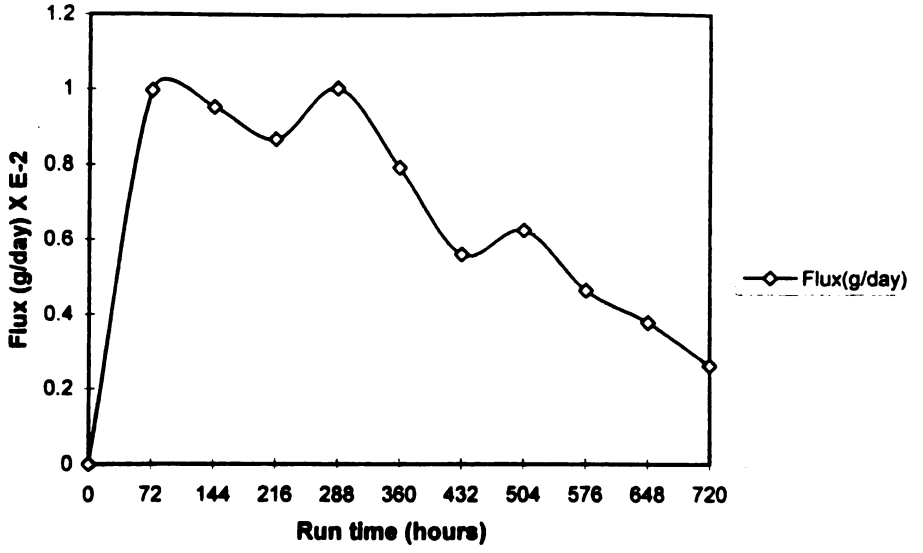


Figure 73.Transmission profile of phenethyl alchol through a film C from fragrance formulation #6 at 50°C and flow rate of 20cc/min

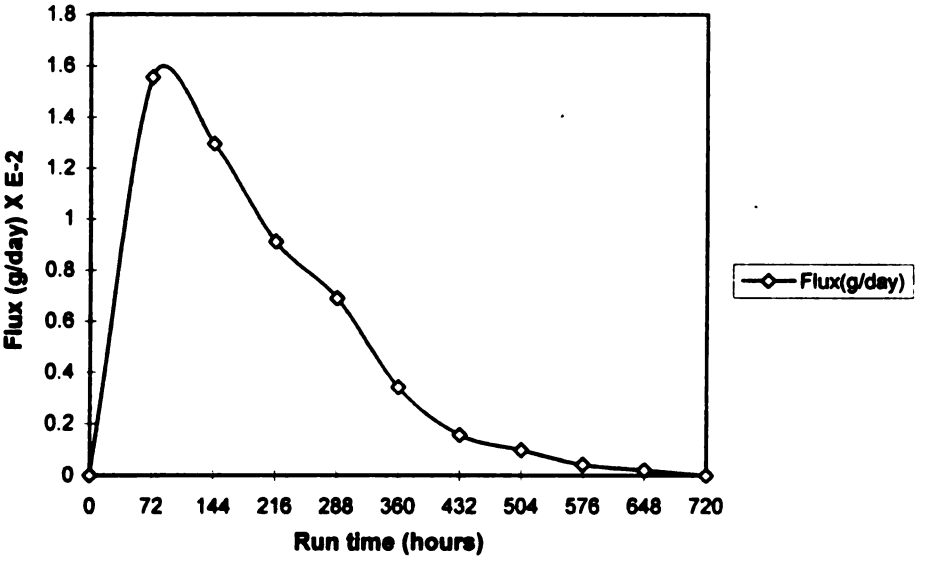


Figure 74.Transmission profile of benzyl acetate through a film C from fragrance formulation #6 at 50°C and flow rate of 20cc/min

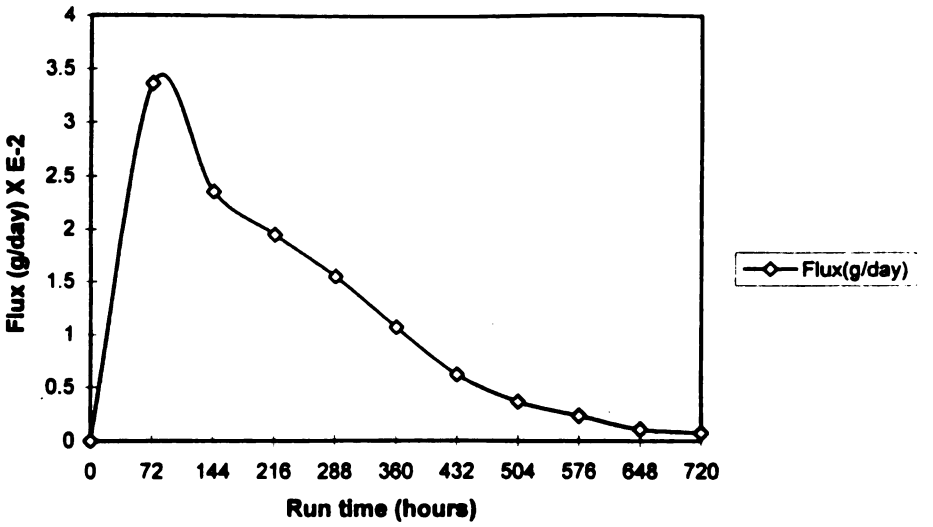


Figure 75.Transmission profile of linalool through a film C
from fragrance formulation #7 at 50°C and flow rate of 20cc/min

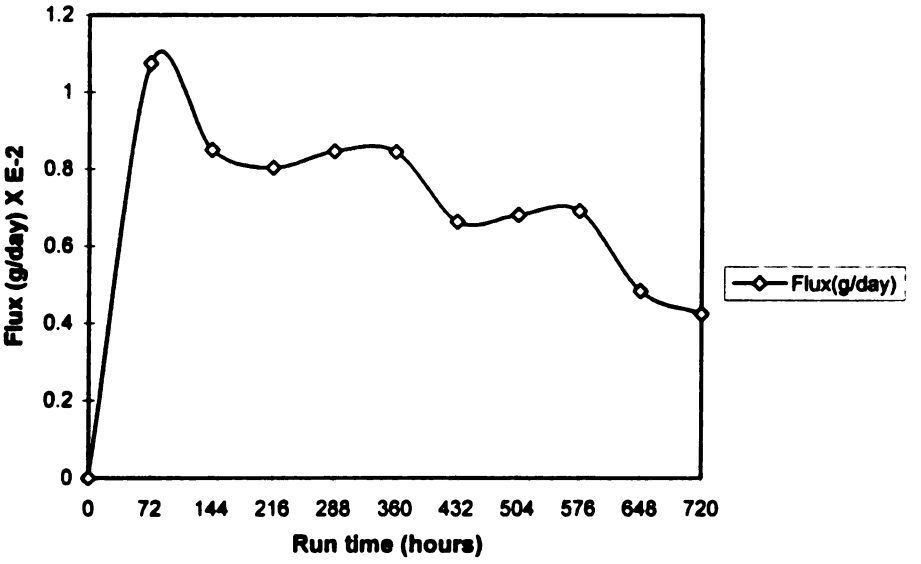


Figure 76.Transmission profile of phenethyl alcohol through a film C
from fragrance formulation #7 at 50°C and flow rate of 20cc/min

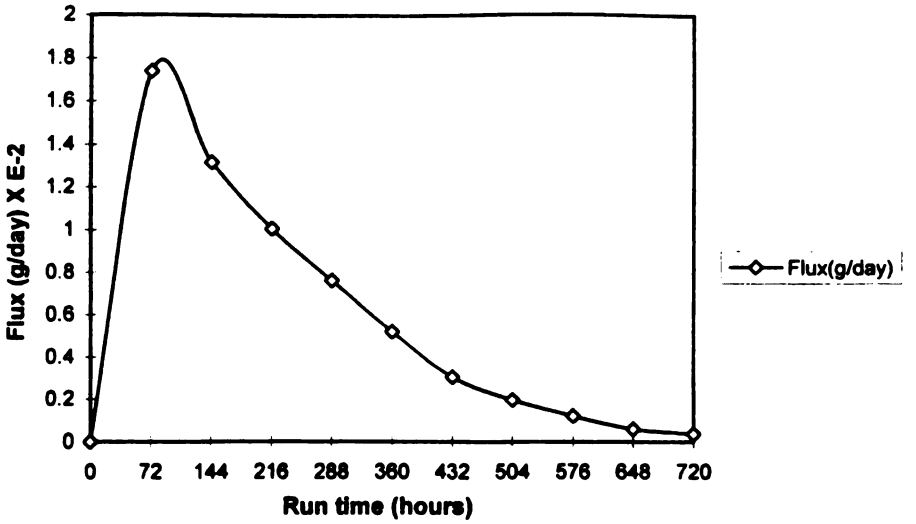


Figure 77.Transmission profile of benzyl aetate through a film C from fragrance formulation #7 at 50°C and flow rate of 20cc/min

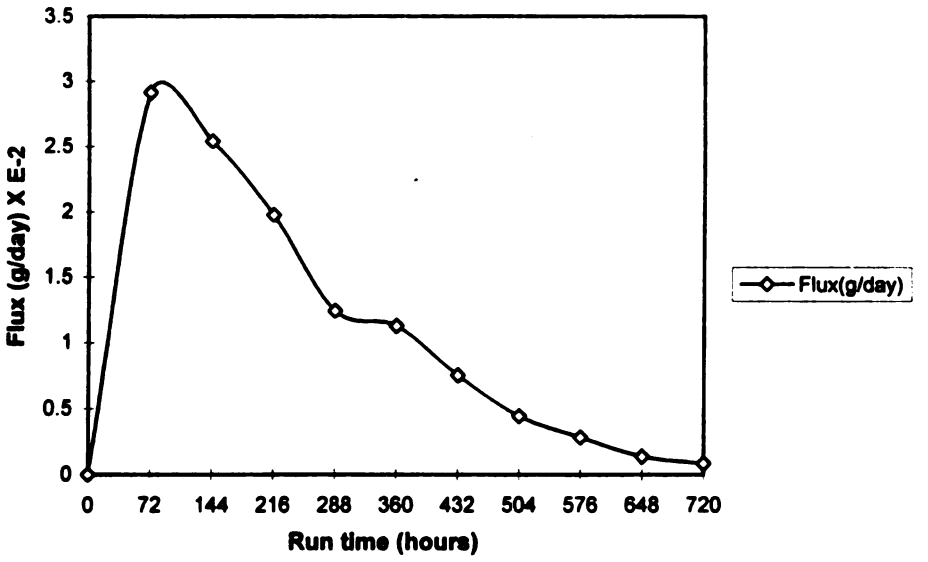


Figure 78.Transmission profile of linalool through a film C from fragrance formulation #8 at 50°C and flow rate of 20cc/min

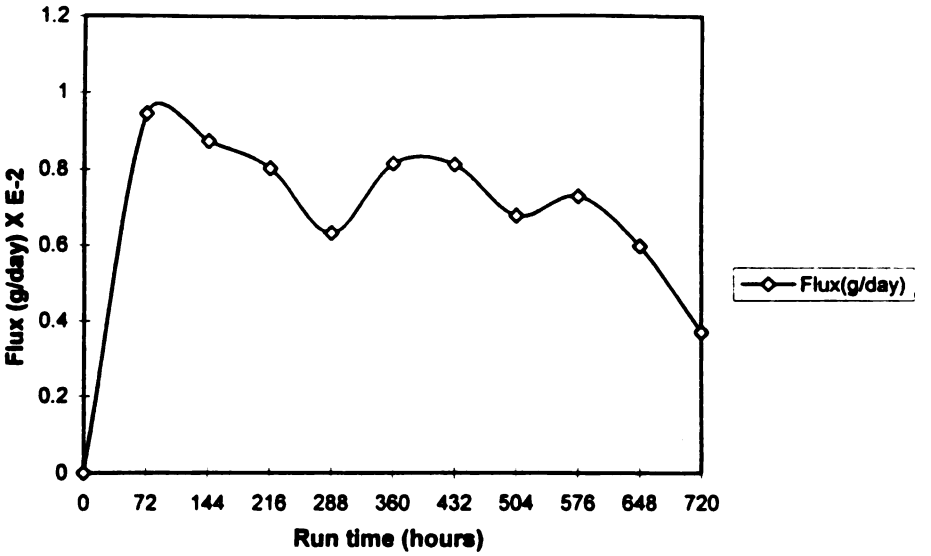


Figure 79.Transmission profile of phenethyl alcohol through a film C from fragrance formulation #8 at 50°C and flow rate of 20cc/min

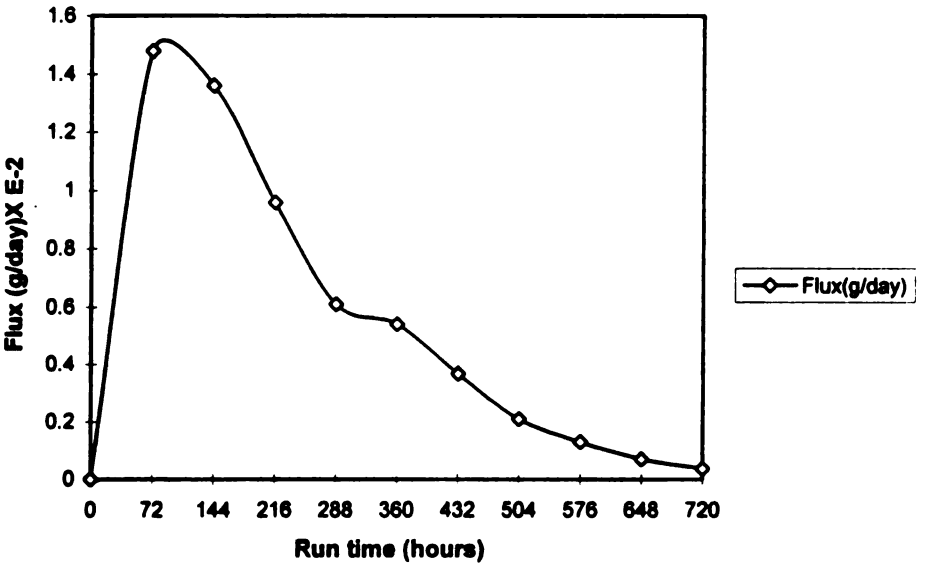


Figure 80.Transmission profile of benzyl acetate through a film C from fragrance formulation #8 at 50°C and flow rate of 20cc/min

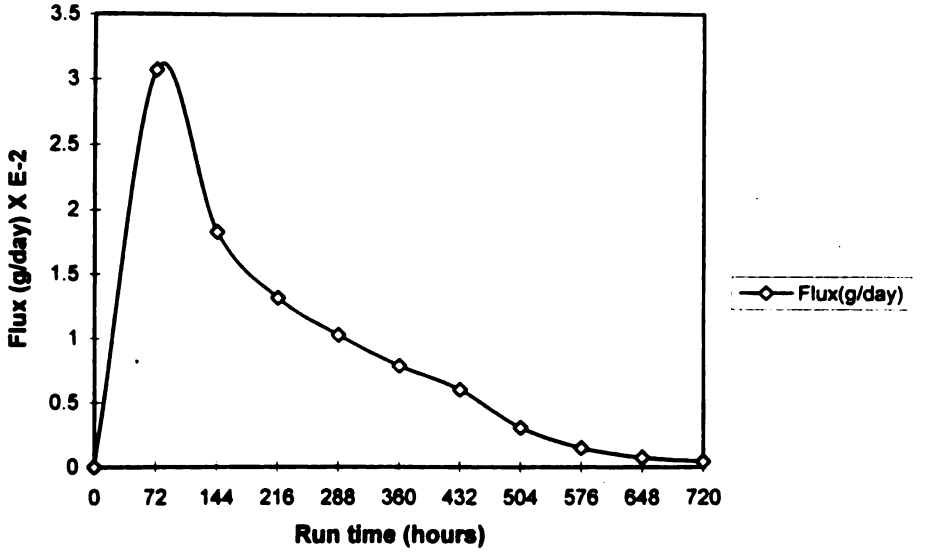


Figure 81.Transmission profile of linalool through a film C
from fragrance formulation #9 at 50°C and flow rate of 20cc/min

