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DEVELOPMENT OF A SIMULATION MODEL
FOR SHELF-LIFE PREDICTION OF PACKAGED
MODEL LIPID FOOD SYSTEMS

presented by

Kiyonori Kogashiwa

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of the requirements for

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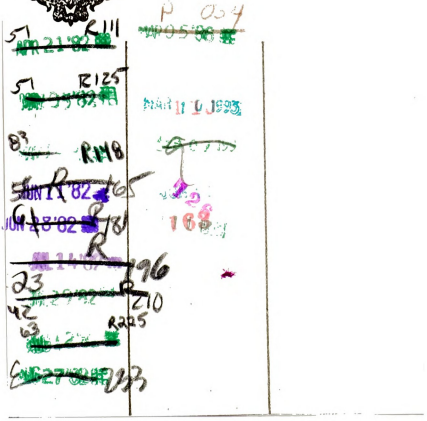

DEVELOPMENT OF A SIMULATION MODEL FOR SHELF-LIFE PREDICTION OF PACKAGED MODEL LIPID FOOD SYSTEMS

By

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ABSTRACT

DEVELOPMENT OF A SIMULATION MODEL
FOR SHELF-LIFE PREDICTION OF PACKAGED
MODEL LIPID FOOD SYSTEMS

By

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A simulation model was developed which considered the influence of both package permeability to oxygen and the product oxidation rate on product quality. Relative humidity and temperature were held constant and the package permeability and product oxidation rates were determined as a function of oxygen partial pressure within the package. A computer-aided simulation model was developed, based on these kinetic data, to predict the extent of oxygen uptake by the food product, under selected package storage conditions.

The oxygen uptake levels by the model food system, obtained from experiment and by calculation were compared and a fair agreement was obtained. Knowledge of the acceptable level of oxygen uptake of the product and the package permeability can be used for an estimate of product shelf-life.

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INTRODUCTION

Packages affect the quality of food products, mainly by controlling moisture, oxygen and light transfer. In addition, packaging provides protection from biological attack as well as providing protection of the product in the mechanical environment. Package selection can therefore determine or influence the shelf-life of a food product. The most desirable package would maintain product quality for the required shelf-life period most economically. Traditionally, shelf-life has been determined by storage tests, carried out under either real or accelerated storage conditions. Storage tests under actual environmental conditions of time, temperature and relative humidity, are more accurate, but time-consuming and costly. The accelerated storage tests would be less time-consuming and less costly. However, prediction errors may be introduced.

In comparing these traditional techniques for shelf-life determination, shelf-life prediction by calculation, based on a simulation model of environment-package-product interaction, has a number of advantages. For example, this technique is less costly and much less time-consuming. In some applications, the calculation method was reported to be even more accurate than the accelerated

test method (Clifford et al., 1977). It may also be an advantage that the calculation technique expresses shelf-life prediction mathematically, especially with the recent development of highly mathematical, statistical, decision-making systems.

For example, the factors which must be taken into consideration for package design are shown in Figure 1 (Gyeszly, 1980). As shown, the total cost of the package system should be minimized by optimizing the package design. Package optimization can be obtained by mathematical processing, such as linear or non-linear programming. While storage stability studies carried out under real time-temperature conditions or under accelerated conditions might be applied in such model building, it would require that an extensive number of tests be carried out, due to the inflexibility of such studies to variable change. As described above, a major advantage of computer simulation is that it allows for a rapid assessment of the influence of environmental change in product or package conditions.

This study will deal with the interaction of oxygen permeation through a package and oxygen consumption by a food product. Specifically, the factors: Time, External Environment, Permeability of the Package Material, Permeability of the Package, Permeation Rate Through the Package Wall, Internal Environment, Interaction Between the Product and Components of Headspace, and Quality of Product (c.f. Figure 1), will be considered. Several assumptions have been made in this study concerning shelf-life prediction,

as the critical acceptable quality level for the model food system was not determined.

The oxidation rate plays an important role in developing a simulation model for lipid-containing food products, and thus, it is necessary to determine the rate of lipid oxidation under well defined storage environmental conditions. Rate data were therefore obtained in a system, where temperature and relative humidity were held constant and the rate of oxidation was monitored as a function of continuously changing oxygen partial pressure. A number of assumptions were also made for the simulation model. Computed results were then compared to the experimental data.

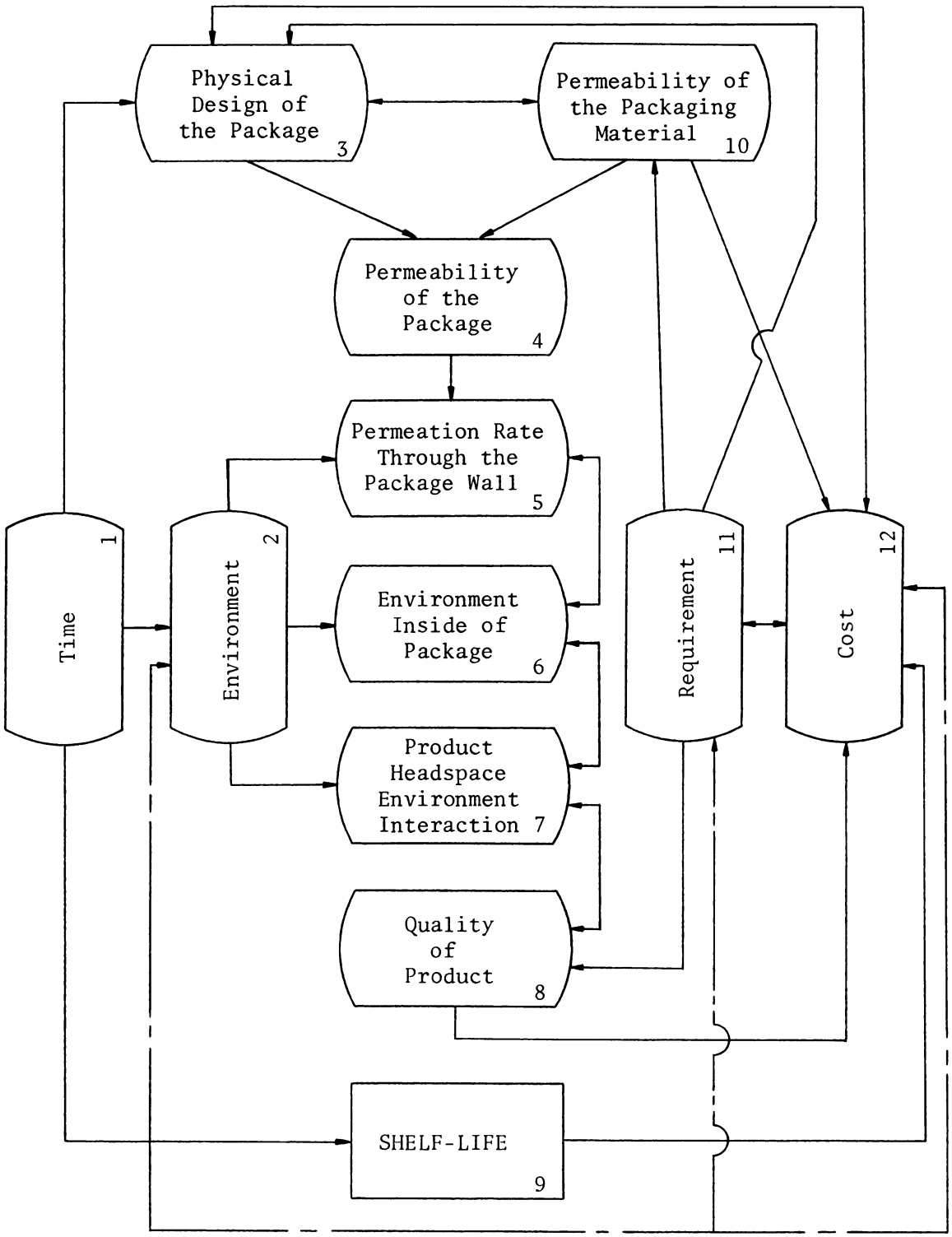


Figure 1. Factors for the Package System Design.

LITERATURE REVIEW

Shelf-life prediction has been conducted by accelerated storage tests or through calculation based on physical or chemical properties of the product and package. Clifford et al. (1977) compared the shelf-life prediction by accelerated storage tests to that of the calculation method and evaluated the agreement with experimental data obtained from storage under ambient conditions. They indicated that the calculation method not only required much less time and resources, but was also more accurate. The calculation method has been used for about forty years; Felt et al. (1945) used the linear relationship between the permeation rate of water vapor and the water vapor partial pressure difference to predict the shelf-life of a cereal product. In this study, shelf-life was determined solely by the moisture content of the product. Numerous studies have since been reported in the area of product storage stability and shelf-life prediction, following the publication of this work.

