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DETERMINATION OF MOISTURE CONTENT OF DRY FOODS IN AN OVERWRAPPED MULTIPACK BY CALCULATION BASED ON SIMULATION

presented by

JOHN SCOTT WILES

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M.S. degree in PACKAGING

Bruce R. Harte

Dr. Bruce R. Harte

Major professor

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DETERMINATION OF MOISTURE CONTENT OF DRY FOODS IN AN OVERWRAPPED MULTIPACK BY CALCULATION BASED ON SIMULATION

Bу

John Scott Wiles

51.0 s.

A THESIS

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

MASTER OF SCIENCE

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ABSTRACT

DETERMINATION OF MOISTURE CONTENT OF DRY FOODS IN AN OVERWRAPPED MULTIPACK BY CALCULATION BASED ON SIMULATION

By

John Scott Wiles

The objective of this study is to investigate the effect of barrier placement in a packaging system consisting of a series of small packages sealed within a larger one and to predict by calculation the rate of moisture uptake by a dry food product contained in the small packages.

Results show that lower product moisture contents are achieved when superior moisture barrier properties are built into the inner package rather than the overwrap and the outcome of calculations based on a system simulation demonstrates that moisture levels of the product can be predicted with acceptable accuracy. The results indicate that the accelerated technique for predicting shelf life is inaccurate and may lead to improper packaging when prediction of product moisture content over time is based upon this method of prediction.

DEDICATION

This thesis is dedicated to my wife, Cheryl, and my parents, Mr. and Mrs. John Wiles, in appreciation for their encouragement and especially their patience in this and other efforts.

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INTRODUCTION

The ultimate quality of any processed food product is dependent upon a variety of factors including the condition of the raw materials, methods of processing, pre and post process handling and environmental influence such as heat, light, humidity and mechanical conditions.

Obviously, the manufacturer has some control over the first three factors but the package must bear the burden of protecting the product from environmental hazards encountered in distribution. One of the most important functions of the package when viewed in this context is its ability to act as a barrier, preventing exchange between the product and the external environment.

In the case of dried food products, the uptake of moisture by the product is a consideration of major importance to the processor due to the intimate relationship between the product moisture content and susceptibility to spoilage. The primary reason for removal of water from food systems is the inhibition of microbial growth which may result in enzymatic degradation of fats and proteins or, most importantly, may be of a pathogenic nature so as to pose a threat to public health. However, even if water levels are reduced to a point where microbial activity is unlikely, there are other spoilage mechanisms which are not necessarily dangerous to health but which may adversely affect the food in terms of nutritional

value, functional properties and attractiveness to the consumer. Such mechanisms include non-enzymatic browning, hydrolysis of fats and sugars, oxidation of unsaturated fats and enzymatic degradation of nutrient and structural components of the food product. On a simpler scale, moisture exchange through a package can result in staling of foods in which moisture content is responsible for the characteristic textures and mouth feel that we associate with these stale products.

Traditionally, protection against environmental exchange was built into the package ultimately reaching the consumer. It is an intent of this thesis to examine the concept of barrier placement upon the packaging system in terms of moisture protection. The approach taken here is that it may be more economical to use a superior barrier material to overwrap several consumer packages rather than using the better (and more expensive) barrier in each small package, since the total surface area of many small packages would be greater than the surface area of the overwrap. As a practical application, one might consider the overwrapping of pallets or unitizing multipacks in an effort to reduce costs. This concept of pallet-level protection is further supported by the fact that extremes of temperature and humidity will most likely be encountered when the product is on the pallet (such as warehousing and shipping) rather than on the retail shelf or in the consumer's home. Also the product spends more time on the pallet than it does as a primary package in the store or home.

In addition to examining the placement of barrier materials, this experiment also intends to attempt a calculation of moisture gain based upon a knowledge of the variables of the simulated system in an effort to predict package performance. Traditional methods of system simulation have involved the use of actual field testing of the product/package or the accelerated technique which involves exposure of the system to conditions of high temperature and relative humidity. However, the time and expense involved in field testing and the questionable accuracy of the accelerated test make them of limited value in predicting the performance of a particular system.

In light of these facts, system simulation would be a valuable tool in packaging system development. This method not only gives a rapid and relatively inexpensive view of the performance of a package, but also offers increased flexibility in design since several alternative systems can simultaneously be evaluated, thus allowing the selection of the package that is best suited to the requirements of your operation.

LITERATURE REVIEW

Prediction of the shelf life of a product is important to a packager since the success of that product requires that it be presented to the consumer in a safe, nutritious and attractive form. Also, recent years have seen an increasing demand by consumer and regulatory agencies for fresh dating many food items. Viewed in this light, knowledge of shelf life is important in the product marketing effort since the open dating reduces consumer risk. Shelf life data is also of importance to the manufacturer for economic reasons too. A product which is inadequately protected may be subject to chargeback by grocers, recall by government agencies or loss of consumer confidence. Conversely, an over protected product is also undesirable since it represents an increased and unnecessary operating cost. Often the reduction of single package cost by only a fraction of a cent can result in significant savings when one considers the tremdendous volume of packages that may be processed in a year's time.

One of the simplest ways of shelf life evaluation is the field test method in which the packaged product is actually sent through the distribution system. Upon completion of this test, the package's ability to protect the product is evaluated and needed alterations in the package properties are made. A major drawback of this method is the high cost of monitoring the

condition of the product and package over widespread areas. Also, the length of time (up to 2 years in some cases) required to perform the test and analyze the results is often too great since short lead times do not allow this amount of time for package development.