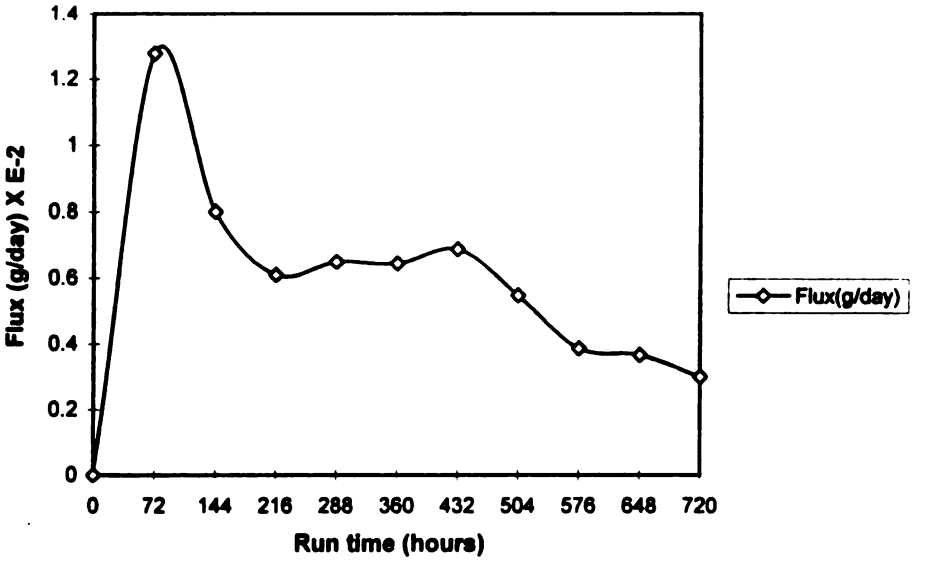


Figure 82.Transmission profile of phenethyl alcohol through a film C
from fragrance formulation #9 at 50°C and flow rate of 20cc/min

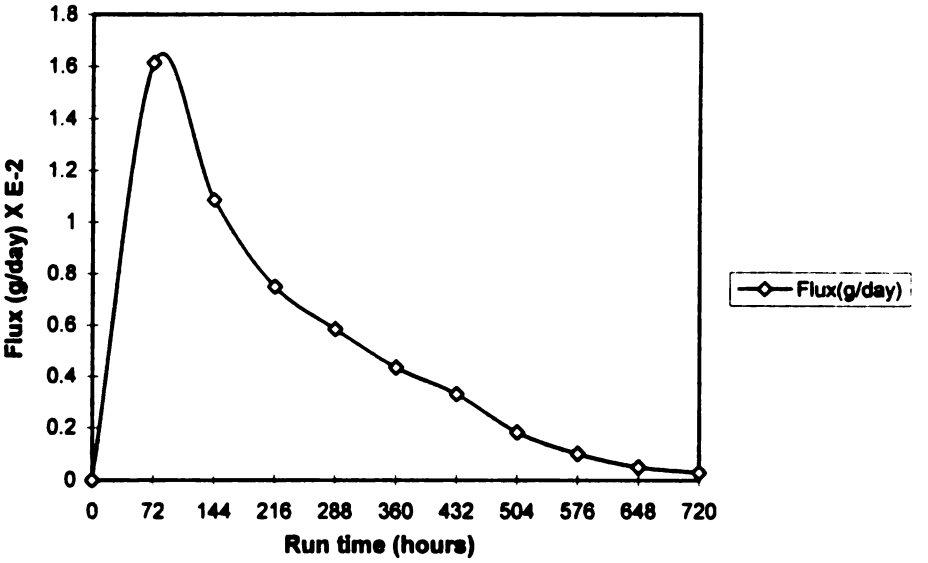


Figure 83.Transmission profile of benzyl acetate through a film C from fragrance formulation #9 at 50°C and flow rate of 20cc/min

be expected to have high transmission rates through the polar ethylene-vinyl acetate (EVA) film structures.

In multi-component organic mixtures, like the fragrance formulations, each penetrant has the capacity of altering the transport properties of the co - pentrants, which makes the mass transport process complicated. The influence on the transport properties of one penetrant by another, as well as the constant change in the driving force concentration and composition of organic mixtures comprising the fragrance formulations, are contributing factors to the complexity of the mass transfer properties of the test systems studied.

A comparison of barrier characteristics of films A, B, and C for the respective probe compounds in the individual fragrance formulations is presented graphically in Figures 84-110 when flux rate is plotted as a function of run time. As the figures illustrate, the transmission rates for the respective probe compounds, which exclude α-hexyl cinnamaldehyde, through film A (vinyl acetate content 6.5%) were significantly lower than through film B (vinyl acetate content 9%) and film C (vinyl acetate content 12%).

To further illustrate the barrier characteristics of the respective test films to the probe volatiles, the relative concentration of probe volatiles permeated through selected fragrance formulation/polymer membrane systems as a function of run time are presented graphically in Figures 111-113, respectively. As demonstrated by both the transmission rate profile curves (Figures 3-83) and histograms presented in Figures 111-113, the barrier properties vary significantly

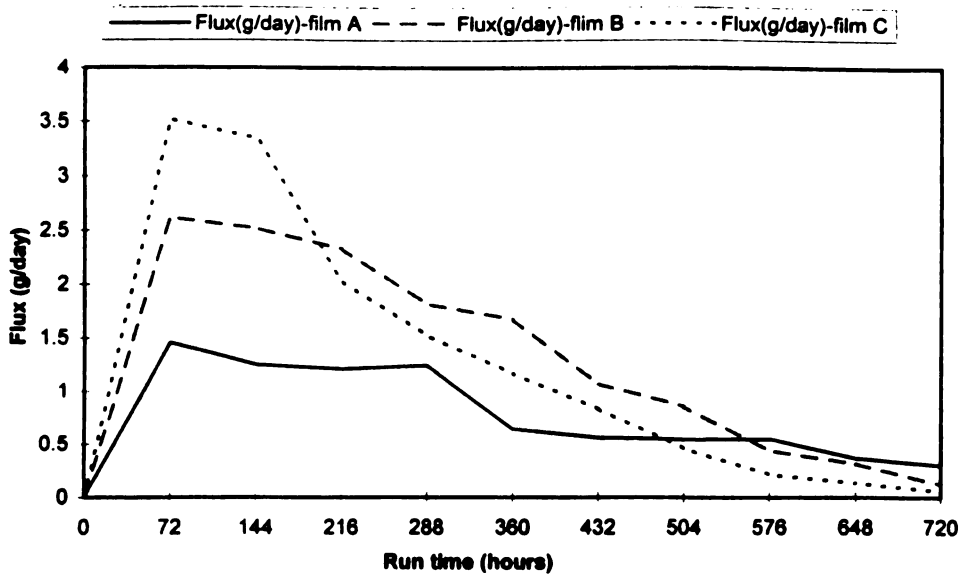


Figure 84. Comparsion of barrier charactieristics of film A, film B, and film C; linalool vapor transmission profile (fragrance formulation #1)

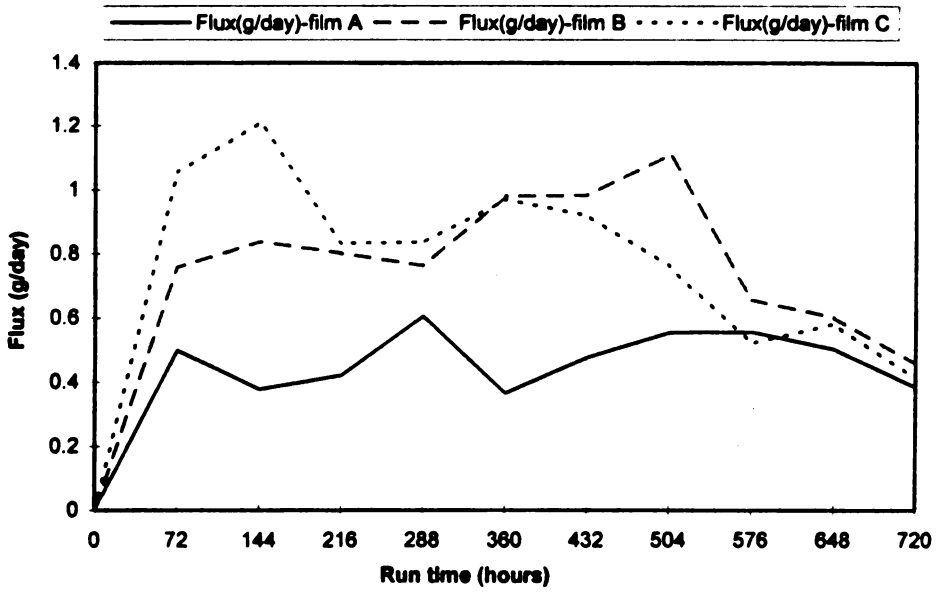


Figure 85. Comparsion of barrier charactieristics of film A, film B, and film C; phenethyl alcohol vapor transmission profile (fragrance formulation #1)

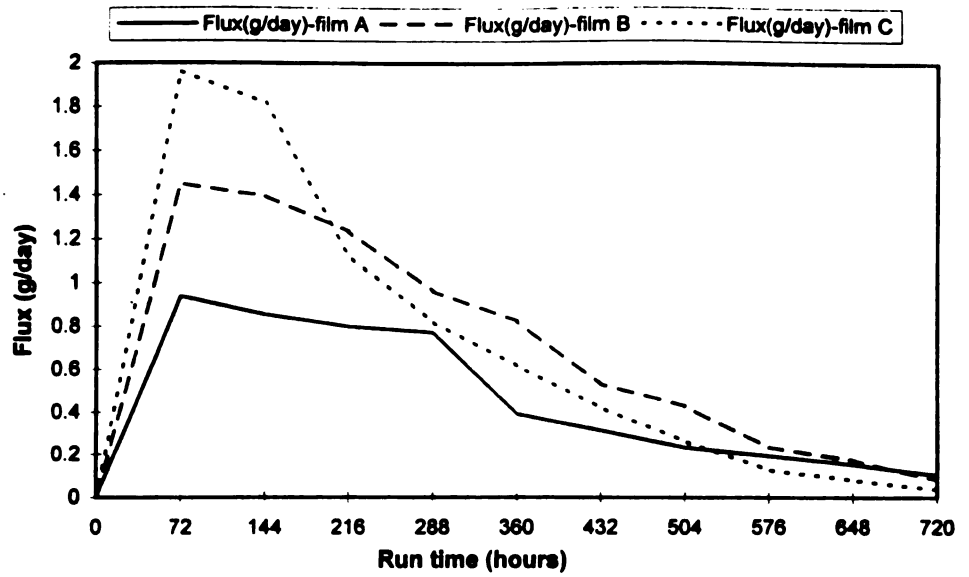


Figure 86. Comparsion of barrier characteristics of film A, film B, and film C; benzyl acetate vapor transmission profile (fragrance formulation #1)

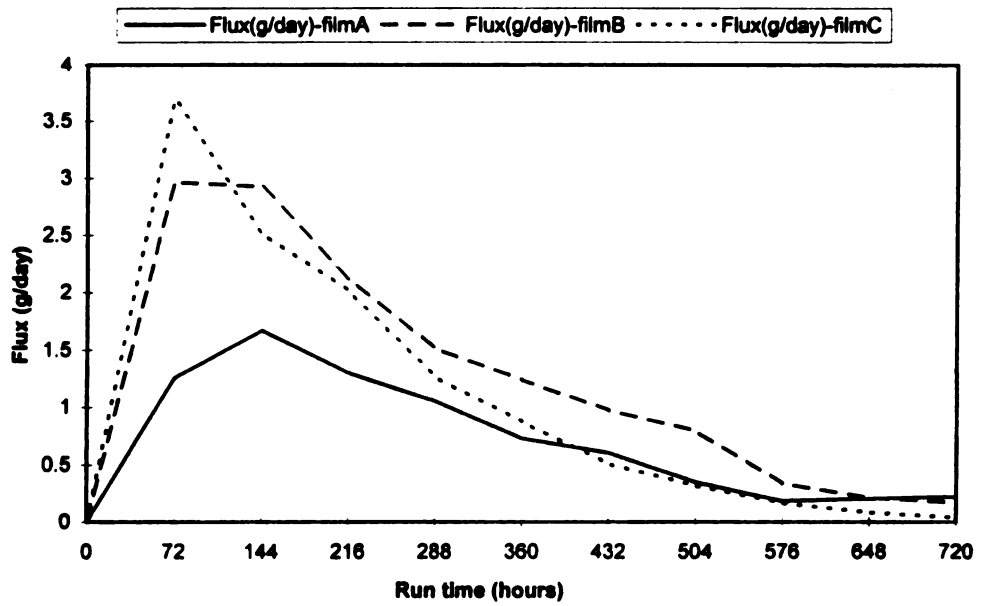


Figure 87. Comparsion of barrier characteristics of film A, film B, and film C; linalool vapor transmission profile (fragrance formulation #2)

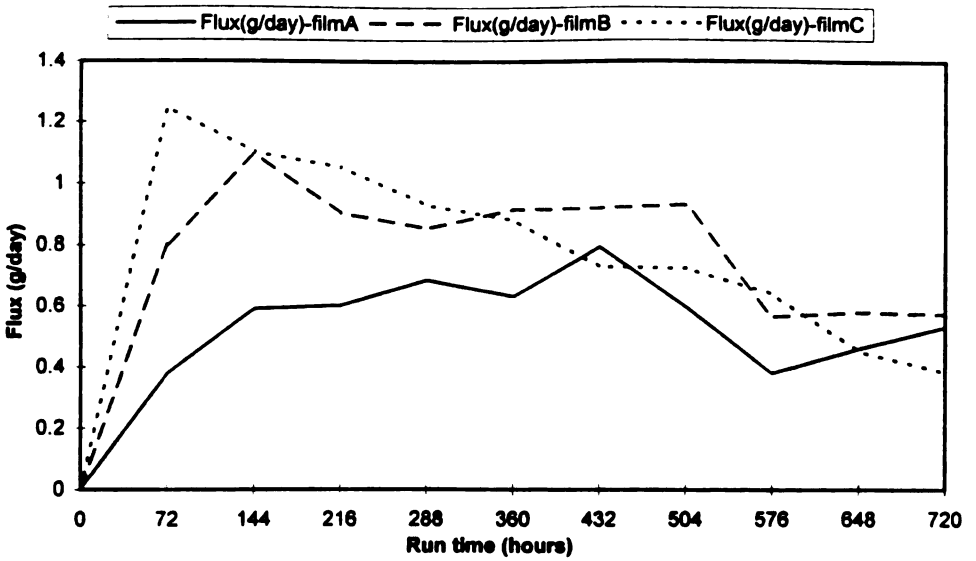


Figure 88. Comparsion of barrier characteristics of film A, film B, and film C; phenethyl alcohol vapor transmission profile (fragrance formulation #2)