In this regard, emphasis has been focused primarily on lipid oxidation of freeze-dried foodstuffs. Karel (1967) has reviewed the theoretical aspects of lipid oxidation, a principal deteriorative mechanism in the storage stability of dehydrated food products. Quast and Karel (1971)

determined the rate of oxygen uptake and the effective diffusivity of oxygen in some dehydrated food products. Maloney et al. (1966) studied the autoxidation of methyl linoleate as a function of water activity. Labuza (1971) reported on the effects of both water activity and glycerol content on the oxidation of lipids. Zirlin and Karel (1969) described the oxidation of a freeze-dried model system consisting of methyl linoleate and gelatin. Cabral et al. (1979) determined the performance of various packages for potato chips, a very oxygen and moisture sensitive product, in terms of selected chemical and physical properties, such as peroxide value, hexanal formation, and texture evaluation. Martinez and Labuza (1968) studied several deteriorative mechanisms affecting the quality of freeze-dried salmon, such as lipid oxidation and non-enzymatic browning. Tuomy and Walker (1970) dealt with the effects of storage time, moisture level, and headspace oxygen concentration on the quality of a dehydrated egg mix.

The storage stability studies have also been extended to include the development of simulation models for the prediction of product shelf-life. Karel (1967, 1974) and his co-workers (Karel, Mizrahi and Labuza, 1971; Quast and Karel, 1972a, 1972d; Quast, Karel and Rand, 1972b; Labuza, Mizrahi and Karel, 1972) used computer-aided mathematical models for the evaluation of package requirements. These models were based on a combination of a kinetic equation of deterioration (Marcuse and Fredriksson, 1968; Labuza et al., 1969) and the permeability characteristics

of packages. The resultant differential equations were solved by the use of a computer. The computer-aided iteration technique enabled the prediction of deterioration of a product under defined package requirements and defined storage conditions. The procedure was applied to several deterioration mechanisms of a food product, such as lipid oxidation in dehydrated shrimp (Simon et al., 1971) and potato chips (Quast et al., 1972a, 1972b), and non-enzymatic browning in dehydrated cabbage (Mizrahi, Labuza and Karel, 1970a, 1970b) and dehydrated tomatoes (Mizrahi and Karel, 1977). Singh (1974) applied a similar procedure to Vitamin C degradation in a liquid food product. Further, Quast, Karel and Rand (1972b) introduced a new model for predicting oxidative deterioration to include the effect of equilibrium relative humidity. In this study, to better simulate actual storage conditions, the rate of oxidation was determined as a function of oxygen partial pressure, extent of oxidation, and equilibrium relative humidity. They reported that the experimental and predicted values agreed reasonably well.

Henig et al. (1973) applied the computer-aided simulation model for the permeation-respiration interaction in packaged bananas. The study predicted equilibrium oxygen and carbon dioxide concentrations in the package headspace. The calculated result was validated by experimental test. In addition, Henig and Gilbert (1975) have employed this technique to packaged tomatoes.

In all the studies described above, the predictions were made under constant temperature conditions. However,

Kwolek and Bookwalter (1971) suggested that the quality change can be expressed as a function of storage temperature. They applied their proposed technique to published data and reported exceptional agreement between the predicted and experimental results. Labuza (1979) reviewed the mathematical models for fluctuating temperature sequences. Further, he developed equations to calculate the quality change in a product undergoing either random, sine, or square wave time-temperature distribution for both zero and first order reactions.

As reviewed, mathematical models have been employed for simulating environmental factors, as well as for product properties and package properties, in order to predict the quality index change of various products.

THEORETICAL BACKGROUND

Mechanism in Lipid Oxidation

Oxidation of unsaturated fatty acids proceeds through a free-radical chain mechanism involving initiation, propagation and termination steps (Gray, 1978). These can be formulated as:

Step 1. $RH + O_2 \longrightarrow R\cdot + \cdot OOH$ (Initiation)

Step 2. $R\cdot + O_2 \longrightarrow ROO\cdot$

$ROO\cdot + RH \longrightarrow ROOH + R\cdot$ (Propagation)

Step 3. $R\cdot + R\cdot \longrightarrow RR$

$R\cdot + ROO\cdot \longrightarrow ROOR$

$ROO\cdot + ROO\cdot \longrightarrow ROOR + O_2$ (Termination)

where: RH = unsaturated fatty acid,

R· = alkyl radical,

ROO· = peroxy radical,

ROOH = hydroperoxide.

As presented above, the degree of lipid deterioration, as a result of oxidation, can be determined by the concentration of hydroperoxide (i.e. peroxide value), the major reaction product formed during the initial stages of oxidation.

Further, there is a stoichiometric relationship between the peroxide value and oxygen uptake by an unsaturated fatty acid (lipid). If all of the oxygen, which was consumed during product oxidation, is incorporated into a hydroperoxide, each molar equivalent of peroxide corresponds to half a mole of oxygen uptake by the product. Consequently, a peroxide value of one corresponds, stoichiometrically, to an oxygen uptake of 11.2 μl O_2 (STP)/g dry product [or 0.5 μ mole O_2 (STP)/g dry product] (Quast and Karel, 1972a). Therefore, it is theoretically possible to determine the degree of oxidative deterioration by monitoring oxygen uptake by a lipid-containing food product. Assumption 1, in SIMULATION MODELING, was made based on this relationship.

Oxidation Rate

The rate of lipid oxidation has been shown by Marcuse and Fredriksson (1968) and Labuza et al. (1969) to be dependent on the oxygen partial pressure, moisture content, and the extent of oxidation of product.

The classic form for expressing the rate of lipid oxidation, as developed by Bollard (1949), is shown below, and considers the rate of oxidation as a function of only oxygen partial pressure.

$$\frac{dVO_2}{dt} = \frac{1}{C + D/PO_2} \qquad (1)$$

where: VO_2 = volume of oxygen uptake by the food,

C, D = constants found by data curve fitting,

PO_2 = oxygen partial pressure within the package.

More recently, Quast and Karel (1972b) developed an equation for expressing the rate of oxidation as a function of all three aforementioned variables. This relationship is given by Equation (2).

$$\frac{dE}{dt} = \frac{K_3 + K_4 E}{RH^{1/2}} + E \frac{PO_2}{K_1 + K_2 PO_2} \qquad (2)$$

where: E = extent of oxidation expressed as microliters of oxygen uptake per g of product [μl O_2 (STP)/g product],

RH = equilibrium relative humidity within the package,

PO_2 = oxygen partial pressure (atm.) within the package,

K_1, K_2, K_3, K_4 = constants found by data curve fitting.

Permeation Rate

The driving force for gases and vapors penetrating or diffusing through permeable packages is the concentration difference between the internal and external environment of the package. The rate of transfer of a diffusing substance can be expressed mathematically by Equations (3), (4), commonly referred to as Fick's first and second laws of diffusion.

$$F = -D \frac{\partial C}{\partial X} \qquad (3)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} \qquad (4)$$

where: F = flux (the rate of transfer of diffusing substance per unit area),

D = diffusion coefficient,

C = concentration of diffusing substance,

t = time,

X = space coordinate measured normal to the section.

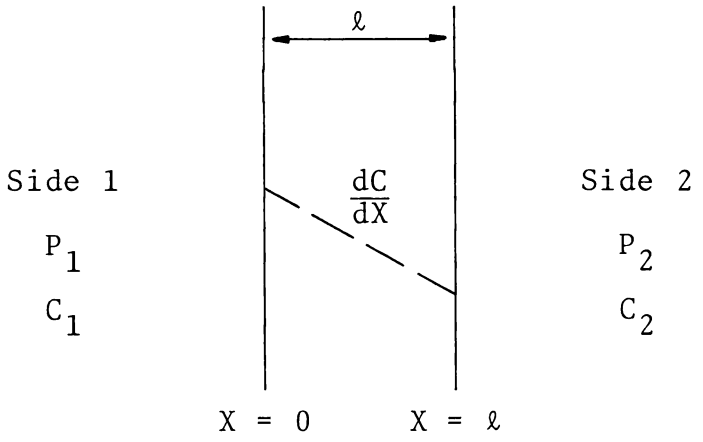
The boundary conditions for Fick's first and second laws of diffusion can be illustrated, as shown in Figure 2. In this analysis, it is assumed that at steady state, the concentration of gas or vapor remains constant at all points of the sheet. Therefore, the diffusion Equation (4) reduces to:

$$\frac{d^2C}{dX^2} = 0 \qquad (5)$$

Assuming D is constant, Equation (6) is then obtained by integrating Equation (5) twice with respect to X, and introducing the boundary conditions, X = 0 and X = ℓ.

$$\frac{C-C_1}{C_2-C_1} = \frac{X}{\ell} \qquad (6)$$

where: ℓ = film thickness.



where: C_1, C_2 = concentration of gas or vapor on the surfaces X = 0, X = ℓ, respectively ($C_1 > C_2$),

P_1, P_2 = partial pressure of gas or vapor at the surfaces X = 0, X = ℓ, respectively ($P_1 > P_2$),

ℓ = film thickness.

Figure 2. Boundary Conditions for Gas Permeation of Plastic Film.