The accelerated technique offers an improvement in testing in that it is relatively inexpensive and can be performed in a matter of a few months. Under this method, the package and its contents are subjected to conditions of high temperature and relative humidity and a correlation is drawn between the time spent under these conditions and the time spent under ambient distribution conditions. For example, one might hear a claim that 16 weeks at accelerated conditions is equal to 2 years at normal conditions. This method is based upon the erroneous assumption that these excessive conditions of temperature and humidity equally affect the rate of deteriorative reactions of the product and package. In reality, however, we can expect the product to undergo isothermal changes and the package materials to exhibit reduced levels of performance. This method thus leads to wasteful overpackaging of the product which can result in unnecessary production costs. Labuza et al (1972) found that many prodcuts that were packaged based on these tests were overprotected by a factor of from 10-100 times.

In the past, several investigations have been undertaken in an effort to predict shelf life on the basis of certain properties of the food, package material and package construction.

Oswin (1946) developed a simulation for the prediction of shelf life based upon the absorption of moisture by the food product to a previously determined limit. Felt et al (1946) proposed a more elaborate calculation in which storage life was predicted on the basis of package permeation, product formulation and knowledge of prevailing relative humidity in the locale in which the product was stored.

Salwin and Slawson (1959) provided a foundation for future work by formulating a mathematical model for predicting equilibrium moisture content of individual components of heterogeneous mixtures of dried foods in impermeable containers. Iglesias et al (1979) further developed this concept by constructing a model which allowed prediction of moisture content of these components when packaged in permeable packages.

Most of the early attempts at prediction of shelf life were based upon a dry product's uptake of moisture to some critical level where loss of functional properties such as crispness or flowability caused the product to be deemed unacceptable. While these factors are of considerable importance in product acceptability, it should be noted that it is a very simplistic approach to shelf life termination since food products can undergo spoilage due to several other factors including oxidative, enzymatic and non-enzymatic reactions which may be more limiting to shelf life than the arrival at a critical moisture content. Mizrahi et al (1970a) successfully designed a series of equations

to predict the extent of non-enzymatic browning in freeze-dried cabbage in permeable packages. This model was further expanded (1970b) to improve the accuracy of accelerated testing by allowing extrapolation of product behavior to lower temperatures and humidities based upon knowledge of product reaction kinetics and mass transfer properties of the package. Karel et al (1971) further pursued this concept by designing a mathematical model which allowed accurate correction of package permeability rates as humidity changed.

Prediction of extent of fat oxidation was investigated by Quast et al (1972a) in which oxidative deterioration of potato chips was predicted based on a knowledge of oxygen pressure, extent of oxidation and equilibrium relative humidity. This model was then expanded (1972b) to allow simultaneous prediction of extent of oxidation and moisture gain, since the product's shelf life can be terminated by either phenomenon. This article also points out that when packaging a product which undergoes spoilage by two mechanisms, we ideally desire both reactions to reach their critical level at the same time. Otherwise, the package provides overprotection from one reaction in relation to the other, resulting in uneconomical use of packaging material. Quast and Karel (1973) have further shown how these models can be used to select a packaging film based upon relative rates of deterioration due to oxygen and moisture uptake by potato chips and desired length of shelf life.

A movement in recent years has seen increasing emphasis placed upon the nutrient content of foods and its importance in

the determination of shelf life. Previous indications of shelf life termination have been based on the development of adverse tastes, odors, textures or functional properties of the food. While these considerations are of great importance, growing concern has been focused upon using nutrient and vitamin content as a basis for shelf life determinations. This further complicates shelf life determinations, yet is one which must be addressed by the processor since today's consumers are increasingly demanding proper nutrient quality in addition to good sensory characteristics. Wanniger (1972) developed a model for predicting ascorbic acid (vitamin C) levels in a food product based upon temperature, moisture content and oxygen concentration. Singh et al (1976) developed a model which accurately predicted ascorbic acid loss in a liquid food based upon light transmission and oxygen permeability properties of the package. Riemer and Karel (1977) also have constructed a model for prediction of ascorbic acid levels in dehydrated tomato juice based upon knowledge of the mass transfer characteristics of the package material and the kinetics of the degradative reaction as related to water activity, oxygen concentration and time.

METHOD OF CALCULATION BASED ON SIMULATION

The storage stability of any food product is directly influenced by the moisture content. Ideally moisture content is reduced to some level where microbial activity, oxidation and browning reactions are all at a minimum, thus ensuring maximum shelf life for the product. One attempt at predicting this level applies the adsorption theory of Brunauer, Emmet and Teller to food products. The result of this investigation was the finding by Salwin (1959) that the moisture contents required for maximum stability were in very close agreement with that amount of water which was found to represent a monomolecular layer of water absorbed by the food product. This monolayer may be regarded as a protective film of water that represents a moisture content that is low enough to prevent microbial activity and browning but is high enough to protect the food from attack by oxygen. In truth however, this monolayer is not actually a continuous film of water but instead represents a condition in which reactive adsorption sites on fat, protein and carbohydrate fractions of the food are occupied by water molecules.