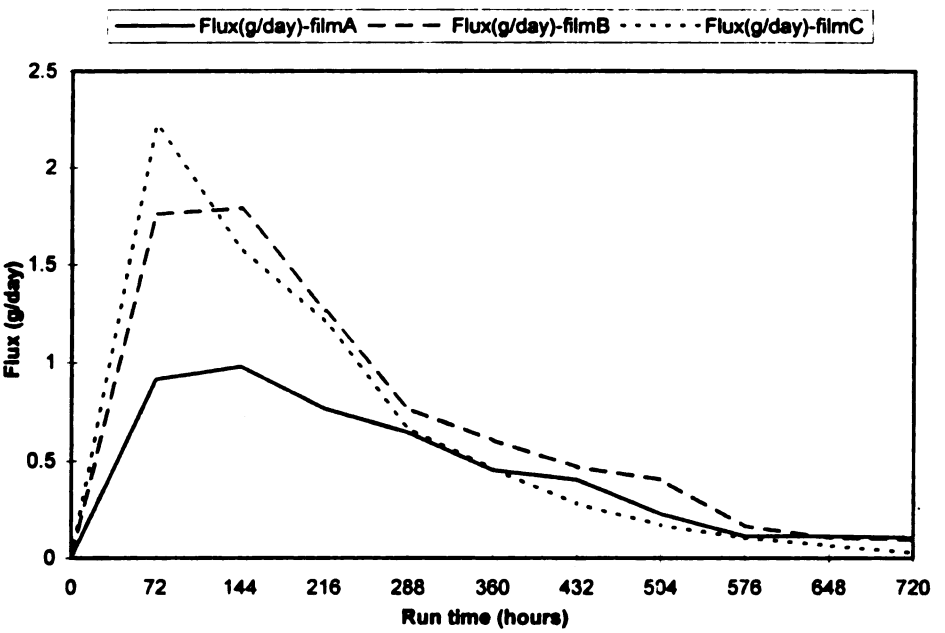


Figure 89. Comparsion of barrier characteristics of film A, film B, and film C; benzyl acetate vapor transmission profile (fragrance formulation #2)

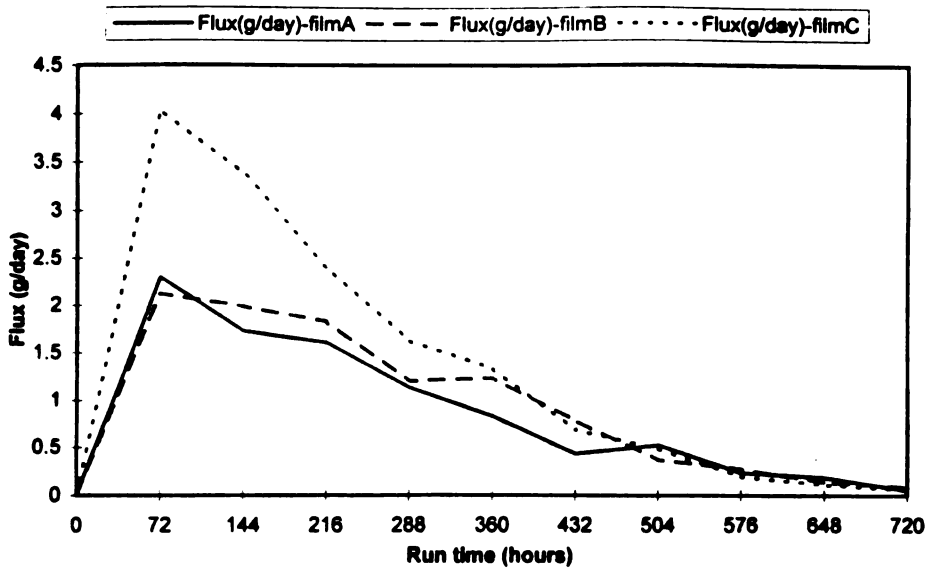


Figure 90. Comparsion of barrier characteristics of film A, film B, and film C; linalool vapor transmission profile (fragrance formulation #3)

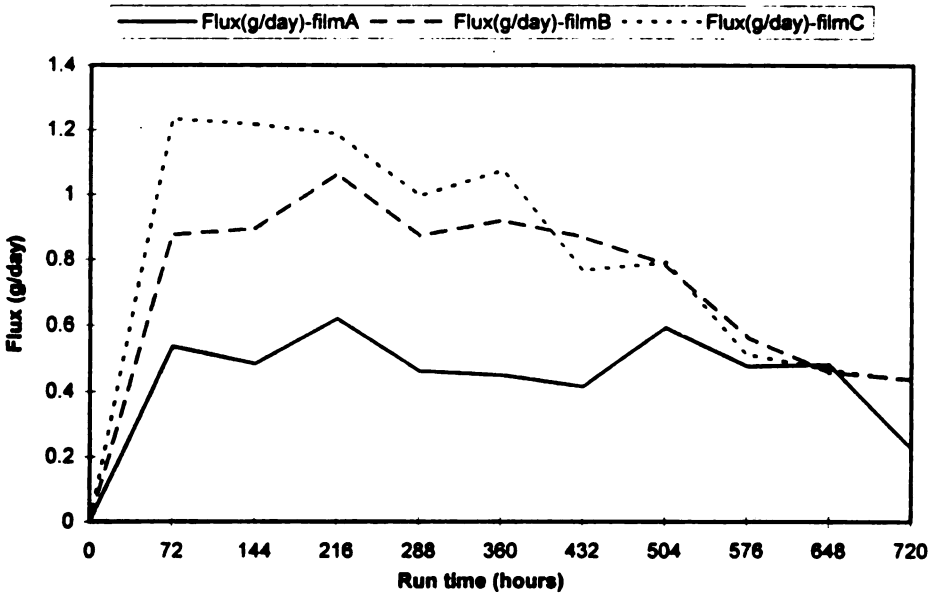


Figure 91. Comparsion of barrier characteristics of film A, film B, and film C; phenethyl alcohol vapor transmission profile (fragrance formulation #3)

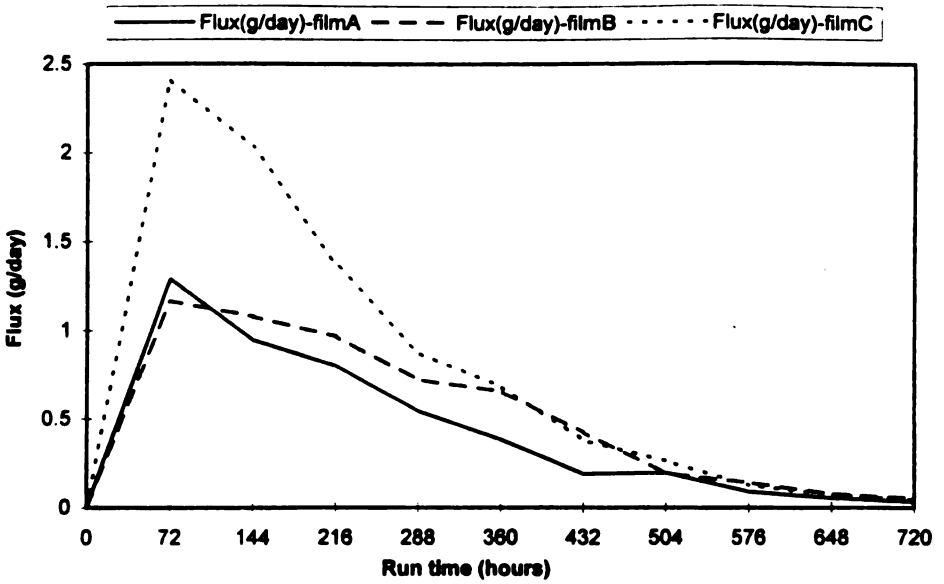


Figure 92. Comparsion of barrier characteristics of film A, film B, and film C; benzyl acetate vapor transmission profile (fragrance formulation #3)

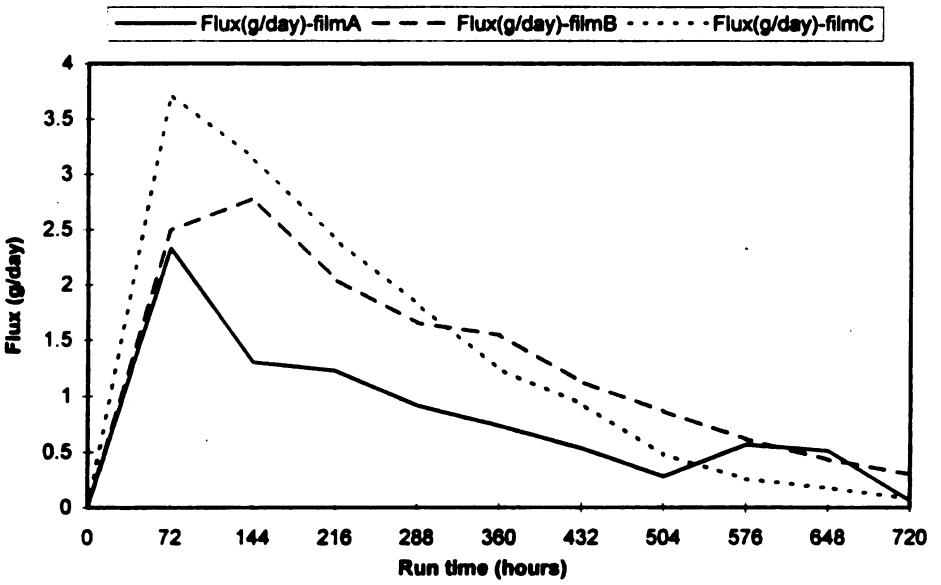


Figure 93. Comparsion of barrier characteristics of film A, film B, and film C; linalool vapor transmission profile (fragrance formulation #4)

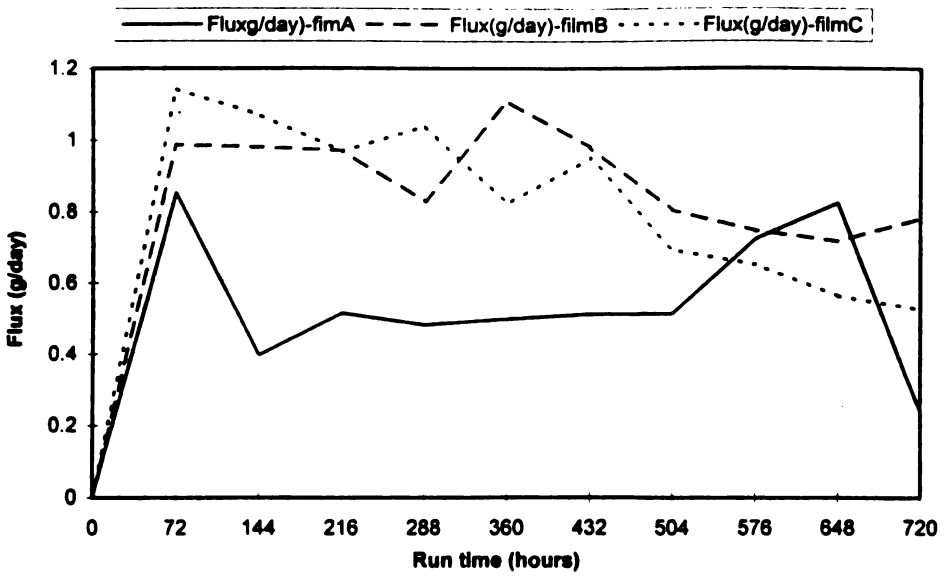


Figure 94. Comparsion of barrier characteristics of film A, film B, and film C; phenethyl alcohol vapor transmission profile (fragrance formulation #4)

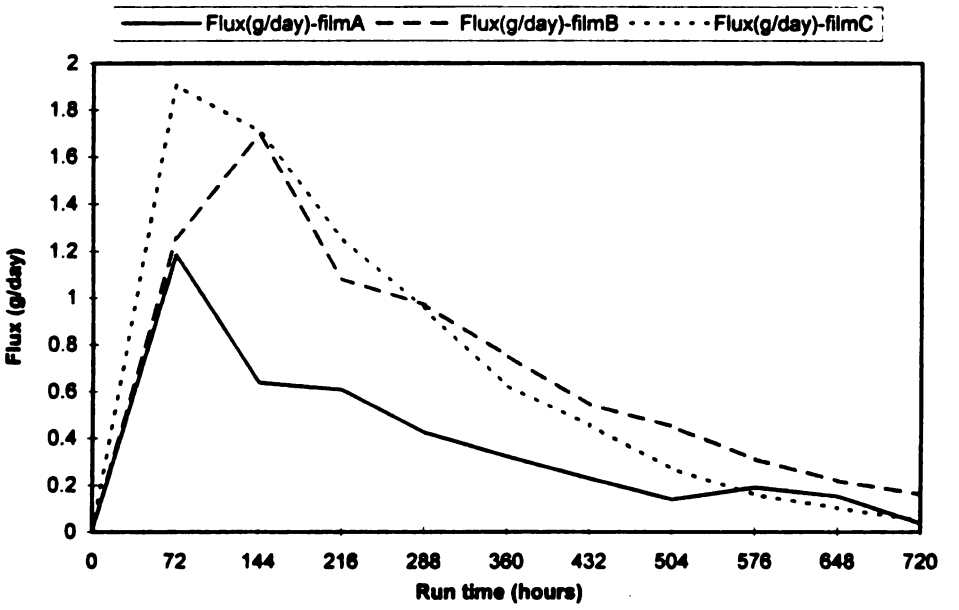


Figure 95. Comparsion of barrier characteristics of film A, film B, and film C; benzyl acetate vapor transmission profile (fragrance formulation #4)

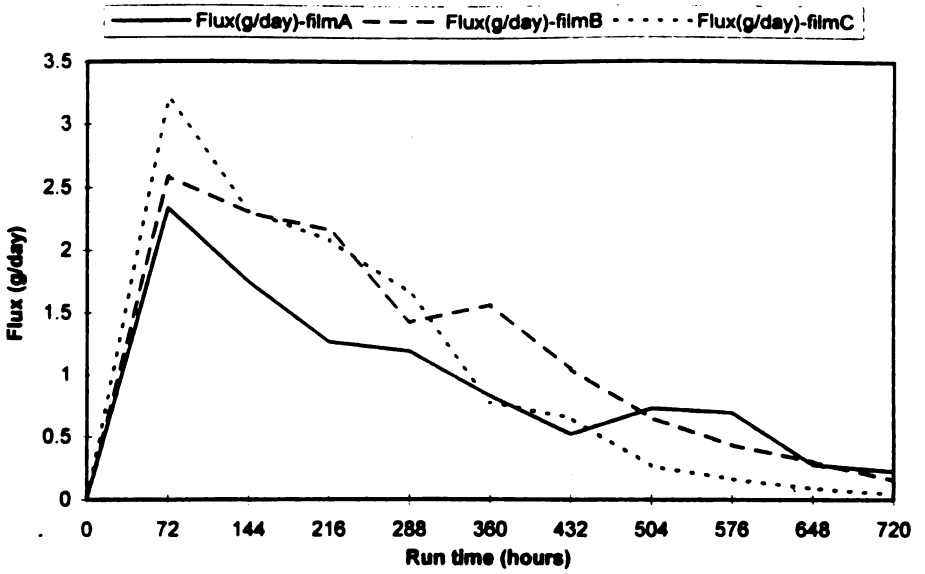


Figure 96. Comparsion of barrier characteristics of film A, film B, and film C; linalool vapor transmission profile (fragrance formulation #5)