Equations (3) and (6) can be combined to give Equation (7):

$$F = -D \frac{dC}{dX} = D \frac{C_1 - C_2}{\ell} \quad (C_1 > C_2) \tag{7}$$

Further, from the Henry's law relationship, Equation (8), the rate of transfer of a diffusing species can be expressed in terms of the permeant partial pressure at the surface X = 0 and X = ℓ, Equation (8a).

$$C = S \cdot P \tag{8}$$

$$F = D \cdot S \frac{P_1 - P_2}{\ell} \quad (P_1 > P_2) \tag{8a}$$

where: S = solubility.

By definition, the permeability constant ($\bar{P}$) = D·S. Therefore,

$$F = \bar{P} \frac{P_1 - P_2}{\ell} \tag{9}$$

where: $(P_1 > P_2)$.

The relationship between the permeation rate through the defined film and the permeability constant ($\bar{P}$) can be expressed by the following equation:

$$P = \frac{Q}{t} = \frac{\bar{P} \cdot A}{\ell} (P_1 - P_2) = Pp\ (P_1 - P_2) \tag{10}$$

where: Q = quantity of diffusing substance transferring through the film,

t = time,

A = area,

P = film permeation rate (= $\frac{Q}{t}$ by definition),

$$Pp = \text{package permeability } (= \frac{\bar{P} \cdot A}{\ell}).$$

In this study, Equation (10) was used for the simulation modeling, with $\bar{P} \cdot A/\ell$ being defined as the package permeability. A more detailed discussion of these and other diffusion coefficients is given by Crank and Park (1963) and Talwar (1974).

SIMULATION MODELING

Assumptions

The following assumptions were made prior to the model building.

Assumption 1: The amount of oxygen consumed by a model lipid food system is directly proportional to the degree or extent of lipid oxidation (Quast and Karel, 1972a).

Validity of Assumption 1: As previously discussed, theoretically a linear relationship between oxygen uptake and the extent of lipid oxidation is assumed in the early stage of oxidation.

Assumption 2: The rate of oxidation can be expressed mathematically as a function of oxygen partial pressure.

Validity of Assumption 2: The classical form of the oxidation rate equation is shown in Equation (1). In this study, the simplest form,

$$RO = m \cdot PO_2 + b,$$

was employed which was based on the results of the oxidation rate equation study,

where: RO = oxidation rate,

PO_2 = oxygen partial pressure within the package,

m, b = constants experimentally obtained.

Assumption 3: Oxygen permeation rate of the package can be expressed mathematically as follows:

$$OP = Pp\ (P_1 - P_2)$$

where: OP = oxygen permeation rate of the package,

Pp = package permeability,

P_1, P_2 = oxygen partial pressure outside and inside the package, respectively.

Validity of Assumption 3: The equation is widely used, proven, and accepted in the literature.

Assumption 4: The headspace volume change is only due to oxygen volume change. (The effect of nitrogen permeation on the headspace volume is ignored.)

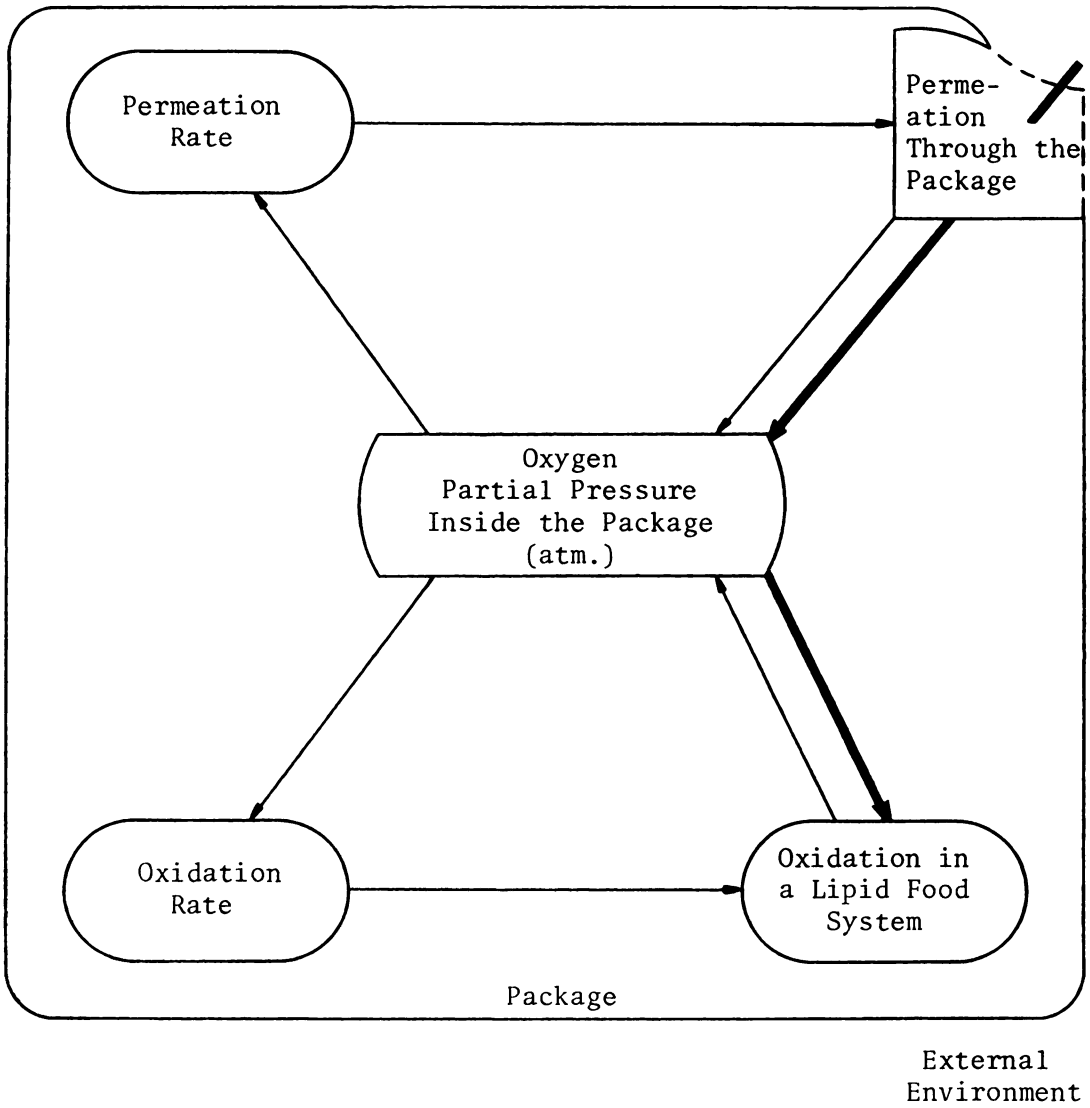
Validity of Assumption 4: The validity of this assumption will be further discussed.

Assumption 5: There is no interaction between packaging material and a product.

Validity of Assumption 5: Since both selected films (Mylar and Saran) have good oil resistance properties (Agranoff, 1977), it can be assumed that the interaction is too low to influence the oxygen permeability of these films within the experimental conditions of this study.

Simulation Model

The relationship between oxygen consumption and oxygen permeation can be represented schematically as follows (Figure 3):



Where: → represents influence on,

⟹ represents the flow of oxygen.

Figure 3. Relationship Between Oxygen Consumption and Oxygen Permeation.

As shown in Figure 3, the various factors interact with each other and their relationship is time-dependent. Therefore, the system can be simulated, assuming the variables remain constant during a short period of time (this is referred to as a time-step). Based on this assumption, the system can be simulated discretely by an iteration technique. The resultant simulation model is shown below in sequential order.

Step 1: Quantity of oxygen consumed by a food system during a time-step (Δt) can be calculated as follows:

$$OC_{\Delta t} = [a \cdot PO_2(t) + b] \cdot \Delta t$$

where: $OC_{\Delta t}$ = oxygen consumption during Δt,

PO_2 = oxygen partial pressure within the package at time = t,

a, b = experimentally obtained constants,

Δt = time-step.

Step 2: Quantity of oxygen permeated into the package headspace through the package wall during a time-step (Δt) can be calculated as follows:

$$OP_{\Delta t} = Pp \cdot [0.208 - PO_2(t)] \cdot \Delta t$$

where: $OP_{\Delta t}$ = quantity of oxygen permeated through the package wall during Δt,

Pp = package permeability,

$PO_2(t)$ = oxygen partial pressure within the package at time = t.

Step 3: Change in the absolute quantity of oxygen within the package during a time-step (Δt) is as follows:

$$O_{\Delta t} = OP_{\Delta t} - OC_{\Delta t}^*$$

where: $O_{\Delta t}$ = change in the absolute quantity of oxygen within the package during a time-step.

*Notation (-) is dependent on the direction of the oxygen flow.

Step 4: Quantity of oxygen within the package at time $(t + \Delta t)$ can be expressed as follows:

$$TO(t + \Delta t) = TO(t) + O_{\Delta t}$$

where: $TO(t + \Delta t)$ = quantity of oxygen within the package at time, $t + \Delta t$,

$TO(t)$ = quantity of oxygen within the package at time, t.