It is generally recognized that overall stability of a food product is more closely associated with the water activity (Aw) than with total moisture content. Aw can be expressed as follows: Equation (1) $Aw = \frac{p}{po}$

Where: p = partial pressure of water in the food
po = saturated vapor pressure of water at the
 specified temperature

More simply Aw may be thought of as the relative humidity exhibited by the food and gives some indication of the degree to which water is available for participation in various chemical reactions or for use by microorganisms. In examining food stability it is known that the Aw of a product will give a better indication of which specific spoilage mechanism will predominate than does moisture content. Labuza (1968) and Labuza et al (1970) have reviewed this relationship between Aw and various types of deterioration including lipid oxidation, nonenzymatic browning and microbial spoilage.

If it is assumed that the moisture within a packaged product is in equilibrium with the relative humidity present within the package, moisture content can be determined since m = f(H), where m = the product moisture content and H = the relative humidity (or Aw) within the package. This correlation between m and H for a specific product at a specific temperature can be graphically represented by the sorption isotherm of the product which describes the amount of water held by the product when it has reached equilibrium with the relative humidity of its surroundings. Thus, if the product moisture content is known, the Aw of that product can readily be obtained and vice versa. This relationship is very important in the food industry since accurate determination of Aw is difficult, requiring the use of delicate manometric equipment while moisture content can be easily determined by several For purposes of calculation of moisture content, if a straight methods. line can be fitted to the curve of the isotherm the relationship between m and H can be expressed as follows:

Equation (2)

 $m = a + b \cdot H$

Where: m = equilibrium moisture content

a = y intercept of the line

b = slope of the line

H = equilibrium relative humidity

Labuza (1968) has reviewed the methods available for constructing isotherms and various equations for describing isotherms have been presented by Labuza (1968) with further reviews given by Iglesias and Chirife (1976), Chirife and Iglesias (1978) and Boquet, Chirife and Iglesias (1978).

The permeation of water vapor through a polymeric packaging material can be described by Fick's First Law of Diffusion and Henry's Law of Solubility and depends upon the concentration gradient that exists across the film. A well known equation to describe this permeation through a plastic film is given by Felt et al (1945): Equation (3)

$$W = R \cdot A \cdot T \cdot (pi - po)$$

Where: W = the weight of water transferred
R = the permeance of the barrier material, weight
 of moisture per area per unit of time per unit
 of vapor pressure difference
A = permeable area of the package
T = time
pi= vapor pressure of higher humidity atmosphere
po= vapor pressure of lower humidity atmosphere

For this investigation a similar equation was used having the form:

Equation (4)

$$\frac{dQ}{dt} = P \cdot A \cdot \frac{ps}{100} \cdot (He - Hi)$$

Where: Q = quantity of water transferred, g
t = time, hrs.
P = permeance of the film, g/cm² hrs ▲atm
A = area of package, cm²
ps = saturated vapor pressure at the temperature of
interest, atm
He = external relative humidity, percent
Hi = internal relative humidity, percent

Equation (4) is useful only in the calculation of moisture permeation through a single wall and the study requires that moisture transfer through two walls be calculated. In beginning this experiment, a series of smaller packages was overwrapped with another material resulting in packages within a package. Due to practical limitations however, it was impossible to obtain the weight of each individual package within the larger package. However, since the inner packages are all nearly identical in terms of fill weight, headspace and surface area, they can be treated as a single package by multiplying each of these values by the number of packages within the larger package. Therefore, there are three relative humidities of interest:

Hi = relative humidity of the innermost package
Hb = relative humidity between the inner and outer
package

He = relative humidity of the external environment When calculating the moisture gain of the product, the amount of water which will penetrate the innermost package, A, must be known. This value can be obtained by the following equation: Equation (5)

$$Q_A = P_A \cdot A_A \cdot \frac{ps}{100} \cdot (Hb-Hi) \cdot t$$

Where: Q_A = the quantity of water that penetrates package A, g P_A = permeance of the material of package A, g/cm²·time.∆atm A_A = area of package A, cm² ps = saturated vapor pressure at the temperature of interest, atm Hb = relative humidity between the walls of packages A and B, percent Hi = relative humidity inside package A, percent ∆t = the time, hrs.

Next an expression must be found which describes the amount of water that will penetrate package B, the outer package. This expresion must also take into account that even though there is passage of water vapor through package B into the headspace between the packages, there is a simultaneous loss of moisture from this headspace as a certain amount of water is passing into package A. This equation must describe the net amount of water passing into the headspace between the packages during the time step, Δt , and can be represented as follows: Equation (6)

$$Q_B = P_B \cdot A_B \cdot \frac{ps}{100} \cdot (He - Hb) \cdot \Delta t - \Delta Q_A$$

Where: Q_B = the quantity of water that penetrates package B, g

- P_B = permeance of the material of package B, g/cm².time. Δ atm
- A_B = area of package B, cm²
- He = external relative humidity, percent
- Hb = relative humidity between the walls of packages A and B, percent

 Δt = the time, hrs.

 ΔQ_A = the quantity of water that penetrates package A, g

In equations (5) and (6) the interval of interest is referred to as Δt or the time step. During this interval it is assumed that conditions of equilibrium exist within the packages and so Δt must be very small if this assumption is to be correct. This point is of great importance in the calculation since the new equilibrium relative humidities are used to calculate ΔQ_A and ΔQ_B for the next time step. If these relative humidities do not represent equilibrium conditions, then all subsequent calculations would be incorrect since the humidities would not be constant during the time step. It is for these reasons that Δt must be very small since the accuracy of the calculation increases as Δt decreases.