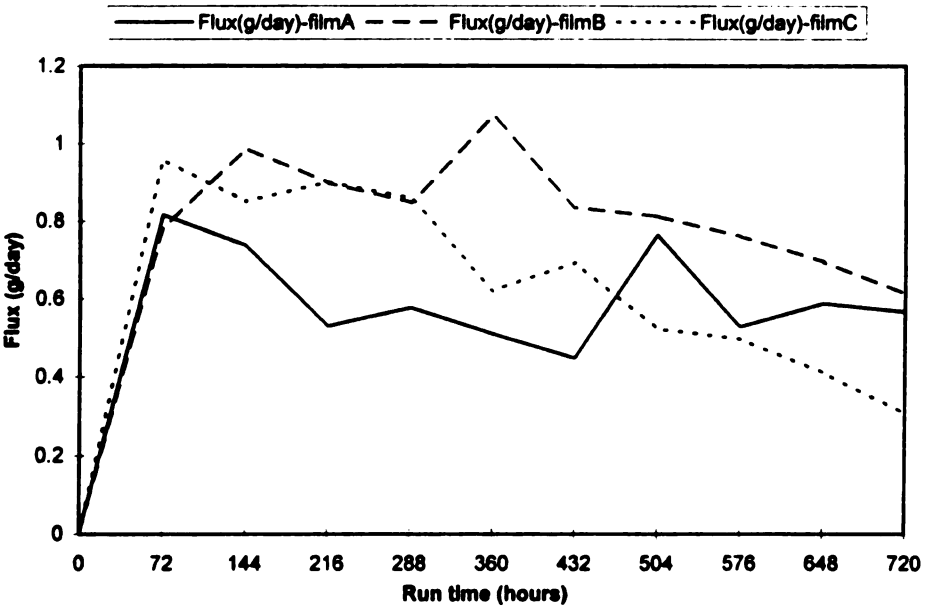


Figure 97. Comparsion of barrier characteristics of film A, film B, and film C; phenethyl alcohol vapor transmission profile (fragrance formulation #5)

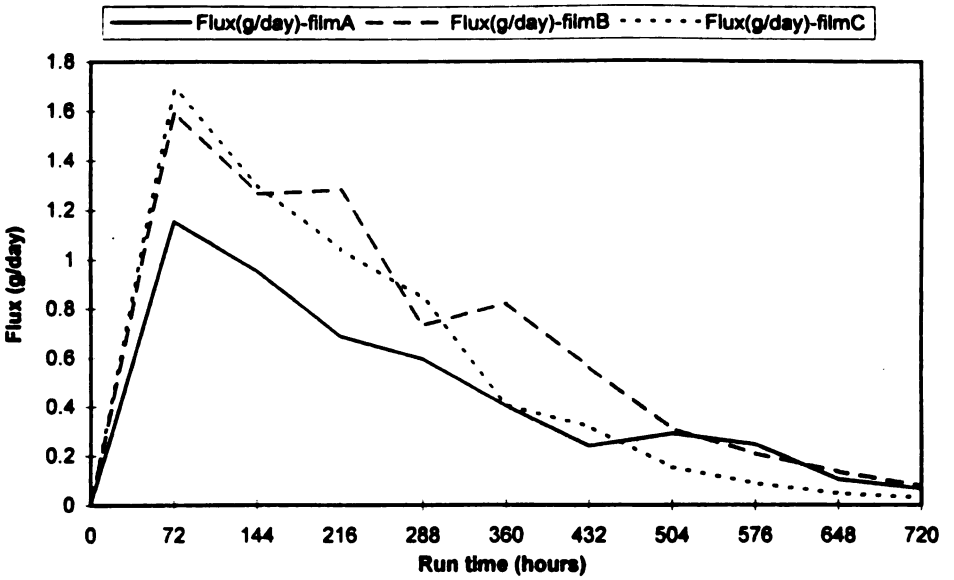


Figure 98. Comparsion of barrier characteristics of film A, film B, and film C; benzyl acetate vapor transmission profile (fragrance formulation #5)

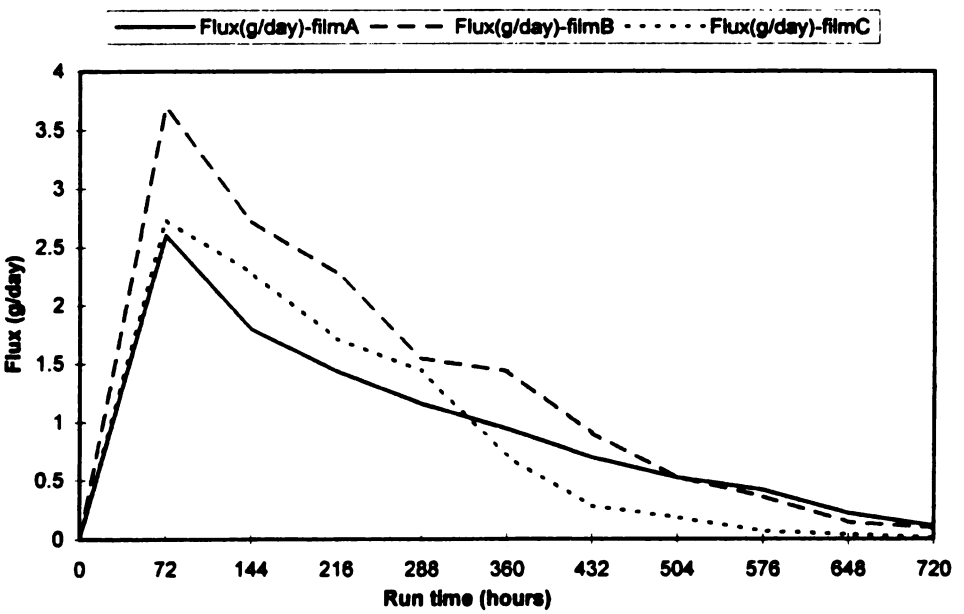


Figure 99. Comparsion of barrier characteristics of film A, film B, and film C; linalool vapor transmission profile (fragrance formulation #6)

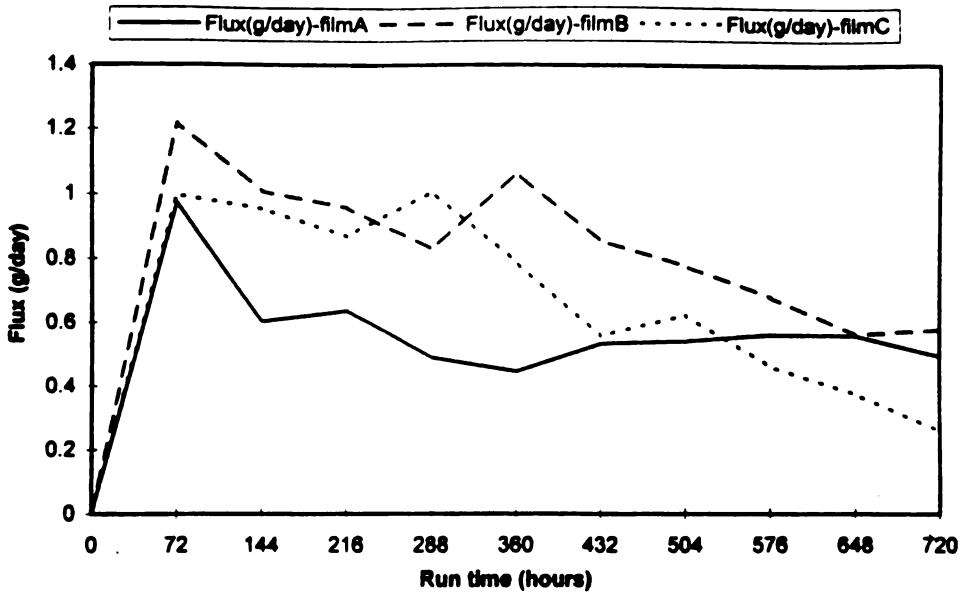


Figure 100. Comparsion of barrier characteristics of film A, film B, and film C; phenethyl alcohol vapor transmission profile (fragrance formulation #6)

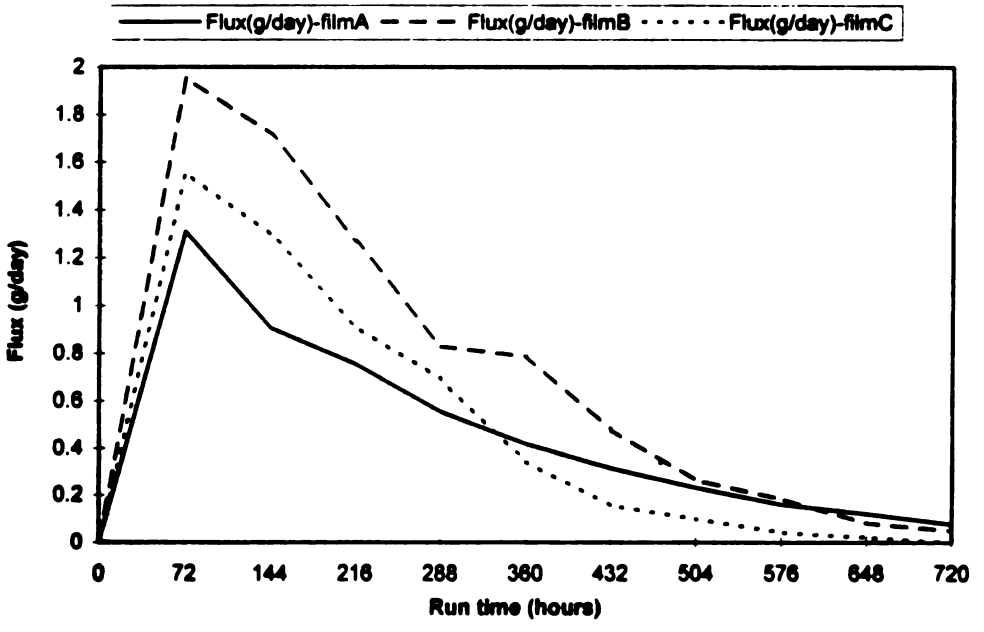


Figure 101. Comparsion of barrier characteristics of film A, film B, and film C; benzyl acetate vapor transmission profile (fragrance formulation #6)

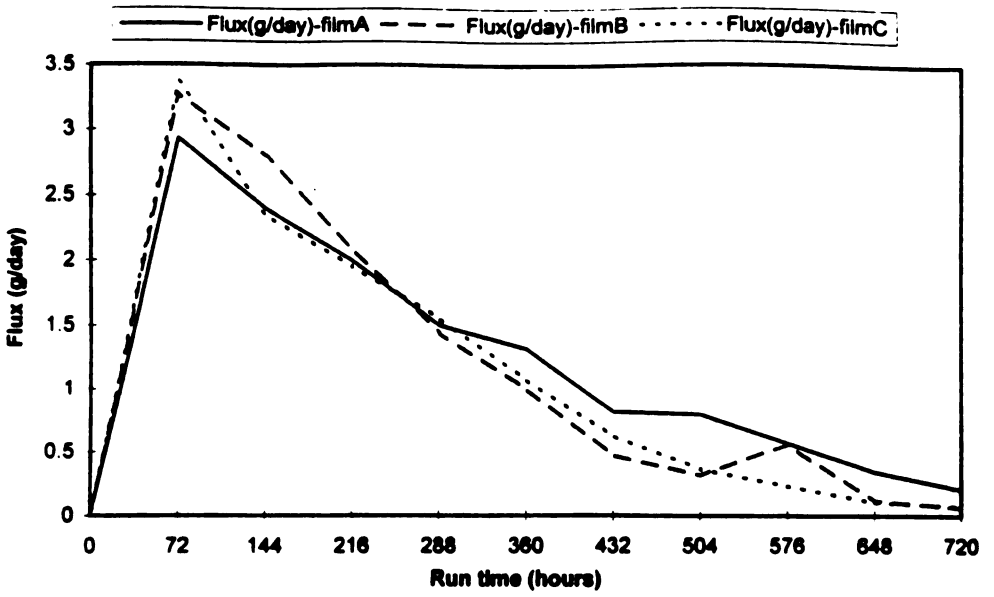


Figure 102. Comparsion of barrier characteristics of film A, film B, and film C; linalool vapor transmission profile (fragrance formulation #7)

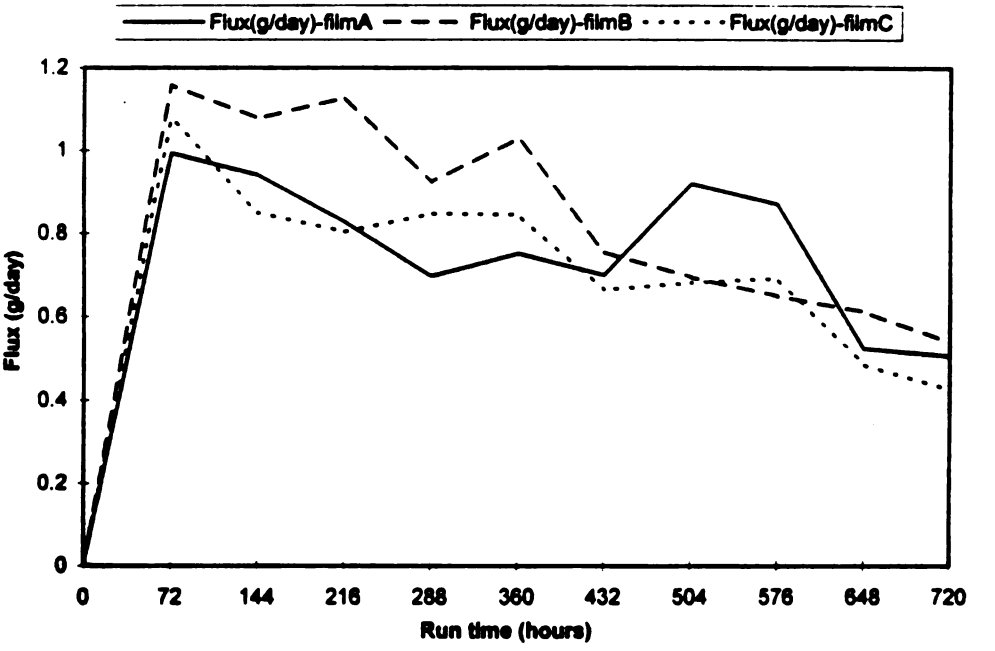


Figure 103. Comparsion of barrier characteristics of film A, film B, and film C; phenethyl alcohol vapor transmission profile (fragrance formulation #7)