Step 5: Headspace volume at $t + \Delta t$ is expressed as follows:

$$V(t + \Delta t) = V(t) + O_{\Delta t}$$

where: $V(t + \Delta t)$ = headspace volume within the package at time, $t + \Delta t$,

$V(t)$ = headspace volume within the package at time, t.

Step 6: Oxygen partial pressure within the package at time, $t + \Delta t$ is expressed as follows:

$$PO_2(t + \Delta t) = \frac{TO(t + \Delta t)}{V(t + \Delta t)}$$

where: $PO_2(t + \Delta t)$ = oxygen partial pressure within the package at time, $t + \Delta t$.

A computer program was written based on the above simulation model. Calculations were performed following Steps 1 to 6 for each package, using experimentally obtained data.

MATERIALS AND METHODS

Preparation of Model Lipid Food System

The major components used in preparation of the model food system were: soybean oil (Hain Food Co., Inc., Los Angeles, California) and carboxymethyl cellulose (CMC) (Hercules Incorporated, Wilmington, Delaware; Type 7HF). Tween 20 (polyoxyethylene sorbitan monooleate, Fisher Scientific Co., Fairlawn, New Jersey) was used as an emulsifying agent.

Soybean oil, 30 g, was mixed with CMC, 3 g, Tween 20, 1.5 g, and phosphate buffer of pH 6.0, 600 g. The resultant slurry was mixed for 1 minute in a laboratory blender (Waring Products Division, Dynamics Corporation, New Hartford, Connecticut). Two hundred grams (200 g) of the mixed slurry was then transferred to an aluminum pan (O.D. = 20 cm), and the sample was dehydrated by freeze-drying. The sample remained in the freeze dryer (Virtis Model II, Repp Industries Inc., Gardiner, New York) for 3 days. Operating conditions for freeze-drying were as follows: glycol temperature, -120°F; platen temperature, 100°F; vacuum, 5 μ.

Freeze-dried samples were stored at -20°C prior to usage. Blank samples, which served as positive controls, were prepared in a similar manner, except that no soybean oil was added to the control samples.

For determination of the composition of the freeze-dried model food system, the percent of oil was determined by the official method of A.O.A.C. 24.005. The water content was determined by drying the sample to constant weight in a conventional oven (50°C), and the percentage of the CMC, Tween 20 and buffer salt was determined based on the slurry composition. The resultant composition is presented in Table 11 (Appendix A).

To determine whether the model food system had a homogeneous distribution of lipid, a sample was cut into four (4) pieces and the respective portions were weighed. The oil in each of the portions was extracted by the standard procedure (A.O.A.C. 24.005) and weighed. As shown in Table 12 (Appendix A), the oil appears to be fairly uniformly distributed throughout the freeze-dried sample.

Oxidation Rate Studies

Package Design and Structure. The oxidation rate studies were carried out using the following flexible package: Reynolds FLEX-CAN Retort Pouch (polyester/aluminum/-polypropylene laminate film). This package design and structure was used for the rate studies, since for all intents and purposes the pouch can be assumed to be impermeable. Prior to usage, a gas sampling septum was provided by application

of a globe of silicon rubber (General Electric Company, Waterford, New York) to the pouch surface, and it was cured overnight at 25°C.

Water Activity Control. The water activity of the freeze-dried model system was carefully controlled by equilibration over a saturated salt solution (potassium nitrite; RH of 48% at 25°C) (Greenspan, 1977). In order to prevent potential oxidation during the equilibration period, the following procedure was employed. A sample was charged into the FLEX-CAN Retort Pouch, and the pouch was placed in a vacuum desiccator which contained the saturated salt solution. The air within the desiccator was evacuated by a vacuum pump and replaced by pure nitrogen. The operation was repeated three times. The samples in the open pouches were then allowed to equilibrate for 3 days under nitrogen, at a temperature of 25°C, and a RH of 48%. The equilibration maintained the model lipid food system at an equilibrium RH of 15% at 50°C, the temperature at which the oxidation studies were conducted.

Temperature Control. Oxidation rate studies were carried out at 50°C. Preliminary studies showed that the temperature within the pouch was 50°C, when the pouch was placed in a constant temperature water bath, maintained at 50±1°C.

Monitoring Oxygen Consumption Levels. The model freeze-dried food system (approximately 15 g), equilibrated to defined water activity, was weighed and added to the FLEX-CAN Retort Pouch (flat dimension of 4¼" x 7").

Six pouch samples containing the model lipid system (Samples, No. 1 to 6, in Table 1) and a pouch containing the positive control (blank in Table 1) were employed in this study. The pouches were then sealed and placed in a constant temperature bath, maintained at 50±1°C. At predetermined time intervals, the pouches were removed from the constant temperature bath, and an aliquot of headspace gas within the FLEX-CAN Pouch was removed with a gas tight syringe through the silicon rubber septum. The gas samples were injected directly into a gas chromatograph and the concentration of oxygen in the sample determined. A Hewlett Packard Gas Chromatograph, Model 5830A, equipped with dual thermal conductivity detection, was used for determination of oxygen concentration. Gas chromatographic conditions: 3 feet x 1/4 inch O.D. stainless steel column, packed with Molecular Sieve 5A (Supelco, Inc., Bellefonte, Pennsylvania); helium flow rate of 30 ml/min.; injection port temperature of 150°C; detector temperature of 350°C; column temperature of 70°C; oxygen retention time of 1.78 minutes. The percent of oxygen was computed from the oxygen peak area, and this value was used directly for the concentration of oxygen. The experiment was terminated when the oxygen concentration within the FLEX-CAN Retort Pouch was reduced to a level of 1%.

Headspace Volume Determination. Following termination of the rate studies, the headspace volume of each FLEX-CAN Retort Pouch was determined by a modification of the procedure of Davis and Hunington (1978). The initial carbon dioxide concentration within the FLEX-CAN Pouch was determined

by gas chromatography using a 1.0 ml headspace gas sample. A known volume (1.0 ml) of pure carbon dioxide was then introduced into the headspace of the FLEX-CAN, and after an equilibration period of 20 minutes, the carbon dioxide concentration was determined again by gas chromatography. A Hewlett Packard Gas Chromatograph, Model 5830A, equipped with dual thermal conductivity detection, was used for determination of carbon dioxide concentration. Gas chromatographic conditions were as follows: 6 feet x 1/8 inch O.D. stainless steel column, packed with Chromosorb 102, 80-100 mesh (Johns-Manville, Celite Division, Denver, Colorado); helium flow of 10 ml/min.; injection port temperature of 150°C; detector temperature of 350°C; column temperature of 70°C; carbon dioxide retention time of 0.97 minute. The concentration was obtained based on an external standard of 100% carbon dioxide.

The volume of the FLEX-CAN was calculated from the relationship:

$$V = \frac{Va \times 100}{C_1 - C_0} \qquad (11)$$

where: V = headspace volume (ml),

Va = volume of carbon dioxide added (ml),

C_1 = final carbon dioxide concentration (volume/volume %),

C_0 = initial carbon dioxide concentration (volume/volume %).

The validity of this procedure was established during development of the method, and the results of those studies are summarized in Appendix B.

Actual Storage Studies

Films with high oxygen-barrier properties were selected for the actual storage studies. These were a vinylidine chloride/vinyl chloride copolymer (Saran, 1 mil), and a Saran-coated polyethylene terephthalate (Mylar M24, 0.5 mil), respectively. Oxygen permeability of the films was measured on the Oxtran-100 (Modern Control, Inc., Minneapolis, Minnesota). The measurements were done under the conditions similar to those of the storage studies: temperature of 50°C (the average of upper and lower chamber temperatures) and 0% relative humidity (RH).

Film samples were cut and sealed on three sides according to a master template (12 cm x 8 cm) using a Sentinal Impulse Heat Sealer (Packaging Industries, Montclair, New Jersey). Conditions for sealing were as follows: impulse time of 0.3 second for Saran, 0.4 second for Mylar, respectively; pressure of 30 psi. for both films. A sampling septum of silicon rubber was provided in a manner similar to that employed for the FLEX-CAN Pouch. The water activity of the model lipid system was also controlled by equilibration over the saturated salt solution, as previously discussed. Samples were triplicated for both Saran and Mylar film packages. (Results are repeated for Samples Mylar M24-1, 2 and 3, and for Saran-2 in the RESULTS Section.)

The packaged samples were placed in a conventional oven maintained at 50±2°C. The samples were removed from the oven, and the oxygen concentration within the package was monitored at predetermined time intervals. After 611 hours of storage, the packaged samples were removed from the oven, allowed to cool to ambient conditions, and the headspace volume of each package was determined. The determination of oxygen concentration and headspace volume was carried out in the same manner as for the FLEX-CAN Pouches.

RESULTS

Experiments were carried out according to the procedure described in the previous section. Results are shown as follows:

Oxidation Rate Studies Results

Oxygen partial pressure change within the FLEX-CAN as a function of time was obtained experimentally and the results summarized in Table 1. Oxidation rates, as a function of oxygen partial pressure, were then derived from the experimentally obtained data in the way presented in Appendix C. The results are tabulated in Table 2.