Now that the quantities of vapor that pass through the packages are known, the relative humidities Hi and Hb must be calculated since these are the only unknowns in equations (5) and (6), assuming that He is constant. In package A which contains the product, the total moisture within the package at time = 0 can be expressed by the following equation:

Equation (7)

$Mo = M_P + M_H$

Where: Mo = total moisture in the package at time = 0, g M_p = total moisture in the product, g M_H = total moisture in the headspace, g

Since the initial moisture content of the product is known in terms of grams of water per hundred grams of dry product matter, the total product moisture, Mp, can be determined by the following expression:

Equation (8)

$$M_{\rm P} = \frac{\rm m \cdot \rm D}{100}$$

Where: m = moisture content of the product, g water/100g dry matter

D = weight of dry material in the product, g

The weight of water in the headspace, M_H , can be calculated by using the ideal gas law as shown in the next equation. (It should be noted that water is not an ideal gas but for purposes of this calculation it can be considered as one without significant error). Equation (9)

$$P \cdot V = n \cdot R \cdot T$$

Where: P = pressure, atm
V = volume, cm³
n = number of moles
R = the Regnard gas constant, atm⋅cm³/degrees K
T = temperature, degrees Kelvin

Substitution into this equation will make it more useful for this calculation since grams of water instead of moles and relative humidity instead of pressure in atmospheres are required in this case. The expression of n, number of moles, may be expressed by equation (10): Equation (10)

$$n = \frac{M}{18}$$

Where: M = weight of water, g

18= molecular weight of water, g/mole

Similarly, pressure, P, may be converted from atmospheres to relative humidity according to equation (11):

Equation (11)

$$P = \frac{ps}{100} \cdot H$$

Where: P = pressure, atm
ps = saturated vapor pressure at the temperature of
 interest, atm
H = relative humidity, percent

Substituting equation (10) and (11) into equation (9) allows (9) to be rewritten:

Equation (12)

$$\frac{\text{ps} \cdot \text{H}}{100} \cdot \text{V} = \frac{\text{M}}{18} \cdot \text{R} \cdot \text{T}$$

Where: ps = saturated vapor pressure at the temperature of interest, atm

H = relative humidity, percent = Hi

 $V = headspace volume, cm^3$

M = the weight of water in the headspace, g

18 = molecular weight of water, g/mole

R = the Regnard gas constant, $atm \cdot cm^3/degrees$ Kelvin

T = temperature, degrees Kelvin

Equation (12) can then be rearranged to a form more useful to this calculation.

Equation (13)

$$M = \frac{18 \cdot ps \cdot H \cdot V}{100 \cdot R \cdot T}$$

Substituting equations (13) and (8) into equation (7) results in an expression which solves for the sum of the water in the headspace of the package and that in the product at t = 0: Equation (14)

$$M_{O} = \frac{m \cdot D}{100} + \frac{18 \cdot ps \cdot H \cdot V}{100 \cdot R \cdot T}$$

Next, the permeation of water into package A during the first time step, Δt , must be determined as shown by equation (15):

Equation (15)

Where: $M(\Delta t)$ = the water in package A at the end of the time step, g

Mo = the water in package A at t = 0, g
Q_A = the quantity of water that penetrates package A during the time step **\Delta**t,g

Since $M(\Delta t)$, the weight of water in the package, is known and equilibrium conditions are assumbed to exist between the product and the headspace due to the small time step, the humidity inside package A and the new product moisture content must now be determined. To calculate the humidity, an equation is needed which relates the weight of water in package A to the humidity in A, such as equation (14). There is a need for a slight modification of this expression which will allow the determination of the relative humidity (or Aw) exhibited by the product instead of its moisture content, m. This conversion of relative humidity to moisture content can easily be made by using equation (2), the sorption isotherm of the product which relates moisture content and relative humidity.

In constructing the isotherm, it was found that a straight line could be fitted to this curve in the area of interest, thus allowing conversion between moisture content and equilibrium relative humidity. Incorporating equation (2) into equation (14), the following expression is obtained:

Equation (16)
$$M(\Delta t) = \frac{(a+bHi(\Delta t))\cdot D}{100} + \frac{18\cdot V \cdot ps \cdot Hi(\Delta t)}{R \cdot T \cdot 100}$$

Rearranging and solving for the humidity within the package, Hi, gives a form more convenient for the purposes of this calculation: Equation (17)

$$Hi(\Delta t) = \frac{M - \frac{a \cdot D}{100}}{\frac{b \cdot D}{100} + \frac{18 \cdot V \cdot ps}{R \cdot T \cdot 100}}$$

Now that $Hi(\Delta t)$ inside package A is known, the isotherm equation (2) can be used to determine the moisture content of the product at Δt . The only step remaining is to calculate the relative humidity between packages A and B. The weight of water in the headspace between the package at Δt may be expressed by the equation: Equation (18)

$$M_{R}(\Delta t) = M_{R} + Q_{R}$$

Where: $M_B(\Delta t) =$ the amount of water in the headspace between the packages at the end of the time step, g $M_B =$ the amount of water in the headspace between the packages at t = 0, g $Q_B =$ the quantity of water that penetrates package B during the time step Δt , g

Equation (13) can now be solved for H using the headspace volume of package B for "V" and $M_B(\Delta t)$ for "M" in the equation.