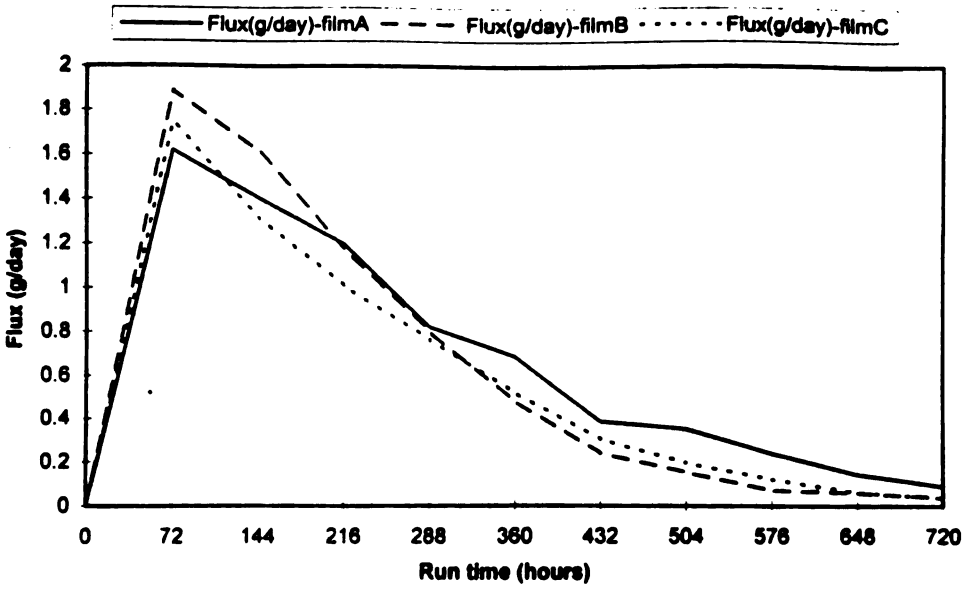


Figure 104. Comparsion of barrier characteristics of film A, film B, and film C; benzyl acetate vapor transmission profile (fragrance formulation #7)

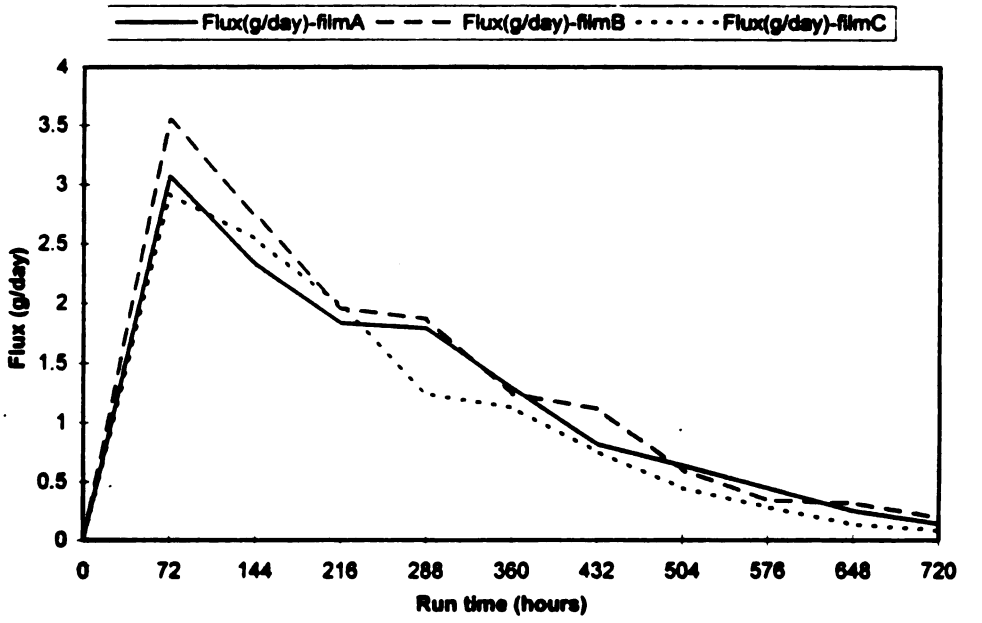


Figure 105. Comparsion of barrier characteristics of film A, film B, and film C; linalool vapor transmission profile (fragrance formulation #8)

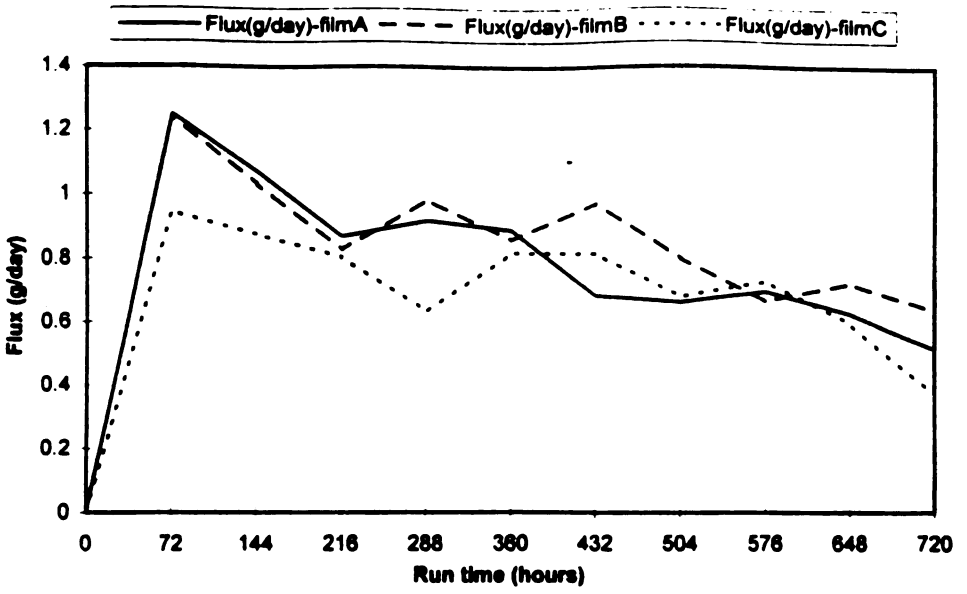


Figure 106. Comparsion of barrier characteristics of film A, film B, and film C; phenethyl alcohol vapor transmission profile (fragrance formulation #8)

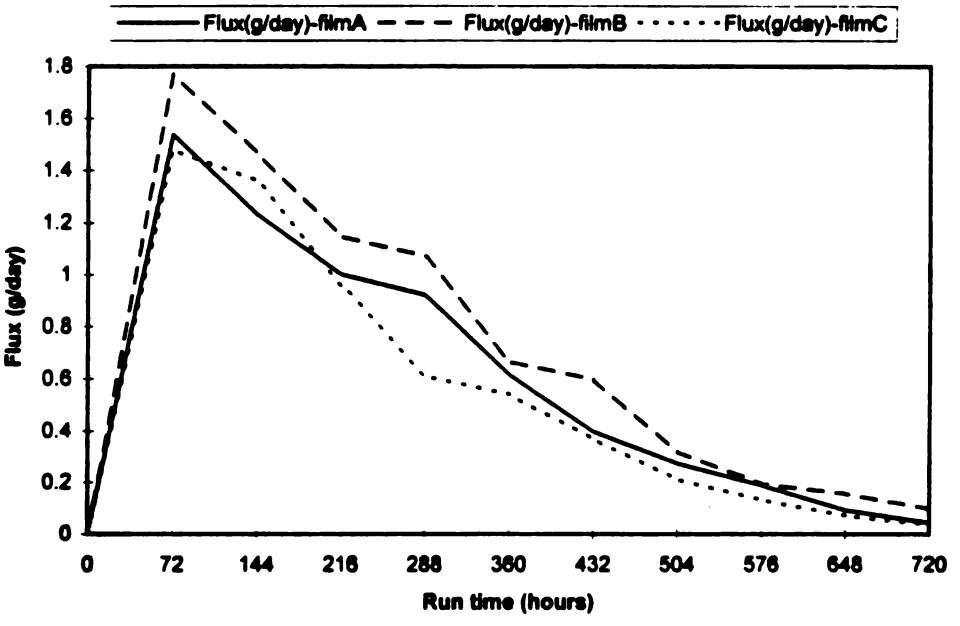


Figure 107. Comparsion of barrier characteristics of film A, film B, and film C; benzyl acetate vapor transmission profile (fragrance formulation #8)

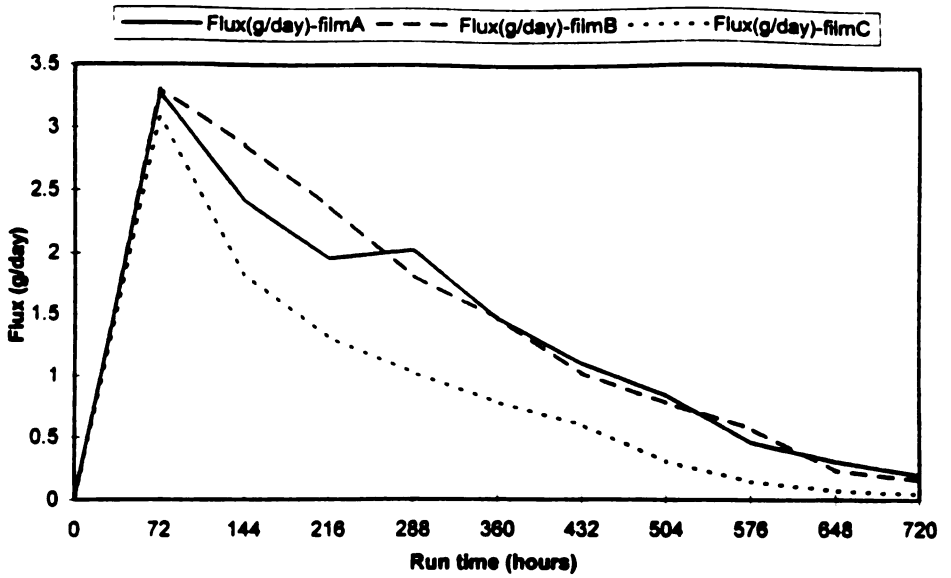


Figure 108. Comparsion of barrier characteristics of film A, film B, and film C; linalool vapor transmission profile (fragrance formulation #9)

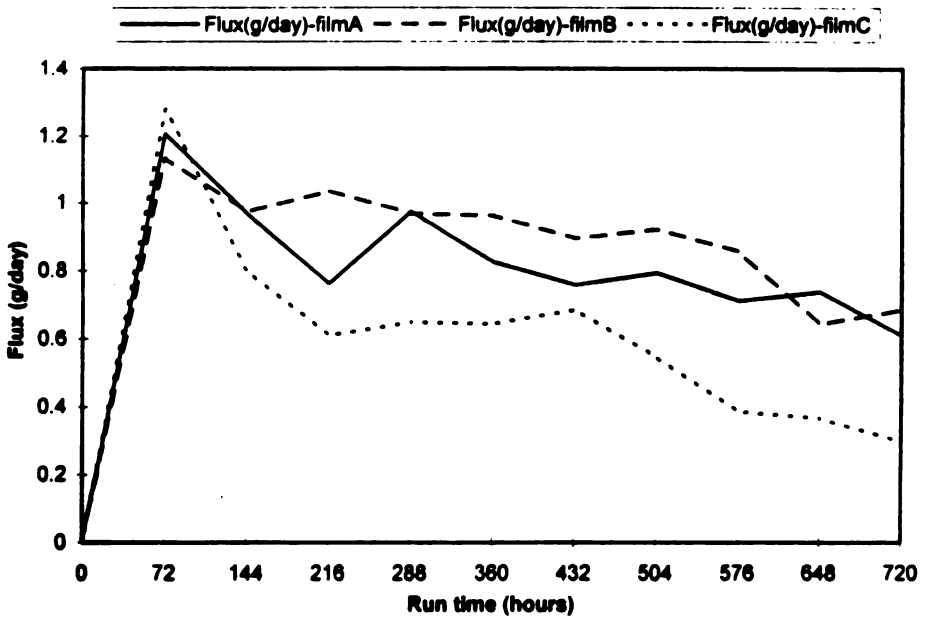


Figure 109. Comparsion of barrier characteristics of film A, film B, and film C; phenethyl alcohol vapor transmission profile (fragrance formulation #9)

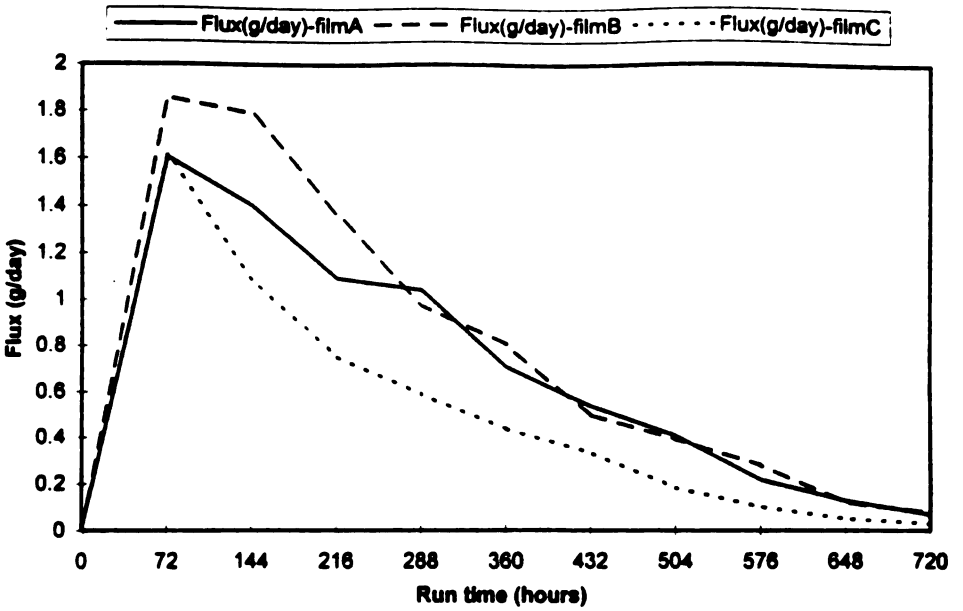


Figure 110. Comparsion of barrier characteristics of film A, film B, and film C; benzyl acetate vapor transmission profile (fragrance formulation #9)

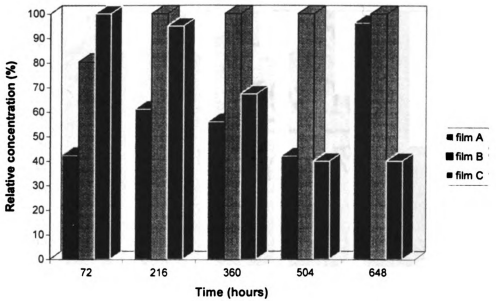


Figure 111. Relative concentration of linalool permeated through film A, film B, and film C permeated from fragrance formulation #2 at 50°C and flow rate of 20cc/min

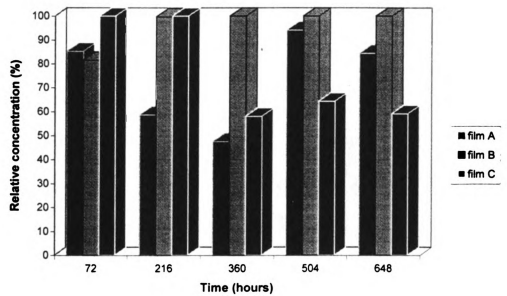


Figure 112. Relative concentration of phenethyl alcohol permeated through film A, film B and film C permeated from fragrance formulation #5 at 50°C and flow rate of 20cc/min

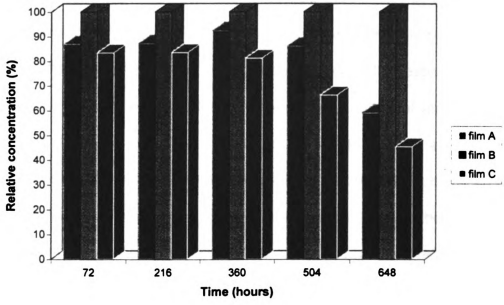


Figure 113. Relative concentration of benzyl acetate permeated through film A, film B and film C permeated from fragrance formulation #8 at 50°C and flow rate of 20cc/min

with time and membrane composition. This is further illustrated below where the global loss and the percent loss of the individual probe volatiles are discussed. The global loss through film A, film B, and film C were found to be approximately 45-50%. However, the relative rates of transmission of the respective probe compounds through the test membranes varied as function of vinyl acetate content of the EVA copolymers. It is assumed therefore, that the difference in the relative transmission rates between each film is due to the difference in percent crystallinity of the films. Polymer morphology refers to the physical state by which amorphous and semi-crystalline regions coexist and relate to each other and depends not only on its stereochemistry, but also on whether the polymer has been oriented or not, and at which conditions of temperature, strain rate, and cooling temperature the film has been oriented, as well as the melt cooling temperature.