Table 1. Oxygen Partial Pressure (Atm.)[a] Change within the FLEX-CAN as a Function of Time.

Time (Hours)	Sample Number						
	Blank	1	2	3	4	5	6
0	.207	.207	.206	.207	.206	.207	.207
44	.205	.179	.175	.179	.187	.189	.192
69	.205	.164	.155	.160	.178	.182	.187
93	.205	.147	.137	.142	.171	.174	.178
119	.204	.128	.117	.123	.164	.163	.168
142	.204	.110	.094	.104	.156	.154	.160
161	.204	.096	.079		.149	.146	.152
186	.204	.077	.052		.139	.136	.142
196	.204	.065	.042		.135	.130	.137
208	.204	.055	.031		.130	.124	.132
219	.203	.044	.023		.124	.118	.126
234	.204	.030	.014		.118	.109	.119
246	.203	.018	.015		.111	.106	.114
258	.204	.013	.013		.108	.103	.108
269	.203	.012	.012		.100	.093	.099

(a) Oxygen partial pressure was obtained based on oxygen concentration (volume/volume %). National Weather Service in East Lansing, Michigan reported that the atmospheric pressure during the experiment period was 0.97 atm. with standard deviation of 0.0089 atm. Therefore, the atmospheric pressure can be assumed to be 1 atm.

Table 2. Oxidation Rate as a Function of Oxygen Partial Pressure[a].

Sample Number					
Sample 1		Sample 2		Sample 3	
Oxygen Partial Pressure (atm.)	Oxygen Consumption Rate (ml O_2/hr. per gram of oil)	Oxygen Partial Pressure (atm.)	Oxygen Consumption Rate (ml O_2/hr. per gram of oil)	Oxygen Partial Pressure (atm.)	Oxygen Consumption Rate (ml O_2/hr. per gram of oil)
.207	.0077	.206	.0066	.207	.0077
.179	.0072	.174	.0068	.179	.0086
.164	.0076	.155	.0063	.160	.0083
.147	.0078	.137	.0061	.142	.0076
.128	.0080	.117	.0073	.123	.0083
.109	.0070	.094	.0056		
.096	.0070	.079	.0071		
.065	.0067	.052	.0064		
.055	.0084	.042	.0052		
.044	.0073	.031	.0044		
.030	.0076	.023	.0037		

Table 2 (continued)

Sample Number					
Sample 4		Sample 5		Sample 6	
Oxygen Partial Pressure (atm.)	Oxygen Consumption Rate (ml O_2/hr. per gram of oil)	Oxygen Partial Pressure (atm.)	Oxygen Consumption Rate (ml O_2/hr. per gram of oil)	Oxygen Partial Pressure (atm.)	Oxygen Consumption Rate (ml O_2/hr. per gram of oil)
.206	.0072	.207	.0065	.207	.0064
.187	.0058	.189	.0047	.191	.0038
.178	.0050	.182	.0053	.187	.0066
.171	.0043	.174	.0057	.178	.0068
.164	.0054	.163	.0058	.168	.0062
.156	.0055	.154	.0064	.160	.0075
.149	.0061	.146	.0055	.152	.0064
.139	.0063	.136	.0083	.142	.0083
.134	.0059	.129	.0069	.137	.0064
.129	.0073	.124	.0061	.132	.0077
.124	.0053	.118	.0073	.126	.0074
.118	.0077	.109	.0038	.119	.0067
.111	.0040	.106	.0026	.113	.0074
.108	.0069	.103	.0079	.108	.0085

(a) The data processing procedure to obtain the oxidation rate as a function of oxygen partial pressure is presented in Appendix C.

Obtained data, shown in Table 2, were plotted and linear regression analysis was carried out since data suggested that the oxidation rate and the oxygen partial pressure had a linear relationship. The following relationship was obtained.

$$OR = .00453 \times PO_2 + .00705 \qquad (12)$$

where: OR = oxidation rate (ml O_2/hr. per gram of oil),

PO_2 = oxygen partial pressure (atm.).

Prediction Results

Change in the oxygen partial pressure and the oxygen consumption was predicted using a computer program with the obtained Equation (12). Predictions were performed for the respective packages, which were used for the storage studies; namely, Samples Mylar M24-1, Mylar M24-2, Mylar M24-3 and Saran-2. The predicted change in the oxygen partial pressure is presented in Table 3, and the predicted oxygen consumption is shown in Table 4.

The shelf-life of the packaged model lipid system was then determined for the individual packages. In this study, the shelf-life is defined as a period of time required, until oxygen uptake by the packaged, model lipid system reaches an unacceptable quality level. The results are shown in Table 5.

For this study, the product was assumed to be unacceptable after sorption of 2.73 ml O_2 (STP/g oil).

A detailed discussion concerning derivation of this value is presented in Appendix D.

Table 3. Predicted Change in the Oxygen Partial Pressure (Atm.) within the Respective Packages.

Time (Hours)	Oxygen Partial Pressure (Atm.)			
	Mylar M24-1	Mylar M24-2	Mylar M24-3	Saran-2
0	0.208	0.208	0.208	0.208
60	0.178	0.175	0.180	0.187
120	0.149	0.143	0.153	0.165
180	0.121	0.113	0.128	0.144
240	0.097	0.084	0.104	0.122
300	0.073	0.057	0.081	0.099
360	0.052	0.033	0.061	0.076
420	0.034	0.011	0.042	0.054
480	0.017	-	0.025	0.032

Table 4. Predicted Oxygen Consumption within the Respective Packages.

Time (Hours)	Oxygen Consumption (ml O_2/gram oil)			
	Mylar M24-1	Mylar M24-2	Mylar M24-3	Saran-2
0	0	0	0	0
60	0.48	0.48	0.48	0.48
120	0.94	0.94	0.94	0.95
180	1.02	1.40	1.41	1.41
240	1.86	1.85	1.86	1.87
300	2.30	2.29	2.31	2.32
360	2.74	2.73	2.75	2.77
420	3.18	3.16	3.19	3.21
480	3.61	-	3.62	3.65

Table 5. Predicted Shelf-Life of Packaged Model Lipid Food System.

	Packages			
	Mylar-1	Mylar-2	Mylar-3	Saran-2
Shelf-Life (Hours)	358	360	357	360

It can be seen from Table 5 that there is little or no difference in the predicted shelf-life of the model food system packaged in the respective test materials, based on the simulation model developed. These results can be rationalized, if the rate of oxygen consumption (ml O_2/hr./gram product) is slower than the rate of O_2 permeation through the respective packages. The oxygen permeation rates of the two test packages are of the same order of magnitude; namely, 2.25 and 5.16 ml O_2 (STP)/m^2/hr. for Saran and Mylar, respectively.

From these permeation rates and the total package surface area of approximately 192 cm^2 (package dimensions of 12 cm x 8 cm), it can be estimated that for the Mylar package approximately 0.1 ml (STP) of oxygen will permeate through per hour. This represents a minimum value, since the studies were conducted at 50°C. The total oxygen consumption will be approximately 0.076 ml O_2/hr. at this temperature. Further, the oxidation rate is assumed to be independent of oxygen partial pressure.

Actual Storage Studies Results

Actual storage tests were carried out according to the procedure described in the previous Section, under the following package conditions (Table 6).

Table 6. Package Conditions for Actual Storage Test.

Variables	Packages			
	Mylar-1	Mylar-2	Mylar-3	Saran-2
Initial Headspace Volume (ml)	55	57	60	78
Weight of Model Lipid System (g)	4.40	4.98	4.48	4.32
Surface Area (m^2)	0.0199	0.0189	0.0200	0.0153
Oxygen Permeability Rate (ml O_2/m^2 hr. atm.)	5.16	5.16	5.16	2.35

For these studies the initial headspace volume was not determined directly in order to eliminate any effect of the carbon dioxide gas, introduced to the package for the headspace determination. The initial headspace volume was, therefore, calculated based on the final headspace volume, using the following Equation (13).

$$H_i = (H_f + 4.0) \times (1 - PO_{2_f})/(1 - PO_{2_i}) \qquad (13)$$

where: H_i = initial headspace volume (ml),

H_f = final headspace volume (ml),

4.0 = the amount of gas evacuated from the headspace for sampling (ml),

PO_{2i} = initial oxygen partial pressure (atm.),

PO_{2f} = final oxygen partial pressure (atm.).

The change in the oxygen partial pressure within the respective packages is shown as a function of time in Table 7.

Table 7. Change in Oxygen Partial Pressure (Atm.) within the Respective Packages (Actual Storage Test).