The entire calculation of moisture content requires the use of only 3 simple equations (2, 13 and 17). During the time steps, Δt , moisture will penetrate the packages, causing changes in the internal relative humidity conditions of each package. By using very small time steps and assuming that the product is in equilibrium with the relative humidity inside package A, the changes in moisture content of that product can be calculated as can changes in the relative humidities in both packages A and B. These new (Δt) relative humidities can in turn be used to calculate moisture gain for the next time step based upon the change in partial pressure differences.

EXPERIMENTAL DESIGN

The first requirement of this experiment was to find a dry product which, due to its hygroscopic nature, required some form of barrier protection to maintain quality. After examining the sorption isotherms of several commercially available dry products, a non-fat dry milk (NFDM) powder and a dry breakfast cereal product were selected. For the purposes of this test, it was assumed that the shelf life of the product depended only upon moisture content, although no specific limit was specified since the test is concerned only with the rate of moisture uptake.

Since certain unique variables and design features were required for this investigation, it was necessary to construct a packaging system using handmade packages from films of varying water vapor transmission characteristics. The test called for one film with "excellent" water barrier properties, another which exhibited "medium" properties and a third material which was a "poor" barrier to water vapor. It was found that the three films which met these conditions were 1 mil saran (polyvinyldene chloride), 1 mil high-density polyethylene and 1 mil polystyrene respectively. These films were then used to make a series of small pouches in which the product was sealed and a series of larger pouches which were used to overwrap a group of the smaller packages such that all practical combinations of inner and over-packages were represented (see Figure 1). It should be noted, however, that a saran/saran and a polystyrene/polystyrene combination

were not used. It was decided that these two combinations would result in a system that absorbed water vapor much too slowly in the case of the saran/saran and much too rapidly in the case of the polystyrene/ polystyrene to be of use in comparison with the other combinations.

For convenience, the films saran, polyethylene and polystyrene will hereafter be referred to as S, PE and PS, respectively, and combinations expressed as overwrap/inner package.



Overwrap/Inner Package Combinations Used To Obtain Experimental Data

Originally, the experiment was to be based on an actual miniature version of a pallet in which many small packages were to be overwrapped and then opened at predetermined intervals. This approach proved impractical due to the limited space available in the laboratory and the need to destroy a pallet at each weighing. To overcome this difficulty, a non-destructive method was developed in which each of the inner and overwrap packages were weighed accurately and then filled. The nonfat dry milk was filled volumetrically while the cereal product was filled by count. Net product weight was then determined by subtracting the weight of each of the packages from the total weight of one overwrapped unit. Under this system the individual small packages within the overwrap are treated as one large package for purposes of calculation.

After filling and sealing, the overwrapped packages were suspended from wire hangers in racks as shown in Figure 2 so as to prevent any contact with other packages or parts of the racks which would in effect reduce their surface area.





Method of Suspending Packages for Weight Gain Studies

In determining moisture content by calculation, certain parameters of the packaging system must be known including sorption isotherm of the product, initial moisture content of the product, area of packages, permeability constant of each packaging material, package fill weight and headspace volumes. Following is a description of how each of these values was determined.

Initial Moisture Content

One of the most common analytical determinations performed upon any food product is that of moisture analysis. Literature reports a number of methods for arriving at the moisture content, some of which are chemical in nature while others rely upon physical properties. For this experiment, the vacuum oven method was selected due to its wide acceptance and use in the food industry. Four samples of each product, each containing approximately 2 grams, were placed in a vacuum oven at 100°C for 5 hours, with the weight loss reported as the weight of water. All moisture contents are expressed on a dry basis of grams water/100 grams dry product. It should be noted that initial moisture content of each product was redetermined prior to each portion of the experiment due to the fact that all tests were not run simultaneously. Results are reported in Table 1.

Construction of Sorption Isotherms

The sorption isotherm of any food product may be most simply expressed as a plot of the equilibrium moisture content as a function of the relative humidity of the environment surrounding the food at one specific temperature. There are two basic methods available to obtain the information needed to construct this plot and a summary of these procedures has been presented by Taylor (1961).

The first approach involves drying the food to remove all moisture then adding back water until a predetermined moisture content is reached. The vapor pressure exhibited by the food at this moisture content is then determined by manometric equipment. However, the difficulty in adjusting moisture content to the precise level of interest and the delicate procedures required to assure that only the vapor pressure of water is measured make this method impractical.

The second method involves placing the food in a sealed container containing a saturated salt solution which gives a specific relative humidity. The food (of known initial weight) is then weighed periodically until there is no change due to water gain or loss, and the moisture content at equilibrium is then calculated. Numerous
	<u>Cereal</u>	NFDM
Moisture content for isotherms (g moisture/100g dry matter)	1.96	3.01
Moisture content for test @ 75 ⁰ F/50%RH (g moisture/100g dry matter)	1.78	2.87
Moisture content for test @ 100 ⁰ F/85%RH (g moisture/100g dry matter)	1.80	2.97

Table 1 Initial Product Moisture Contents¹

¹Mean determination of four samples.