Fundamental properties which are associated with polymer morphology and will therefore influence the permeability and diffusivity characteristics of the polymer include:

- structural regularity or chain symmetry, which can readily lead to a three-dimensional order of crystallinity. This is determined by the type of monomer(s) and the conditions of the polymerization reaction.
- chain alignment or orientation which allows laterally bonding groups to approach each other to the distance of the best interaction, enchanting the tendency to form crystalline materials.

Semicrystalline polymers consist of a microcrystalline phase dispersed in an amorphous phase. The dispersed crystalline phase decreases the sorption of penetrants, whenever the crystal conformations produce regions of higher density than the amorphous polymer. A closer atomic packing tends to exclude relatively large molecules such as organic permeants. For this reason it is generally accepted that gases and vapors are normally sorbed, and therefore able to diffuse, only in the polymer's rubbery or amorphous phase. The dispersed microcrystals are impermeable to penetrant diffusion and create a more tortuous path for the diffusing molecule. Additionally, the microcrystalline phase also acts as a three dimensional crosslinking agent, increasing the non-isotropism of the polymer. The combined decrease in sorption and diffusion contributes then to a lower permeability.

According to the previous study by Matur(1993), ethylene vinyl acetate copolymer(6.5% vinyl acetate) has a percent crystallinity of about 25.5, which is considered highly amorphous.

The percent crystallinity was obtained by differential scanning calorimetry analysis to give the heat of fusion (ΔH_f) and substitution into Equation (23).

$$\text{Percent crystallinity} = \frac{Actual Hf\,(cal/g)}{Theoretical\,100\%\,Hf\,(cal/g)} \times 100 \qquad (23)$$

The theoretical value of Hf was obtained from the literature. For polyethylene(PE), the heat of diffusion value for the theoretical 100% crystalline polymer was 68.4 cal/g (Troedel, 1984). For the respective vinyl acetate/ethylene copolymers, it was assumed that the theoretical value for the heat of fusion was equivalent to the PE value. The results of heat for fusion

determinations by differential scanning calorimetry (DSC), for the respective vinyl acetate/ethylene copolymers, are presented in Appendix E. The percent crystallinity of the test films were 33.9% (6.5% vinyl acetate content), 31.3% (9% vinyl acetate content) and 27.4% (12% vinyl acetate content) respectively.

The magnitude of the solubility for the penetrant in a polymer increases as the molar volume of the condensed penetrant increases. The measure of molecular size is the constant b of the Van der Waal's equation of state, where b is the effective volume of the molecules in one mole of gas. The molar volumes of linalool, phenethyl alcohol, benzyl acetate and α-hexyl cinnamaldehyde are 177.3 cc/mole, 119 cc/mole, 144 cc/mole, and 227 cc/mole. Therefore, α-hexyl cinnamaldehyde is expected to have the highest solubility in the polymer, . based on concentration of the molar volume. However, the studied fragrance formulations have low concentrations of α-hexyl cinnamaldehyde and correspondingly low vapor pressure values, due to its high boiling point. Also, there are other factors which can influence the mass transport properties of the penetrants, like synergistic or antagonistic effects on permeability by co-penetrants, temperature and penetrant-polymer interaction.

In general, the permeability increases with chemical similarities between the components, for most penetrant-polymer systems. As the solubility parameters of the penetrants and the polymer become closer, the solubility of the penetrant in the polymer is expected to increase. The estimated solubility parameters of linalool, phenethyl alcohol, benzyl acetate and α-hexyl cinnamaldehyde are 5.2 $(Cal/cm^3)^{1/2}$, 6.3 $(Cal/cm^3)^{1/2}$, 5.9 $(Cal/cm^3)^{1/2}$, and 4.5 $(Cal/cm^3)^{1/2}$ respectively.

Also, the solubility parameter of the ethylene/vinyl acetate copolymers is estimated to be between 8.51 and 9.03 $(Cal/cm^3)^{1/2}$. Therefore, it is expected that phenethyl alcohol and benzyl acetate would have a higher solubility in the ethylene/vinyl acetate (EVA) copolymers than linalool and α-hexyl cinnamaldehyde. However, it was found that linalool and benzyl acetate had higher flux values than phenethyl alcohol and α-hexyl cinnamaldehyde through the EVA copolymers. This is due to the fact that permeability through a polymer membrane is affected not only by solubility but also by diffusivity and vapor pressure of the penetrant.

Furthermore, plasticization of the polymer by the sorbed penetrant can result in changes the polymer structure because of swelling and distortion of amorphous region incurred during sorption(Rogers, 1969). In this regard, sorption of the penetrant vapors may disrupt the initial local conformation of crystalline and amorphous regions, so that the effective density and local molecular conformation vary in a nonlinear fashion both with time, and as a function of distance in the sample (Rogers, 1964).

The concentration of organic penetrants is also important in understanding the permeability of organic vapor/barrier membrane combinations. The free volume theory can be used to explain the concentration and temperature dependency of the diffusion coefficient, characteristic of organic vapors in amorphous polymer above their glass transition temperature (Tg) (Meares, 1958, and Fujita et al., 1960). According to the free volume theory, for polymer/penetrant system the mobility of both the polymer chain segments and

diffusant molecules is primarily determined by the free volume of the system. Therefore, the concentration dependency of the diffusion coefficients for polymer/organic vapor systems can be attributed to the extreme sensitivity of the mobility of diffusant molecules and polymer chain segments to a slight change in the average free volume in the system. Also, the free volume theory can be applied to the idea of competition for sorption sites between components of a mixture. In a multi-component organic mixtures like the fragrance formulations studied, each organic component would compete for active centers within the polymer bulk phase. The sorption of one component may reduce the permeability of a second component by effectively reducing the microvoid content and diffusion pathway through the polymer. Factors such as the number of components competing to occupy the available active sites, the change in the driving force concentration, the concentration and temperature dependency of the mass transport process, and the physicochemical characteristics of the components involved in the mass transport process all contributes to the complexity of the transport properties of the fragrance volatiles in the system.

STATISTICAL ANALYSIS

The results of Simple Factorial and One-way ANOVA for each dependent (four probe compounds) are presented in Appendix D.

As indicated in Appendix D, the main effect of the three variables (film, solvent, thickening agent) is presented as a value of significance level. The significance level is the basis for deciding whether or not to reject the null hypothesis. If the observed significance level is less than 0.05 or 0.01, the null hypothesis is rejected, which means that the variable has a significant effect. For each probe compound, the results of the analysis suggest that it is the film group that has the most significant effect on the permeability of the fragrance delivery system, when compared to both the solvent group and thickening agent group, due to the less than 0.05 significance level, obtained for these groups. After deciding that the film group had a significant effect rather than solvent (Isopar) and thickening agent (Cabosil) on the permeability of the fragrance delivery system, a One-way ANOVA procedure (regression) was applied to determine the barrier properties of each film for the probe compounds.

Figures 118-120 presents graphically the relationship between the median slope values(ΔFlux/Δt) obtained from the transmission profile plots of linalool, phenethyl alcohol and benzyl acetate for the respective fragrance formulation as a function of vinyl acetate content of three EVA films evaluated. As shown, the change in rate with time (ΔFlux/Δt) for the respective probe volatiles increases linearly with an increase in vinyl acetate content.

SUMMARY AND CONCLUSIONS

The effect of membrane composition and fragrance formulation composition on the permeation of selected fragrance volatiles through an ethylene vinyl acetate(EVA) copolymer membrane based fragrance delivery system was studied by an isostatic method. The permeation rates of selected fragrance volatiles present in the fragrance formulations, to include: linalool, phenethyl alcohol, benzyl acetate and α-hexyl cinnamaldehyde, were determined as a function of time at 50°C and a constant air flow rate of 20cc/min, over a four week period.

Permeability studies were carried out at 50°C at constant carrier gas flow rate of 20cc/min to insure that the mass transport process is diffusion controlled. A three level, three variable statistical design experiment was carried out to evaluate the three variables(vinyl acetate content in the EVA copolymer, thickening agent content and dispersing solvent content of the fragrance formulations) and their effect on the permeability of fragrance probe volatiles through the fragrance delivery system membrane. A total of nine different fragrance formulations and three EVA membranes were evaluated in the experimental design.

The transmission rates of all probe volatiles through the three test polymer structures were found to be dependent on the partial pressure of the respective fragrance volatiles, which acts as the driving force for the permeation of probe compounds from the fragrance formulations. The finite concentration of the

fragrance volatiles, the constant change in the driving force concentration and composition explain the transmission profile curves obtained. From the transmission profile data, linalool showed the highest transmission rate when compared to phenethyl alcohol, benzyl acetate, and α-hexyl cinnamaldehyde . Linalool is present in the highest concentration in the fragrance formulation and has the highest vapor pressure value, which explains the observed higher transmission rate of linalool. Also, α-hexyl cinnamaldehyde was not detected in the permeated vapor stream, which can be explained by its low concentration in the fragrance formulation and high boiling point(i.e. low vapor pressure).

The global or total loss of volatiles from the fragrance formulations following termination of the permeability studies was between 45-50% for the three test membrane structures. Linalool, benzyl acetate and phenethyl alcohol showed losses greater than 85%, while α-hexyl cinnamaldehyde showed a percent loss of approximately 50% for the three test films. Statistical analysis showed that the vinyl acetate content of the test membrane was a significant variable effecting the permeation rates of fragrance volatiles through the fragrance delivery system. Film A(ethylene vinyl acetate content 6.5%) was found to have significantly lower transmission rates for the respective probe compounds when compared to Film B(vinyl acetate content 9%) and Film C(vinyl acetate content 12%).

In terms of practical importance, from the study of the permeation of the constituents of multi-component organic fragrance formulations through polymeric barrier membranes, a relative comparison of barrier properties of

polymeric packaging materials to organic penetrants of varying molecular structure can be made. Furthermore, as a results of this study, a better understanding can be achieved with respect to the effect of the chemical nature of the fragrance delivery system membrane and fragrance formulation on fragrance volatiles permeability. This knowledge can then be applied to optimize the design of a plug-in type air freshener system to provide the required end-use life.

FUTURE RESEARCH

Numerous, future studies could be conducted which could lead to an increased understanding of the mass transport properties of multi-component, organic vapor mixtures. Studies of the relationship between membrane structure and barrier properties will be important in the development and/or selection of polymeric materials for specific solutions and transport applications. In the fragrance delivery system studied, there was a constant change in the partial pressure gradient or the driving force and film structure as a function of time. Detailed studies on the effect of changes in the vinyl acetate composition of the test films may be necessary to gain a better understanding of, and make relative comparisons between, polymeric packaging materials of varying molecular structure used as barriers to organic penetrants.

APPENDICES

Appendix A

Gas Chromatograph Calibration Procedure

Equipment:

10 ml volumetric flasks with stoppers (20)

100 ml volumetric flasks with stoppers (4)

10 µl liquid sampling syringes

10 ml pipettes with automated pipette fixtures

Materials

Linalool

Phenethyl alcohol

Benzyl acetate

Alpha Hexyl Cinnamaldehyde

Methanol

Concentrations of 1,4,10,20,50, and 100 PPM (v/v) of probe compounds in methanol were used to create the calibration curves.

Procedure

In all cases, a standard curve of area response vs. Quantity injected was constructed form standard solutions of known concentration. The solutions were prepared by dissolution of known quantities of probe compounds in methanol. The following procedure was followed:

1. The volumetric flasks, pipettes and syringes were baked in an oven at 135°C for 12 hours prior to used to remove any residual solvent or permeant and cooled to room temperature.

2. The purity of the solvent is evaluated by using the gas chromatograph to ensure that there are no interfering peaks at the retention times of the probe compounds.

3. The following dilution scheme is adopted for preparing the standard solutions:

a. The 100 ml volumetric flask is partially filled with methanol.

b. 10 µl of the probe compound is added.

c. Stoppered and slightly swirled to mix.

d. The flask is filled to volumetric line with solvent.

e. The contents of the flask are mixed.

This provides the 100 PPM stock solution. From this solution, the other concentrations are obtained. For example:

(a). A 10 ml volumetric flask is partially filled with solvent using a pipette.

(b). The stock solutions swirled to ensure proper mixing.

(c). 1 ml of the stock solution is added to the 10 ml volumetric flask and filled to volumetric line with solvent.

(d). The contents of the flask are mixed.

This provides 10 PPM concentration. The other concentrations are obtained similarly.

4. The GC conditions, as indicated in the Material and Methods section were used.

5. 1 µl of samples were injected directly into the gas chromatography and the area response recorded.

The analyses were done in duplicate and average area response recorded.

6. From he density values of the respective probe compounds, the quantity injected was determined.

V/v X volume injected X ρ = mass injected

7. The average of replicate analyses was taken and the area response is plotted vs. The quantity (g) injected for each samples for the respective compounds. The values obtained, and the calibration factor are tabulated. The reciprocal of the slope of the line gives the calibration factor.

Table 11. CALIBRATION DATA FOR LINALOOL

(Retention Time = 10.64 min.)

Quantity x 10^{-9}	Area Response	Calibration factor (g/AU)
0.87	6931	
3.48	15361	
8.7	46915	2.2027×10^{-13}
17.4	78084	
43.5	200412	

Table 12. CALIBRATION DATA FOR PHENETHYL ALCOHOL

(Retention Time = 11.03 min.)

Quantity x 10^{-9}	Area Response	Calibration factor (g/AU)
1.023	8890	
4.092	19960	
10.23	56810	2.0241×10^{-13}
20.46	105564	
51.15	255381	

Table 13. CALIBRATION DATA FOR BENZYL ACETATE

(Retention Time = 12.78 min.)

Quantity x 10^{-9}	Area Response	Calibration factor (g/AU)
1.04	2619	
4.16	12597	
10.4	33338	3.1514×10^{-13}
20.8	77547	
52.0	163454	

Table 14. CALIBRATION DATA FOR α-HEXYL CINNAMALDEHYDE

(Retention time = 31.53 min.)