Time (Hours)	Packages			
	Mylar-1	Mylar-2	Mylar-3	Saran-2
0	0.206	0.207	0.207	0.207
46	0.196	0.194	0.196	0.175
115	0.174	0.170	0.175	0.162
161	0.162	0.157	0.164	0.149
203	0.148	0.142	0.151	0.133
252	0.139	0.131	0.144	0.119
296	0.126	0.116	0.132	0.108
329	0.114	0.099	0.121	0.094
417	0.096	0.074	0.107	0.067
466	0.080	0.053	0.094	0.049
537	0.044	0.025	0.061	0.013
587	0.015	0.012	0.029	0.012
611	0.013	0.013	0.015	0.011

As shown in Tables 3 and 7, a fairly good agreement was obtained for the oxygen partial pressure change within the packages between predicted results and actual storage

test results. This indicates that oxygen consumption by the model lipid system is also simulated reasonably well by the developed computer program. The shelf-life determination can then be considered fairly reliable.

DISCUSSION

Consideration of Possible Error in the Oxidation Rate Studies

In the system which was employed to determine the oxidation rate and the oxidation rate equation, the temperature and relative humidity were held constant, and the rate of oxidation was monitored as a function of continuously changing oxygen partial pressure. The oxidation rate was determined by a calculation based on the oxygen partial pressure change and the headspace volume of the system. In this procedure, a certain degree of error is introduced due to both sampling and instrument (i.e. gas chromatograph) accuracy.

The oxidation rate was calculated, based on the change in the amount of oxygen within the package as a function of time. The oxidation rate is assumed equal to the slope, where oxygen quantity within the package is plotted as a function of storage time.

The effect of both instrumental and sampling error on the oxidation rate studies are discussed below.

The amount of oxygen within the package headspace is calculated as follows:

$$O_2(t) = V(t) \times PO_2(t) \qquad (14)$$

where: $O_2(t)$ = actual amount of oxygen present within the headspace volume at time, t,

$V(t)$ = actual headspace volume at time, t,

$PO_2(t)$ = actual oxygen partial pressure at time, t.

In the present studies, both headspace volume and oxygen partial pressure were determined by gas chromatography measurements. It is assumed that the percent error of both sampling and instrumentation is ±A% for the headspace volume measurement, and ±B% for the oxygen partial pressure measurement.

The measured headspace volume at time, t, with maximum possible error can be described as follows:

$$V^*(t) = (1 \pm a) \times V(t) \qquad (15)$$

where: $V^*(t)$ = measured headspace volume with maximum possible error at time, t,

$V(t)$ = actual headspace volume,

$a = \frac{A}{100}$.

The measured oxygen partial pressure at time, t, with maximum possible error also can be shown:

$$PO_2^*(t) = (1 \pm b) \times PO_2(t) \qquad (16)$$

where: $PO_2^*(t)$ = measured headspace volume with maximum possible error at time, t,

$PO_2(t)$ = actual headspace volume at time, t,

$b = \frac{B}{100}$.

From Equations (14), (15) and (16), the relationship between $O_2(t)$ and $O_2^*(t)$ can be obtained as follows:

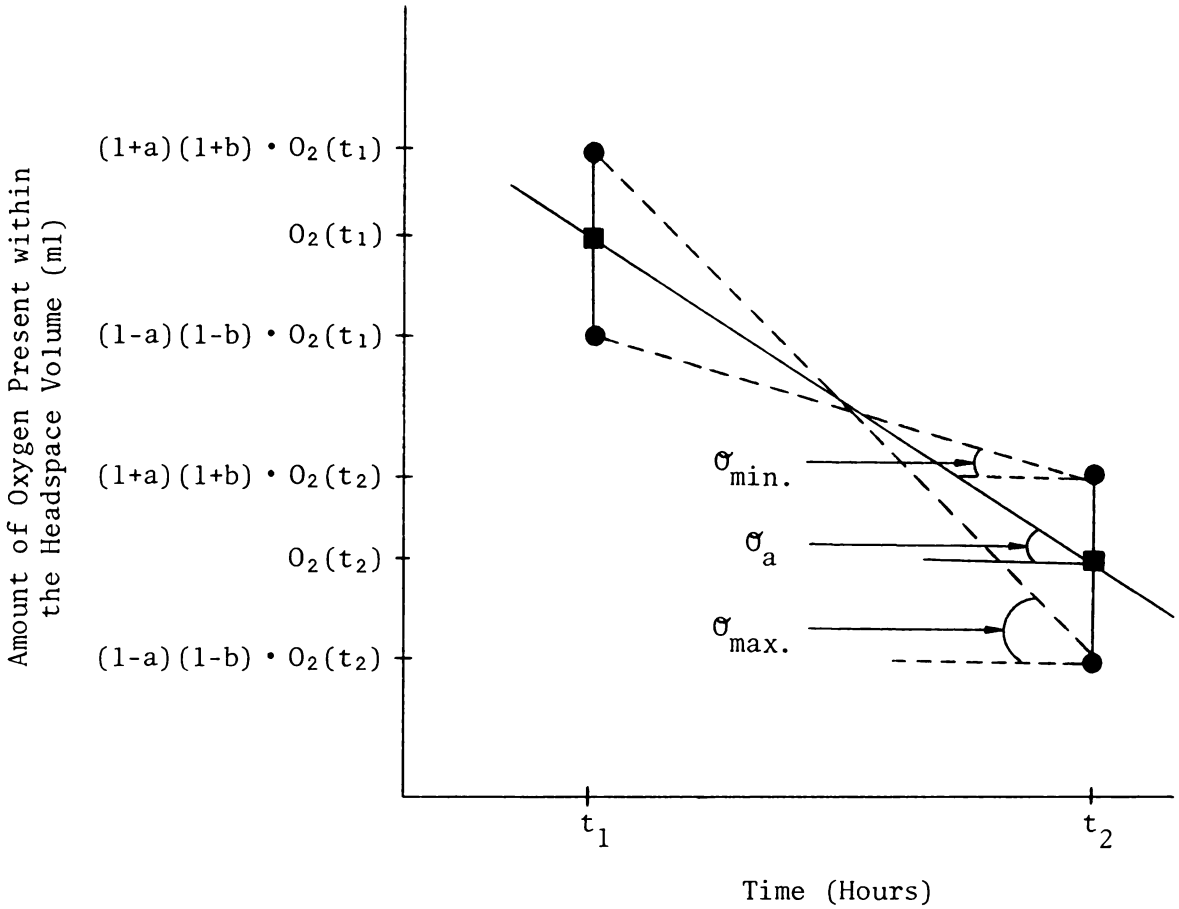
$$O_2^*(t) = V^*(t) \times PO_2^*(t)$$

$$O_2^*(t) = (1\pm a)(1\pm b) \times V(t) \times PO_2(t)$$

$$O_2^*(t) = (1\pm a)(1\pm b) \times O_2(t) \qquad (17)$$

where: $O_2^*(t)$ = measured amount of oxygen present within the headspace volume at time, t.

The amount of oxygen within the headspace was obtained as a function of time. The measured amount of oxygen falling within the region of $(1\pm a)(1\pm b) \cdot O_2(t)$ can be represented graphically for oxygen quantity values, determined at t_1 and t_2.



where: ■ = actual amount of oxygen,

● = minimum or maximum possible measured amounts of oxygen,

$\sigma_{max.}$ = maximum possible calculated oxidation rate,

$\sigma_{min.}$ = minimum possible calculated oxidation rate,

σ_{a} = actual oxidation rate.

Figure 4. Illustration for Determination of Oxidation Rate.

The results presented in Table 8 illustrate how such error factors can affect the oxidation rate, using as an example, data from the FLEX-CAN Sample 1.

Data: t_1 = 119 hours, t_2 = 142 hours;

$O_2(t_1)$ = 11.72 ml O_2, $O_2(t_2)$ = 9.99 ml O_2;

Oxidation Rate = 0.076 (ml O_2/hr.).

Table 8. Effect of Error Factors on the Oxidation Rate.

Error Factor		Possible Measured Value with Error (ml)				Oxidation Rate (ml O_2/hr.)	
		$O_2(t_1)$		$O_2(t_2)$			
a	b	Max.	Min.	Max.	Min.	Max.	Min.
0.005	0.005	11.84	11.60	10.09	9.89	0.085	0.066
0.005	0.01	11.90	11.54	10.14	9.84	0.090	0.061
0.01	0.005	11.90	11.54	10.14	9.84	0.090	0.061
0.01	0.01	11.96	11.49	10.19	9.79	0.094	0.057

As shown, the effect of error factors involving both sampling and instrumentation on the oxidation rate calculation can be significant. In this study, a number of measurements were made and linear regression analysis was carried out on these measurements.

Discussion of Simulation Model

In most examples of predicting shelf-life by calculation, the time-step selected can influence the results. However, there is a critical value for the time-step function, below which it has no influence on the computed

shelf-life value. The magnitude of the time-step, therefore, has to be below this critical value for appropriate application of the iteration technique. The effect of the time-step function on the calculated change in oxygen partial pressure, as a function of time, was determined using data obtained experimentally for the Mylar M24-1 package. The results are summarized in Table 9, where oxygen partial pressure change was computed for time-step values of 0.1, 1.0 and 5.0 hours, respectively.

Table 9. Effect of the Time-Step Function on the Computed Oxygen Partial Pressure Change.