	Relative Hu	umidity, %
Salt Solutions	750F	100 ⁰ F
LiC1	11.1	11.8
к ₂ с ₂ н ₂ он	22.9	22.0
MgCl ₂	32.8	32.8
к ₂ со ₃	43.8	43.5
Mg(NO ₃) ₂	53.1	52.0
NaNO ₂	64.5	63.3

Table 2 Salt Solutions and Relative Humidities at $75^{\rm O}F$ and $100^{\rm O}F$

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book writing divides easily into three large categories: price, and jungle adventue stories. Of the first he "W Berny - attacker, hut, alry, norable, hypers, of stories an entry heating. Note also the emphasis upon the of the work. It must deal with the activities of ed in a compariso boy covered by the category, not of a single presen.

	Equilibrium Moi (g moisture/100	isture Content Og dry matter)
Relative Humidity, %	Cereal	NFDM
11.8 22.0 32.8 43.5 52.0 63.3	2.39 2.90 3.37 4.20 4.74 6.63	3.27 3.98 5.08 6.40 6.87 8.78

Table 3 Equilibrium Moisture Content vs. Relative Humidity at 100⁰F¹

¹Mean determination of four samples.

Table 4 Equilibrium Moisture Content vs. Relative Humidity at 75^oF¹

	Equilibrium Mo (g_moisture/100	isture Content Og dry matter)
Relative Humidity, %	Cereal	NFDM
11.1 22.9 32.8 43.8 53.1 64.5	2.36 3.33 4.31 4.97 5.79 7.57	3.01 3.88 5.40 7.27 8.68 10.56

¹Mean determination of four samples.

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Relative Humidity, %	Cereal	NFDM
11.8 22.0 32.8 43.5 52.0 63.3	2.39 2.90 3.37 4.20 4.74 6.63	3.27 3.98 5.08 6.40 6.87 8.78

Table 3 Equilibrium Moisture Content vs. Relative Humidity at $100^{\circ}F^{1}$

¹Mean determination of four samples.

Table 4 Equilibrium Moisture Content vs. Relative Humidity at 75⁰F¹

	Equilibrium Mo (g_moisture/100	isture Content Og dry matter)
Relative Humidity, %	Cereal	NFDM
11.1 22.9 32.8 43.8 53.1 64.5	2.36 3.33 4.31 4.97 5.79 7.57	3.01 3.88 5.40 7.27 8.68 10.56

¹Mean determination of four samples.





sources are available describing the relative humidities of various saturated salt solutions. Since the equipment for this method was readily available, it was chosen for the determination of the sorption isotherms.

Samples of approximately 2 grams were placed in small aluminum weighing dishes and placed in a sealed bucket containing a saturated salt solution. The samples were then weighed periodically until each showed a constant weight at which time their moisture content was calculated and expressed as grams of water/100 grams dry product. Product isotherms were constructed at 75°F and 100°F using the salt solutions and respective relative humidities shown in Table 2. Construction of Packages

The pouches used in this experiment were constructed from roll stock of saran, polyethylene and polystyrene. In order to assure uniform size, a paperboard template of proper size was used for each package size to assure uniformity of surface area. The film was then heat sealed by the impulse method, the package trimmed of excess material, labeled and accurately weighed. The pouches were periodically inspected under polarized light to evaluate uniformity of seal quality; however, all pouches could not be examined due to the large number involved. Packages were sealed after filling in the same manner. Surface area of the packages was obtained by measuring the filled, sealed pouch along the sealed edges. A random sampling of ten pouches of each size used showed acceptable ($\pm 5\%$) dimensional uniformity was obtained using this method.

Package Fill Weight

The fill weight of each overwrapped unit was obtained by

Table 5 Experimental Design of Package System Specifications

Package	Surface Area, cm ²	<u>Headspace, cm³</u>	Target Fill Wt., g
NFDM Inner Pouch	100	7	10
NFDM Overwrap	175	37	;
Cereal Inner Pouch	255	20	12
Cereal Outer Pouch	300	80	:

subtracting the weight of the empty packages from the weight of the filled packages.

Package Headspace Volume

Calculation of headspace volume of flexible packages is extremely difficult due to the lack of three stable dimensions upon which to base the calculation. It should also be noted that even if headspace could be accurately calculated, the flexible nature of the package will cause changes in the headspace volume as the film bends and the product shifts within the package.

For the purposes of this investigation, the headspace volume of the packages was estimated based upon the dimensions of the filled packages. An attempt was made to determine headspace using CO_2 gas dilution in which the CO_2 concentration of the headspace is determined by gas liquid chromatography. In this procedure, an initial measurement is made of CO_2 in the headspace. Next, a known volume of CO_2 is injected into the headspace and allowed to equilibrate with the gases in the headspace after which time another sample is taken and the CO_2 concentration is again measured. Headspace volume can then be determined using the following equation:

$$V = \frac{(V_A \times 100)}{(0_2 - 0_1)}$$

Where: V = headspace volume, cm^3 V_A = volume of CO_2 added, cm^3 O_2 = % CO_2 after injection and equilibration O_1 = % CO_2 before injection and equilibration However, due to film permeability and the flexibility of the packages, this method did not allow accurate or repeatable results.