Quantity x 10^{-9}	Area Response	Calibration factor (g/AU)
0.95	3480	
3.86	9335	
9.5	28596	2.9644×10^{-13}
19	58913	
47.5	158656	

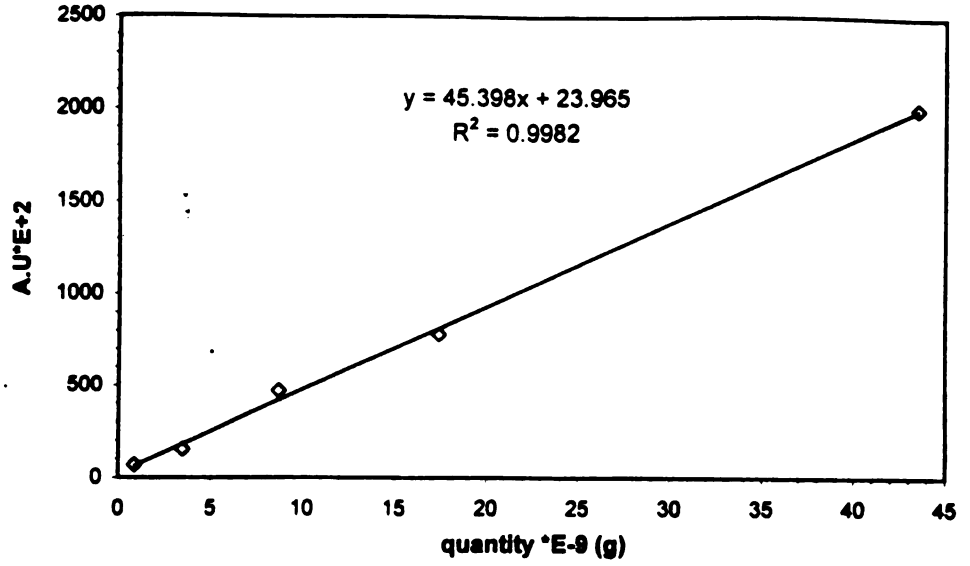


Figure 114. Calibration curve for linalool

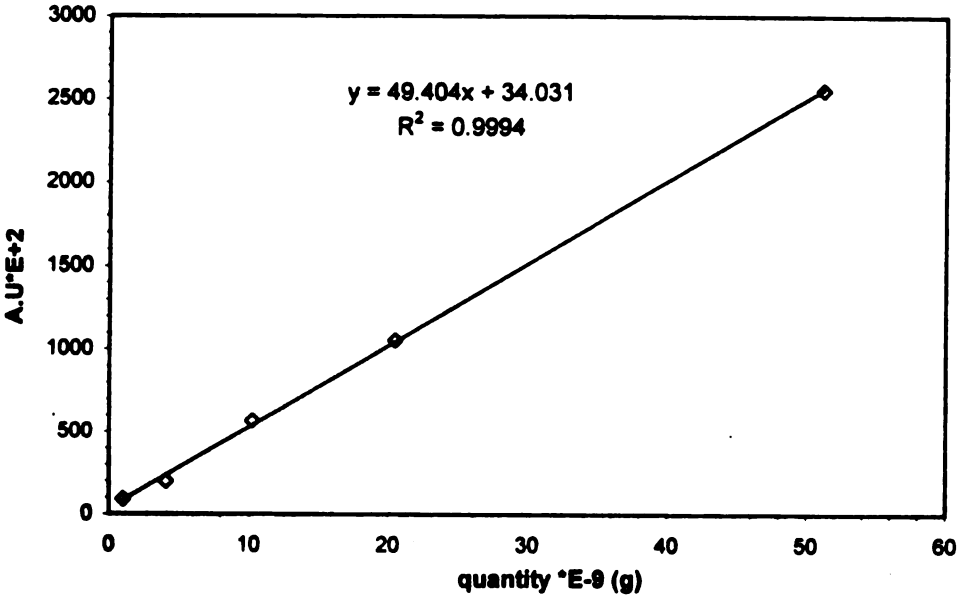


Figure 115. Calibration curve for phenethyl alcohol

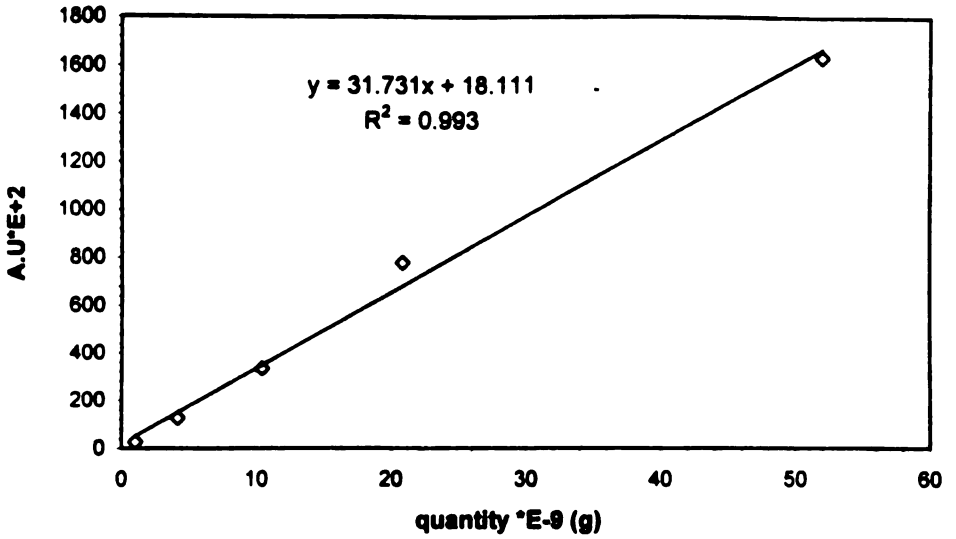


Figure 116. Calibration curve for benzyl acetate

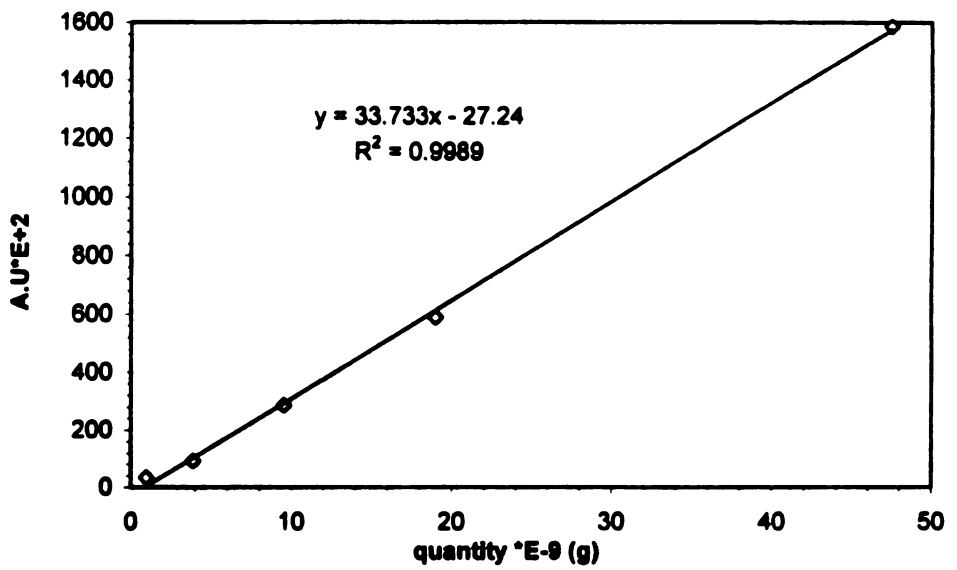


Figure 117. Calibration curve for alpha-hexyl cinnamaldehyde

Appendix B

Vapor pressure and vapor activity

One ml of Linalool, Phenethyl alcohol, Benzyl acetate, Alpha hexyl cinnamldehyde, and the fragrance formulations 1-9 were added to 25 ml septa seal vials. The vials were sealed with Teflon coated silicone septa and aluminum crimp cap. They were then allowed to equilibrate at 50°C. 200 µl of the headspace of these samples was taken and injected directly into the gas Chromatograph for quantification after an equilibration period of 5 days. Five repetitions of each vial were done, making sure to allow equilibrium at temperature before the next injection. For fragrance formulations , 50 µl of the head space was used for analysis.

The average area response is converted to concentration by the following equation:

$$\text{area response X calibration factor X } \left(\frac{1}{V\ inj}\right) = \text{conc.}$$

The saturation vapor concentration was then converted to its corresponding saturation vapor pressure using the ideal gas law: PV = nRT

The saturation vapor pressure values for the respective probe compounds are in table and the plots of temperature vs. Vapor pressure are shown in Figure respectively.

Vapor activity of the probe compound in the fragrance formulation was calculated by dividing the vapor pressure of the probe compound in the fragrance formulation at a temperature by saturation vapor pressure of the pure compound.

$$a = P / P_o$$

APPENDIX C

DATA ON THE TRANSMISSION RATES OF THE PROBE VOLATILES FROM FRAGRANCE FORMULATION 1 - 9 THROUGH FILM A, FILM B, AND FILM C AT 50°C

Table 15. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 1 through film A at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	1.4550	0.4993	0.9373	0
144	1.2504	0.3773	0.8533	0
216	1.2073	0.4211	0.7935	0
288	1.2403	0.6067	0.7653	0
360	0.6402	0.3653	0.3901	0
432	0.5579	0.4785	0.3142	0
504	0.5449	0.5549	0.2332	0
576	0.5487	0.5572	0.1934	0
648	0.3659	0.5034	0.1532	0
720	0.2986	0.3850	0.1036	0

Table 16. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 2 through film A at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	1.2564	0.3804	0.9163	0
144	1.6704	0.5898	0.9798	0
216	1.2996	0.6009	0.7658	0
288	1.0518	0.6828	0.6438	0
360	0.7265	0.6307	0.4543	0
432	0.6008	0.7933	0.4041	0
504	0.3486	0.5973	0.2269	0
576	0.1848	0.3812	0.1131	0
648	0.2038	0.4612	0.1135	0
720	0.2213	0.5292	0.1059	0

Table 17. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 3 through film A at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.2964	0.5356	0.2912	0
144	1.7353	0.4829	0.9468	0
216	1.6111	0.6201	0.8034	0
288	1.1386	0.4614	0.5441	0
360	0.8391	0.4486	0.3828	0
432	0.4358	0.4146	0.1885	0
504	0.5268	0.5929	0.1955	0
576	0.2359	0.4754	0.08944	0
648	0.1864	0.4801	0.0537	0
720	0.0562	0.2274	0.0335	0

Table 18. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 4 through film A at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.3297	0.8529	1.1849	0
144	1.3024	0.3987	0.6380	0
216	1.2253	0.5142	0.6081	0
288	0.9181	0.4796	0.4247	0
360	0.7345	0.4966	0.3233	0
432	0.5347	0.5111	0.2284	0
504	0.2822	0.5145	0.1395	0
576	0.5699	0.7243	0.1906	0
648	0.5111	0.8250	0.1524	0
720	0.0651	0.2392	0.0372	0

Table 19. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 5 through film A at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.3377	0.8163	1.1531	0
144	1.7458	0.7375	0.9511	0
216	1.2686	0.5291	0.6875	0
288	1.1918	0.5774	0.5938	0
360	0.8308	0.5090	0.4032	0
432	0.5217	0.4472	0.2393	0
504	0.7295	0.7644	0.2906	0
576	0.6950	0.5281	0.2462	0
648	0.2763	0.5873	0.1034	0
720	0.2240	0.5661	0.0659	0

Table 20. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 6 through film A at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.6060	0.9730	1.3097	0
144	1.7956	0.6024	0.9064	0
216	1.4344	0.6359	0.7525	0
288	1.1552	0.4904	0.5539	0
360	0.9429	0.4493	0.4176	0
432	0.6966	0.5345	0.3148	0
504	0.5233	0.5417	0.2307	0
576	0.4181	0.5604	0.1597	0
648	0.2187	0.5588	0.1196	0
720	0.1137	0.4976	0.0766	0

Table 21. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 7 through film A at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.9323	0.9930	1.6167	0
144	2.3981	0.9398	1.3992	0
216	1.9881	0.8268	1.1936	0
288	1.4881	0.6968	0.8144	0
360	1.3092	0.7513	0.6817	0
432	0.8151	0.6998	0.3851	0
504	0.7998	0.9198	0.3522	0
576	0.5714	0.8702	0.2392	0
648	0.3430	0.5225	0.1429	0
720	0.2078	0.5042	0.0886	0

Table 22. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 8 through film A at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.069	1.2482	1.5387	0
144	2.3270	1.0699	1.2322	0
216	1.8286	1.8683	1.0008	0
288	1.7848	0.9159	0.9211	0
360	1.2912	0.8862	0.6147	0
432	0.8169	0.6811	0.3968	0
504	0.6394	0.6603	0.2731	0
576	0.4439	0.6953	0.1869	0
648	0.2513	0.6267	0.0919	0
720	0.1415	0.5162	0.0432	0

Table 23. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 9 through film A at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.2692	1.2059	1.6046	0
144	2.4098	0.9689	1.3975	0
216	1.9533	0.7621	1.0846	0
288	2.0223	0.9766	1.0366	0
360	1.4650	0.8261	θ.7072	0
432	1.0987	0.7581	0.5380	0
504	0.8442	0.7935	0.4072	0
576	0.4620	0.7117	0.2176	0
648	0.3058	0.7380	0.1289	0
720	0.1975	0.6107	0.0688	0

Table 24. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 1 through film B at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.6188	0.7561	1.4484	0
144	2.5145	0.8372	1.3945	0
216	2.3177	0.8010	1.2295	0
288	1.8158	0.7620	0.9553	0
360	1.6620	0.9812	0.8214	0
432	1.0640	0.9843	0.5310	0
504	0.8572	1.1109	0.4289	0
576	0.4381	0.6576	0.2359	0
648	0.3140	0.6027	0.1733	0
720	0.1157	0.4589	0.0811	0

Table 25. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 2 through film B at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.9649	0.8004	1.7593	0
144	2.9274	1.0962	1.7904	0
216	2.1213	0.9020	1.2657	0
288	1.5099	0.8508	0.7648	0
360	1.2393	0.9127	0.6062	0
432	0.9713	0.9194	0.4706	0
504	0.7945	0.9297	0.4051	0
576	0.3390	0.5661	0.1639	0
648	0.2118	0.5798	0.1049	0
720	0.1697	0.5720	0.0939	0

Table 26. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 3 through film B at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.1230	0.8759	1.1671	0
144	1.9884	0.8938	1.0776	0
216	1.8298	1.0655	0.9673	0
288	1.2073	0.8723	0.7236	0
360	1.2430	0.9199	0.6574	0
432	0.7901	0.8685	0.4246	0
504	0.3713	0.7848	0.1923	0
576	0.2744	0.5637	0.1400	0
648	0.1397	0.4565	0.0761	0
720	0.0827	0.4352	0.0514	0

Table 27. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 4 through film B at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.4922	0.9881	1.2603	0
144	2.7803	0.9810	1.6924	0
216	2.0444	0.9701	1.0791	0
288	1.6547	0.8263	0.9694	0
360	1.5470	1.1065	0.7520	0
432	1.1257	0.9802	0.5434	0
504	0.8642	0.8042	0.4501	0
576	0.6176	0.7474	0.3106	0
648	0.4315	0.7189	0.2182	0
720	0.3013	0.7828	0.1599	0

Table 28. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 5 through film B at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.5826	0.7804	1.5957	0
144	2.2964	0.9879	1.2642	0
216	2.1542	0.8983	1.2768	0
288	1.4258	0.8479	0.7326	0
360	1.5624	1.0702	0.8234	0
432	1.0466	0.8343	0.5598	0
504	0.5618	0.8119	0.3075	0
576	0.4332	0.7609	0.2074	0
648	0.3011	0.6952	0.1337	0
720	0.1532	0.6128	0.0771	0

Table 29. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 6 through film B at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.6820	1.2169	1.9547	0
144	2.7266	1.0068	1.7162	0
216	2.2795	0.9546	1.2687	0
288	1.5436	0.8284	0.8286	0
360	1.4305	1.0670	0.7853	0
432	0.9042	0.8568	0.4807	0
504	0.5217	0.7776	0.2628	0
576	0.3597	0.6787	0.1828	0
648	0.1444	0.5624	0.0799	0
720	0.0938	0.5812	0.0491	0