Time (Hours)	Oxygen Partial Pressure (Atm.)		
	Time-Step 0.1 Hour	Time-Step 1.0 Hour	Time-Step 5.0 Hours
0	.208	.208	.208
100	.159	.159	.158
200	.114	.113	.113
300	.074	.073	.073
400	.040	.039	.039
500	.012	.012	.011

As shown, there is an average of about 1% difference between the computed values of oxygen partial pressure change as a function of storage time for the three time-step levels evaluated. This indicates that the value of 5.0 hours is already below the critical value. In this study, a time-step of 1.0 hour was used, assuming that the value was well below the critical time-step level.

Another factor which may influence the calculated results is the permeation of nitrogen from the headspace within the package to the external package environment, as a result of a nitrogen partial pressure difference between the internal and external package environments. The nitrogen partial pressure (i.e. concentration) within the package will increase as the oxygen partial pressure decreases because of oxygen consumption by the model lipid food system, resulting in a decrease in the internal volume of the package. Since the nitrogen partial pressure remains constant (= 0.792 atm.) outside the package a nitrogen partial pressure difference occurs, resulting in the permeation of nitrogen through the package into the external environment. Although the permeation rate of nitrogen was not determined, it is possible to estimate the nitrogen permeation rate of the respective films, based on the permeability constants of nitrogen and oxygen, which are available in the literature (Agranoff, 1977). The estimated permeation rates for the respective films are listed below:

Mylar: 62.0 [ml N_2 (STP)/m^2 · 24 hr. · atm.] at 50°C,

Saran: 28.3 [ml N_2 (STP)/m^2 · 24 hr. · atm.] at 50°C.

The effect of the nitrogen permeation was evaluated using these data. The computer program which was written to calculate the oxygen partial pressure change as a function of storage time was modified to include the permeation of nitrogen through the respective permeable materials. The computed oxygen partial pressure values for the Mylar M24-1 are

summarized in Table 10 and compared to the values previously determined, where the quantity of nitrogen within the package was assumed constant.

Table 10. Effect of Permeation of Nitrogen on the Oxygen Partial Pressure Change within the Package[a].

Storage Time (Hours)	Oxygen Partial Pressure (Atm.)	
	With the Effect of Nitrogen	Without the Effect of Nitrogen
0	.208	.208
100	.159	.159
200	.114	.113
300	.075	.073
400	.040	.039
500	.011	.012

(a) Data of Mylar M24-1 Sample are used for the computation.

As shown, there appears to be a negligible effect on the computed oxygen partial pressure change, due to the permeation of nitrogen. Therefore, Assumption 4 for the simulation model was considered valid.

SUMMARY AND CONCLUSIONS

The shelf-life prediction study was carried out by using a mathematical model to simulate the interaction mechanism of oxygen permeation through a package and oxygen consumption by an oxidizable product. The predicted oxygen partial pressure within the package, based on the simulation model developed, showed a fair agreement with experimentally determined values obtained from actual storage test data. The model developed simulates the mechanism of oxygen consumption within the package reasonably well for a first approximation. However, improved agreement may be obtained in future studies by improvement of analytical methodology and/or refinement in the simulation model.

Based on the present studies and results obtained, the following future studies are proposed.

1. The rate of oxygen consumption as a function of extent of oxidation in the food product should be determined prior to the shelf-life studies.
2. The change in quality index should be monitored by following the oxygen partial pressure changes, as well as an independent chemical analysis of the product. Correlation should be established between the oxygen uptake and chemical analysis. Such a correlation

establishes and/or validates the assumption that the loss of quality index due to oxidation is related directly to the extent of oxygen uptake by the product.

3. The influence of other independent variables (i.e. relative humidity and temperature) which were kept constant in the present studies should be studied.
4. After completion of the model food study, an actual food system should be evaluated.

APPENDICES

APPENDIX A

TABLES FOR COMPOSITION AND DISTRIBUTION OF MODEL LIPID FOOD SYSTEM

Table 11. Composition of Model Lipid Food System.

Component	Relative Percent
Soybean oil	65.5
CMC	6.9
Tween 20	3.5
Buffer salt	19.2
Water	4.9

Table 12. Lipid Distribution in Model Lipid Food System.

Sample Number	Weight of Sample (g) [A]	Weight of Oil (g) [B]	[B]/[A] x 100 (%)
1	3.90	2.41	61.79
2	3.59	2.29	63.71
3	3.27	2.07	63.22
4	4.28	2.62	61.33

APPENDIX B

HEADSPACE VOLUME DETERMINATION

Control studies were carried out to determine the effect of sorption of carbon dioxide by the food system. Two FLEX-CAN Pouches containing the model lipid system were prepared as previously described for the oxidation rate studies. Pure carbon dioxide (1 ml) was injected into the headspace of each FLEX-CAN through a sampling septum. The concentration of carbon dioxide within the FLEX-CAN was determined by gas chromatography after 10 minutes, 1 hour and 3 hours. As shown in Table 13, no sorption of carbon dioxide was detected between 10 minutes to 3 hours after pure carbon dioxide injection.

The validity of the relationship, shown in Equation (11), was established by the following preliminary study. Using FLEX-CAN Pouches of known headspace volume [i.e. 50, 100 and 140 ml (STP)], headspace volume determinations were carried out by a serial dilution technique and the calculated and actual headspace volume values compared. As shown in Table 14, the calculated results agreed well with the actual volume.

Table 13. Change in the Concentration of the Carbon Dioxide within the FLEX-CAN by Sorption as a Function of Time.

Time After Pure Carbon Dioxide Injection	Concentration of Carbon Dioxide within the FLEX-CAN (%)
10 minutes	1.48
1 hour	1.47
3 hours	1.50

Table 14. Comparison of the Determined Headspace Volume to the Actual Volume.

Actual Headspace Volume [ml (STP)]	Experimentally Determined Headspace Volume [ml (STP)]	Error (%)
50	50	0
50	50	0
100	104	4.0
100	100	0
140	139	2.9
140	131	6.4
	Average % Error	2.2

APPENDIX C

OXIDATION RATE STUDY DATA PROCESSING

In this study, the oxygen consumption rate (the amount of oxygen consumed per unit of time) is required for the prediction of shelf-life. Since the change in the oxygen partial pressure within the FLEX-CAN was obtained experimentally, the oxygen consumption rate can be calculated if the headspace volume of the FLEX-CAN is known. However, the headspace volume of the FLEX-CAN is changing throughout the experimental period, due to both oxygen consumption by the model lipid system and the sampling of the headspace gas.

The following procedure was employed, which considered the continuously changing headspace volume. The procedure was developed based on the fact that the amount of nitrogen within the FLEX-CAN is relatively constant throughout the experimental period.

Summarized below is the stepwise data processing procedure for FLEX-CAN Sample 1. The resultant data are summarized in Table 15.

Calculation Steps

Step 1: The volume of nitrogen within the FLEX-CAN headspace, at time = 269 hours, can be calculated:

$$73\ (\text{ml}) \times \frac{1 - 0.012\ (\text{atm.})}{1\ (\text{atm.})} = 72.12\ (\text{ml}) \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{a}$$

Step 2: The volume of nitrogen evacuated for sampling at time = 269 hours:

$$0.25\ (\text{ml}) \times \frac{1 - 0.012\ (\text{atm.})}{1\ (\text{atm.})} = 0.24\ (\text{ml}) \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{b}$$

Step 3: The volume of nitrogen at 258 hours is therefore:

$$a + b = 72.12\ (\text{ml}) + 0.24\ (\text{ml}) = 72.36\ (\text{ml}) \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{c}$$

Step 4: The headspace volume at 258 hours:

$$72.36\ (\text{ml})/(1 - 0.013)(\text{atm.})/1\ (\text{atm.}) = 73.31\ (\text{ml}) \quad \ldots\ldots\ldots\ldots \text{d}$$

Step 5: The volume of oxygen present within the FLEX-CAN headspace at 269 hours, at 258 hours:

at 269 hours: $73.00\ (\text{ml}) \times .012 = 0.88\ (\text{ml})$ ..... e

at 258 hours: $73.31\ (\text{ml}) \times .013 = 0.95\ (\text{ml})$ ..... f

Step 6: The oxygen consumption rate between the sampling time of 269 hours and 258 hours can be obtained as follows:

The amount of oxygen consumed (g) between the time of 269 hours and 258 hours:

$$g = f - e = 0.07\ (\text{ml}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{g}$$

The oxidation rate is therefore:

$$g/(269 - 258)\ \text{hours}$$

$$= 0.07\ (\text{ml})/11\ (\text{hours})$$

$$= 0.0064\ (\text{ml}\ O_2/\text{hour} \cdot 9.46\ \text{grams of oil}) \quad \ldots\ldots\ldots\ldots \text{h}$$

Step 7: The oxygen consumption rate obtained above is then converted to one gram of oil basis:

$$i = h/9.46 \text{ (grams)}$$
$$= 0.0064 \text{ (ml } O_2\text{/hour} \cdot 9.46 \text{ grams of oil)/9.46 (grams)}$$
$$= 0.00068 \text{ (ml } O_2\text{/hour} \cdot \text{gram of oil)} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad i$$

Steps 1 to 7 were then repeated for each sampling time to obtain the oxygen consumption rate as a function of sampling time. The same procedure was applied to Samples 2 to 6. The calculated results are shown in Table 1.