Another technique based upon Archimedes Principle, the Combined Gas Law and Boyles Law was also tried. This procedure requires the determination of the weight of the package in water and the pressure at which the package has no weight when it is immersed in water. Once these values are determined, the following equation can be used:

$$V = (\frac{P_2}{P_1 - P_2}) (\frac{W}{PH_20})$$

Where: $V = headspace volume, cm^3$ P_1 = room barometric pressure, mm Hg P_2 = pressure at which package weight = 0, mm Hg w = weight of package in water at P_1 , gm pH_20 = density of water = q/cm^3

However, due to the small size of the packages and the small headspaces involved in this system, it was found that this technique was also unsuitable.

For the purposes of this investigation, the headspace volume of the packages was estimated based upon the dimensions of the filled and sealed packages without adversely affecting the outcome of the calculation. As can be seen in the equations used to calculate the relative humidities between the two packages (13) and within the innermost package (17)

Equation (13)

$$H = \frac{M \cdot 100 \cdot R \cdot T}{18 \cdot ps \cdot V}$$

Equation (17)

$$Hi(\Delta t) = \frac{M - \frac{a \cdot D}{100}}{\frac{b \cdot D}{100} + \frac{18 \cdot V \cdot ps}{R \cdot T \cdot 100}}$$

the headspace value, V, is a very small part of the overall calculation. Also, in both cases the numerical value of V is very small relative to the value of the other variables in the equations. For example, in Equation (17) the value of the quantity " $R \cdot T \cdot 100$ " is over 2 million. This equation also shows that as the product dry weight (D) increases relative to the headspace, the less critical the headspace value becomes. This is especially true in the case of a dry product since the product would act as a sink for any moisture in the headspace.

In order to verify these assumptions that headspace values will have little effect upon the calculated relative humidities, a program was run in which the estimated headspace values were doubled and halved, then put into the calculation so that all possible combinations were represented. It was found that the relative humidities calculated with the altered headspace values were identical to each other to three significant places.

Water Vapor Transmission Rate

The water vapor transmission rate for the 3 film samples was determined by ASTM Method E-96, which describes the testing of flat film samples. Values for all samples were determined at $75^{\circ}F$ at 50%RH and $100^{\circ}F$ at 85%RH.

Experimental Test Conditions

In conducting the experimental portion of this investigation, two temperature/relative humidity conditions were used for each product. An environment of 100° F at 85%RH was maintained in a walk-in chamber while a controlled laboratory atmosphere of 75°F at 50%RH was used for the other condition. Samples of packages representing each

film combination for each product were weighed to determine initial weight before being subjected to the controlled environments. The samples at 75^oF/50%RH were then weighed every 3 days to determine weight gain while those at 100^oF/85%RH were checked each day due to an increased rate of moisture gain.

Determination of Experimental Moisture Content vs. Time

Since the experimental data gathering is designed only to record package weight gain vs. time, this change in weight must be converted to change in moisture content, based upon a knowledge of the initial moisture content (dry basis) of the product and the weight of the filled package and empty package at t=0. The weight of dry material in any given sample of a product of known initial moisture content may be given by the formula

$$D = \frac{W}{1 + \frac{mi}{100}}$$

Where: W = product weight, g
mi = initial moisture content of the product, g
water/100g dry product
D = weight of dry matter, g

Thus, if the weight of the dry matter in the package is known, the new moisture content, m(t+at), can be calculated using the following expression:

$$m(t+at) = \frac{W(t+at) - D}{D} \times 100$$

Where: $m(t+at) =$ the moisture content at $(t+at)$, g water/
100g dry product
 $W(t+at) =$ the product weight at $(t+t)$, g
D = the weight of dry matter in the product, g

Determination of Water Vapor Permeance of Films

Water vapor permeance for the films used in this study is based upon water vapor transmission rates (WVTR) obtained by ASTM Method E-96 which describes the testing of flat film samples by the dish method and reports in units of g water . This value is then $cm^2 \cdot hr$ corrected to account for the partial pressure difference, in atmospheres, that exists across the film based upon knowledge of the temperature and relative humidity of the test conditions. This partial pressure difference can be calculated using the following formula:

 $\Delta p = ps$ (He-Hi)

Where: $\triangle p$ = partial pressure difference, atmospheres

- ps = saturated vapor pressure at temperature of interest, atmospheres
- He = external relative humidity, percent
- Hi = internal relative humidity, percent

The permeance of the film can then be expressed as follows:

$$P = \frac{g}{cm^2 \cdot hr \cdot \Delta p}$$

Where: P = permeance of the film used in the study g = weight of water vapor transferred, grams cm²= area of the sample, square centimeters hr = time, hours

Ap = partial pressure difference, atmospheres

Determination of Slope and Intercept

The equation describing the sorption isotherm of the products is of great importance in this calculation, since it allows the determination of the moisture content of the product if the relative humidity within the package is known. A straight line having the equation

	WVTR (g/c	m ² · hr.)
Film	<u>750F/50%RH</u>	100 ⁰ F/85%RH
Saran	1.279 X 10 ⁻⁶	1.374 X 10 ⁻⁵
Polyethylene	8.648 X 10 ⁻⁶	7.198 X 10 ⁻⁵
Polystyrene	9.586 X 10 ⁻⁵	4.138 X 10 ⁻⁴

Table 6 Water Vapor Transmission Rates of Films

Table 7 Water Vapor Permeance of Films

	g cm ² · hr.	. • ∆atm
Film	75 ⁰ F/50%RH	100 ⁰ F/85%RH
Saran	8.753 X 10 ⁻⁵	2.498 X 10 ⁻⁴
Polyethylene	5.915 X 10 ⁻⁴	1.309 X 10 ⁻³
Polystyrene	6.556 X 10 ⁻³	7.527 X 10 ⁻³

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form

m = a+bH

may be fitted to the isotherm by several methods. For this investigation, it was found that the isotherms for both products could be fitted by a straight line in the area of interest with good agreement. Results are shown in Table 8.