Table 30. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 7 through film B at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.2675	1.1575	1.8862	0
144	2.7973	1.0763	1.6083	0
216	2.0816	1.1275	1.1756	0
288	1.4301	0.9231	0.7942	0
360	0.9947	1.0284	0.4775	0
432	0.4679	0.7543	0.2389	0
504	0.3161	0.6948	0.1520	0
576	0.5612	0.6488	0.0699	0
648	0.1189	0.6109	0.0574	0
720	0.0643	0.5376	0.0362	0

Table 31. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 8 through film B at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.5354	1.2401	1.7699	0
144	1.7325	1.0302	1.4669	0
216	1.9545	0.8257	1.1456	0
288	1.8645	0.9807	1.0707	0
360	1.2412	0.8549	0.6645	0
432	1.1164	0.9716	0.5981	0
504	0.5987	0.7965	0.3170	0
576	0.3446	0.6654	0.1934	0
648	0.3194	0.7210	0.1554	0
720	0.1934	0.6352	0.0963	0

Table 32. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 9 through film B at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.2999	1.1334	1.8565	0
144	2.8553	0.9741	1.7866	0
216	2.3657	1.0362	1.3604	0
288	1.8124	0.9697	0.9719	0
360	1.4690	0.9640	0.8058	0
432	1.0203	0.8967	0.4967	0
504	0.7841	0.9239	0.3927	0
576	0.5753	0.8582	0.2799	0
648	0.2321	0.6436	0.1220	0
720	0.1588	0.6860	0.0753	0

Table 33. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 1 through film C at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.5185	1.0536	1.9594	0
144	3.3461	1.2100	1.8157	0
216	2.0232	0.8318	1.1202	0
288	1.5165	0.8353	0.8145	0
360	1.1638	0.9701	0.6132	0
432	0.8300	0.9191	0.4207	0
504	0.4582	0.7608	0.2639	0
576	0.2119	0.5215	0.1278	0
648	0.1317	0.5828	0.0799	0
720	0.0596	0.4124	0.0382	0

Table 34. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 2 through film C at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.6904	1.2454	2.2206	0
144	2.5171	1.1017	1.5864	0
216	2.0142	1.0521	1.2102	0
288	1.2623	0.9264	0.6647	0
360	0.8720	0.8781	0.4612	0
432	0.5071	0.7297	0.2791	0
504	0.3183	0.7232	0.1696	0
576	0.1649	0.6420	0.1044	0
648	0.0850	0.4526	0.0660	0
720	0.0410	0.3819	0.0283	0

Table 35. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 3 through film C at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	4.0343	1.2336	2.4080	0
144	3.3757	1.2162	2.0313	0
216	2.4026	1.1867	1.3710	0
288	1.6284	0.9958	0.8750	0
360	1.3392	1.0750	0.6859	0
432	0.6921	0.7668	0.3794	0
504	0.4899	0.7899	0.2608	0
576	0.1976	0.5119	0.1255	0
648	0.1120	0.4647	0.0726	0
720	0.0631	0.4323	0.0440	0

Table 36. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 4 through film C at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.7183	1.1415	1.9071	0
144	3.1424	1.0688	1.7064	0
216	2.4074	0.9669	1.2559	0
288	1.8283	1.0379	0.9506	0
360	1.2352	0.8202	0.6232	0
432	0.9304	0.9495	0.4570	0
504	0.4782	0.6941	0.2687	0
576	0.2583	0.6527	0.1587	0
648	0.1757	0.5643	0.1026	0
720	0.0799	0.5265	0.0485	0

Table 37. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 5 through film C at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.2000	0.9572	1.6889	0
144	2.3113	0.8499	1.2986	0
216	2.0746	0.9010	1.0394	0
288	1.6570	0.8593	0.8435	0
360	0.7807	0.6211	0.4077	0
432	0.6507	0.6927	0.3178	0
504	0.2658	0.5222	0.1520	0
576	0.1634	0.4956	0.0879	0
648	0.0882	0.4115	0.0474	0
720	0.0445	0.3080	0.0293	0

Table 38. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 6 through film C at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.7368	0.9971	1.5543	0
144	2.2818	0.9531	1.2966	0
216	1.7137	0.8681	0.9108	0
288	1.4347	1.0034	0.6903	0
360	0.7017	0.7919	0.3414	0
432	0.2820	0.5591	0.1569	0
504	0.1838	0.6236	0.0979	0
576	0.0672	0.4616	0.0418	0
648	0.0406	0.3768	0.0217	0
720	0.0137	0.2624	0	0

Table 39. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 7 through film C at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.3643	1.0748	1.7388	0
144	2.3514	0.8499	1.3146	0
216	1.9420	0.8033	1.0031	0
288	1.5437	0.8463	0.7593	0
360	1.0653	0.8446	0.5184	0
432	0.6210	0.6641	0.3051	0
504	0.3670	0.6815	0.1963	0
576	0.2338	0.6914	0.1199	0
648	0.1065	0.4834	0.0597	0
720	0.0741	0.4244	0.0368	0

Table 40. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 8 through film C at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	2.9128	0.9446	1.4785	0
144	2.5386	0.8723	1.3599	0
216	1.9743	0.8017	0.9586	0
288	1.2417	0.6314	0.6107	0
360	1.1273	0.8151	0.5406	0
432	0.7540	0.8133	0.3679	0
504	0.4442	0.6777	0.2103	0
576	0.2842	0.7276	0.1310	0
648	0.1358	0.5973	0.0708	0
720	0.0845	0.3712	0.0372	0

Table 41. Flux (g/day) X E-2 as a function of run time for probe compounds from fragrance formulation 9 through film C at a cell flow rate of 20 cc/min at 50°C

Hours	Linalool	Phenethyl alcohol	Benzyl acetate	α-Hexyl cinnamaldehyde
72	3.0701	1.2779	1.6235	0
144	1.8263	0.7999	1.0848	0
216	1.3138	0.6097	0.7478	0
288	1.0272	0.6493	0.5842	0
360	0.7873	0.6444	0.4341	0
432	0.6031	0.6865	0.3313	0
504	0.3046	0.5471	0.1821	0
576	0.1460	0.3866	0.1016	0
648	0.0736	0.3663	0.0510	0
720	0.0439	0.2992	0.0297	0

APPENDIX D.

STATISTICAL ANALYSIS

Table 42. Slope of transmission profile curve

Variable No	Linalool	Phenethyl Alcohol	Benzyl Acetate
1	-0.1337	0.003	-0.1035
2	-0.166	-0.0046	-0.1086
3	-0.2431	-0.0191	-0.1356
4	-0.1897	-0.0083	-0.1016
5	-0.2053	-0.017	-0.1511
6	-0.2466	-0.0286	-0.1251
7	-0.2942	-0.0393	-0.1758
8	-0.3143	-0.0699	-0.1677
9	-0.3256	-0.0475	-0.1763
10	-0.3077	-0.0241	-0.1678
11	-0.3363	-0.0431	-0.2031
12	-0.2548	-0.0597	-0.1395
13	-0.2793	-0.0302	-0.1566
14	-0.2865	-0.0278	-0.1725
15	-0.3862	-0.0641	-0.2184
16	-0.3579	-0.0739	-0.2133
17	-0.3578	-0.0536	-0.1899
18	-0.3583	-0.0451	-0.2129
19	-0.4012	-0.0726	-0.2197
20	-0.3777	-0.0917	-0.2277
21	-0.4465	-0.1016	-0.2628
22	-0.4158	-0.0699	-0.2161
23	-0.3504	-0.072	-0.1856
24	-0.3188	-0.0852	-0.1771
25	-0.3506	-0.0585	-0.1844
26	-0.3242	-0.0444	-0.1667
27	-0.2891	-0.0801	-0.1578

Table 43. RESULTS OF ANALYSIS OF VARIANCE

Source Of Variation	Sig Of F		
	Linalool	Phenethyl alcohol	Benzyl acetate
Main Effects	.007	.001	.014
Film Group	.001	.000	.002
Solvent Group	.687	.067	.787
Thickening Agent Group	.246	.176	.332
2-Way-Interactions	.157	.109	.182
Film And Solvent Group	.425	.7334	.891
Film And Thickening Agent Group	.029	.018	.025
Solvent And Thickening Agent Group	.868	.4336	.814

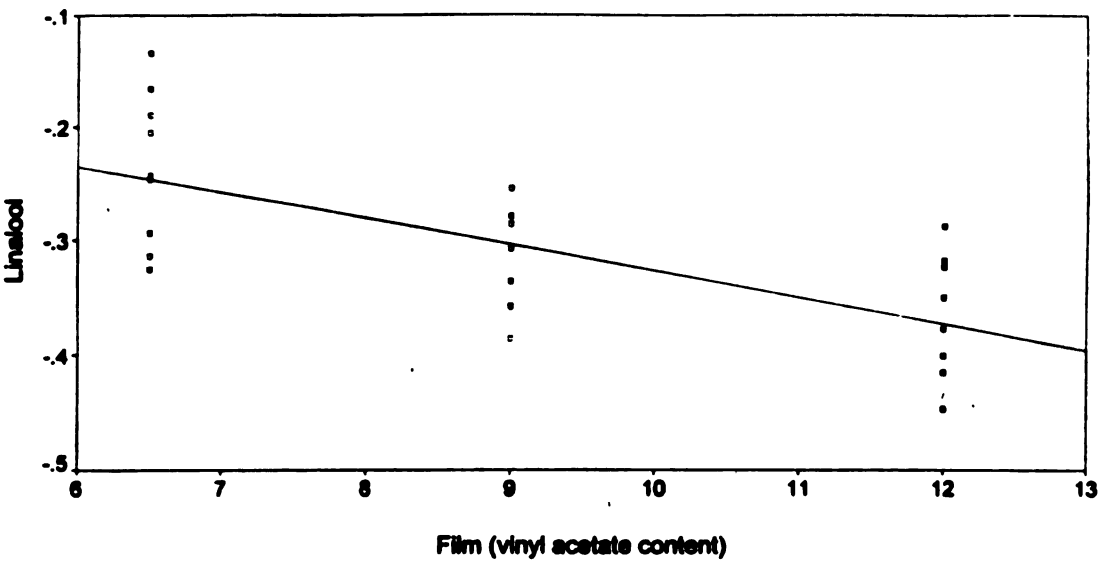


Figure 118. Comparsion of barrier characteristics of film content (linalool)

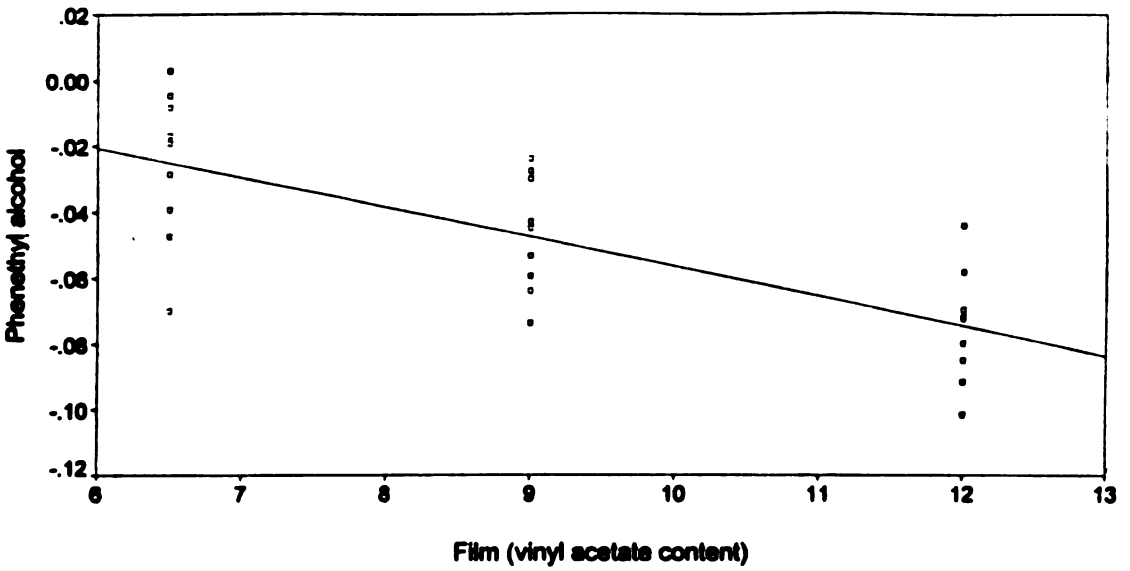


Figure 119. Comparsion of barrier characteristics of film content (phenethyl alcohol)

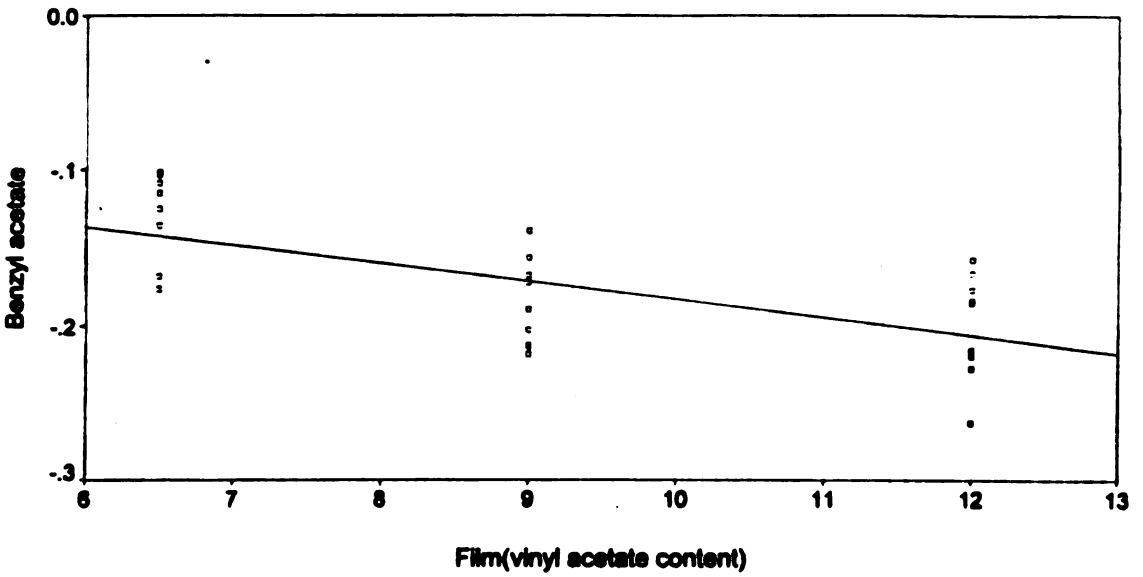


Figure 120. Comparsion of barrier characteristics of film content (benzyl acetate)

APPENDIX E

Melt profile of film samples

The melt profile of film samples film A(6.5% vinyl acetate content), film B(9% vinyl acetate content) and film C(12% vinyl acetate content) were determined by Differential Scanning Calorimetry (DSC) analysis. Analysis was carried out on a Dupon 9900 computer/thermal analyzer. The melt profile of the films are shown in Figures , and the melt temperatures of the films are summarized below:

Film sample	Heat of fusion(J/g)	Melt temperature(°C)	Percent crystallinity
Film A	97.17	102.35	33.93
Film B	89.54	102.98	331.27
Film C	78.48	94.47	27.39

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