Table 15. Oxidation Rate Study Data Processing for FLEX-CAN Sample 1.

Time[a] (Hours)	Oxygen[a] Partial Pressure (Atm.)	Headspace Volume (ml) (Step 1)	Volume of Nitrogen within the Headspace (ml)	Volume[a] of Sample Evacuated (ml)	Volume of Oxygen within the Headspace (ml) (Step 5)	Volume of Oxygen Consumption (ml) (Step 6)	Oxygen Consumption Rate (ml/hr. per 9.46 grams oil) (Step 7)	Oxygen Consumption Rate (ml/hr. per gram oil)
0	.	.	.	.	.	.	.	.
44	.	.	.	.	.	.	.	.
69	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.
234	.302	75.09	72.82	0.25	2.27	0.908	0.074	0.0076
246	.018	73.95	72.58	0.25	1.36	0.420	0.113	0.0120
258	.013	73.31	72.36	0.25	0.95	0.040	0.006	0.0068
269	.012	73.00[a]	72.12	0.25	0.88	.	.	.

(a) Data was obtained experimentally.

APPENDIX D

ACCEPTABLE QUALITY LEVEL OF MODEL LIPID FOOD SYSTEM

The acceptable quality level can be determined by either chemical analysis or sensory analysis, or by a combination of both. However, it was not considered totally appropriate for the evaluation of a model food system. Therefore, an acceptable quality level was assumed, based on the literature value of a dehydrated food system. In this case, the acceptable quality level was expressed in terms of oxygen uptake. The acceptable quality level of potato chips containing cottonseed oil was used for this purpose.

Acceptable quality level of potato chips (Quast et al., 1972b).

1.200 ml O_2 (STP)/gram Sample*

2.727 ml O_2 (STP)/gram Oil*

*Oil content of potato chips is 44 grams of oil/100 grams of food system.

LIST OF REFERENCES

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Agranoff, J., 1977. (See Modern Plastics Encyclopedia.)

Bollard, J. L., 1949. Kinetics of olefin oxidation. Quarterly Rev. (London) 1: 1.

Cabral, A. C. D., Orr, A., Stier, E. F. and Gilbert, S. G., 1979. Performance of metallized polyester as a fatty food packaging material. Package Development and Systems 9(2): 18.

Clifford, W. H., Gyeszly, S. W. and Manathunya, V., 1977. Accelerated test vs. calculations based on product-package properties. Package Development and Systems 7(5): 29.

Crank, J. and Park, G. S., 1963. Diffusion in Polymers, Academic Press, New York.

Davis, E. G. and Hunington, J. H., 1978. New cell for measuring permeability of film materials. Australian Packaging 26(6): 35.

Felt, C. E., Buechele, A. C., Borchardt, L. F. and Koehn, R. C., 1945. Determining shelf-life of packaged cereal. Cereal Chem. 22(3): 261.

Gray, J. I., 1978. Measurement of lipid oxidation...a review. J. Amer. Oil Chemists' Soc. 55(6): 539.

Greenspan, L., 1977. Humidity fixed points of binary saturated aqueous solutions. Journal of Research of the National Bureau of Standards 81A: 89.

Gyeszly, S. W., 1980. Shelf-life simulation, predicts packaging total performance. Pkg. Eng. 25(6): 70.

Henig, Y. S. and Gilbert, S. G., 1975. Computer analysis of the variables affecting respiration and quality of produce packaged in polymeric films. J. Food Sci. 40(5): 1033.

Henig, Y. S., Gilbert, S. G., Ashkenazi, Y. A. and Daun, H., 1973. Storage quality of bananas packaged in selected permeability films. J. Food Sci. 38(7): 1247.

Karel, M., 1967. Use tests only way to determine effect of package on food quality. Food in Canada 4: 43.

Karel, M., 1974. Packaging protection for oxygen-sensitive products. Food Tech. 28(8): 50.

Karel, M., Labuza, T. P. and Maloney, J. F., 1967. Chemical changes in freeze-dried foods and model systems. Cryobiology 3(4): 288.

Karel, M., Mizrahi, S. and Labuza, T. P., 1971. Computer prediction of food storage. Mod. Pkg. 44(8): 54.

King, C. J., 1970. Freeze-drying of foodstuffs (a review). CRC Critical Reviews in Food Technology 1(3): 379.

Kwolek, W. F. and Bookwalter, G. N., 1971. Predicting storage stability from time-temperature data. Food Tech. 25(10): 1025.

Labuza, T. P., 1971. Kinetics of lipid oxidation in foods (a review). CRC Critical Reviews in Food Technology 2(3): 355.

Labuza, T. P., 1979. A theoretical comparison of losses in food under fluctuating temperature sequences. J. Food Sci. 44(4): 1162.

Labuza, T. P., Heidelbaugh, H. D., Silver, M. and Karel, M., 1971. Oxidation at intermediate moisture contents. J. Amer. Oil Chemists' Soc. 48(2): 86.

Labuza, T. P., Mizrahi, S. and Karel, M., 1972. Mathematical model for optimization of flexible film packaging of foods for storage. Transactions. American Society of Agricultural Engineers 15(1): 150.

Labuza, T. P., Tsuyuki, H. and Karel, M., 1969. Kinetics of linoleate oxidation in model systems. J. Amer. Oil Chemists' Soc. 46(8): 409.

Lundberg, W. O., 1962. Lipids and Their Oxidation, edited by H. W. Schultz, AVI Publishing Co., Westport, Connecticut.

Maloney, J. F., Labuza, T. P., Wallace, D. H. and Karel, M., 1966. Autoxidation of methyl linoleate in freeze-dried model systems. J. Food Sci. 31(6): 878.

Marcuse, R. and Fredriksson, P., 1968. Fat oxidation at low oxygen pressure. Kinetic studies on the rate of fat oxidation in emulsions. J. Amer. Oil Chemists' Soc. 45(5): 400.

Martinez, F. and Labuza, T. P., 1968. Rate of deterioration of freeze-dried salmon as a function of relative humidity. J. Food Sci. 33(3): 241.

Mizrahi, S. and Karel, M., 1977. Accelerated stability tests of moisture-sensitive products in permeable packages by programming rate of moisture content increase. J. Food Sci. 42(4): 958.

Mizrahi, S., Labuza, T. P. and Karel, M., 1970a. Computer-aided predictions of extent of browning in dehydrated cabbage. J. Food Sci. 35(6): 799.

Mizrahi, S., Labuza, T. P. and Karel, M., 1970b. Feasibility of accelerated tests for browning in dehydrated cabbage. J. Food Sci. 35(6): 804.

Modern Plastics Encyclopedia, 1977. Edited by J. Agranoff, McGraw-Hill Publishing Corporation, New York.

Official Methods of Analysis of the Association of Official Analytical Chemists. Edited by W. Horwitz, published by Association of Official Analytical Chemists, Washington, D. C.

Quast, D. G. and Karel, M., 1971. Effect of oxygen diffusion on oxidation of some dry foods. J. Food Tech. 6(1): 95.

Quast, D. G. and Karel, M., 1972a. Effects of environmental factors on the oxidation of potato chips. J. Food Sci. 37(4): 584.

Quast, D. G., Karel, M. and Rand, W. H., 1972b. Development of a mathematical model for oxidation of potato chips as a function of oxygen pressure, extent of oxidation and equilibrium relative humidity. J. Food Sci. 37(5): 673.

Quast, D. G. and Karel, M., 1972c. Techniques of determining oxygen concentration inside a package. J. Food Sci. 37(3): 490.

Quast, D. G. and Karel, M., 1972d. Computer simulation of storage life of food undergoing spoilage by two interacting mechanisms. J. Food Sci. 37(5): 679.

Quast, D. G. and Karel, M., 1973. Simulating shelf-life. Mod. Pkg. 46(3): 50.

Ragnarsson, J. O. and Labuza, T. P., 1977. Accelerated shelf-life testing for oxidative rancidity in foods...a review. Food Chem. 2(4): 291.

Simon, I. B., Labuza, T. P. and Karel, M., 1971. Computer-aided prediction of food storage stability: oxidative deterioration of a shrimp product. J. Food Sci. 36(2): 280.

Singh, R. P., 1974. "Computer simulation of quality degradation in liquid foods during storage." Ph.D. Thesis, Michigan State University, East Lansing, Michigan.

Talwar, R., 1974. Plastics in packaging: gas and vapor permeability. Package Development and Systems 4(5): 29.

Tuomy, J. M. and Walker, G. C., 1970. Effect of storage time, moisture level and headspace oxygen on the quality of dehydrated egg mix. Food Tech. 24(11): 1287.

Zirlin, A. and Karel, M., 1969. Oxidation effects in a freeze-dried gelatin-methyl linoleate system. J. Food Sci. 34(2): 160.