Table 8 Least Square Regression of Slope and Intercept of Isotherm Parameters

Product	Temperature, ^O F	Slope	Intercept	
Non-Fat Dry Milk	75	0.146	0.90	
Non-Fat Dry Milk	100	0.104	1.78	
Cereal	75	0.095	1.13	
Cereal	100	0.076	1.14	

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RESULTS AND DISCUSSION

In examining the results of this experiment it seems that the placement of barrier materials affects the level of moisture protection afforded by a given packaging system of an overwrapped set of smaller pouches. The results in Tables 11-14 show that for any combination of films, the best moisture barrier properties (that is lower moisture content at the end of the investigation) occur when the more impermeable film composes the inner pouch with the poorer barrier as the overwrap. For example, a PS/PE combination gave superior performance in comparison to the PE/PS system for both products at both conditions. Similar results can be seen for other combinations.

This result can be explained by the humidity differences that exist in the package system and their significance in determining moisture transfer as described by Equations 4 and 5. As we can see from Figure 5 there are three humidities of interest in this particular packaging system. For purposes of illustration, let us assume that



External Humidity

Figure 5 Packaging and Humidity Variables of the Packaging System

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Package A contains a perfectly dry (0%RH) product and that the External Humidity is greater than or equal to Humidity B so that certain partial pressure differences exist. The External Relative Humidity is assumed constant. Therefore, when Package A is made of a highly permeable material and Package B is of a very low permeability, we expect that there will be a transfer of moisture into Package A due to the partial pressure differences of Humidity A and B. This condition results in an increase in Humidity A (and the product moisture content) and a decrease in Humidity B relative to their initial values. This decrease in Humidity B consequently results in an increase in the partial pressure difference between the External Humidity and Humidity B. If we use a very small time step and assume equilibrium at the end of each step, we would then expect that this difference would result in the transfer of moisture across Package B which would in turn increase Humidity B. This would then re-establish a partial pressure difference between Humidity A and B which would again result in the passage of moisture across Package A. Recalling in the illustration that Package A is a poor barrier to water vapor and Package B is a good barrier, it can be seen that for any given time step sequence a rapid transfer of moisture would be observed across Package A due to the partial pressure difference between Humidities A and B. This would consequently result in a reduction in Humidity B and the establishment of new partial pressure difference between the External Humidity and Humidity B. Therefore, with this combination of films we expect any water vapor passing through Package B to quickly find its way into Package A via the sequence of events described above.

In examining the opposite case when Package A is composed of

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the superior barrier and Package B of the inferior material, several points become evident which explain why less moisture is transferred to the product. Again, it will be assumed that Package A contains a perfectly dry product and that neither Humidity B nor the External Relative Humidity is zero. The sequence of moisture transfer and humidity changes are basically the same; however, the relative rates at which they occur are different than those described earlier. Because Package A is a better barrier in this case, there is much less moisture transferred to the product. Because of this, Humidity B is reduced very slowly so that the partial pressure difference between B and the External Humidity is very small. This results in a reduced rate of moisture transfer across Package B (as described by Equation 5) and a subsequently reduced rate of overall water vapor transferred into the package.

Table 9 shows these results as calculated for the simulation in the case of the PS/S system which represents a good barrier material overwrapped by a poor one. As can be seen, the humidity between the packages (Humidity B) has changed very little from its initial value of 50%, and the value of the relative humidity within the package has gone only to a level of 21.54%. Conversely, in the case of a poor barrier overwrapped by a good one (as represented in Table 9 by the S/PS system), it can be seen that the humidity between the packages has dropped rapidly after the first 3 day interval and then rises slowly but always maintains a larger humidity. (Humidity A) rises more rapidly and to a higher level than in the PS/S system, thus accounting for the higher moisture levels found when the superior barrier material forms the overwrap.

		ystem as kelated to Flim For Non-Fat Dry Milk at J	Lombination 750F, 50%RH	
	Saran/Po	lystyrene	Polystyre	ne/Saran
Time, Days	Humidity Inside Inner Pkg., %	Humidity Between Packages, %	Humidity Inside Inner Pkg., %	Humidity Between Packages, %
0	8.41	50.0	8.41	50.0
с	11.03	11.91	10.26	49.70
9	12.71	13.56	11.26	49.71
6	14.33	15.14	12.24	49.71
12	15.87	16.65	13.20	49.72
15	17.35	18.08	14.14	49.73
18	18.76	19.47	15.05	49.74
21	20.11	20.79	15.93	49.74
24	21.40	22.05	16.80	49.75
27	22.64	23.26	17.63	49.75
30	23.82	24.42	18.46	49.76
33	24.95	25.53	19.26	49.77
36	25.48	26.04	20.04	49.77
39	25.96	26.52	20.80	49.78
42	26.45	26.98	21.54	49.78

Table 9 Humidities of the Package System as Related to Film Combination

In the case of industrial applications of the concept of barrier placement in pallet loads and unit packs, economics and conditions unique to the system in question may dictate a change in the location of barrier films. In this investigation, the ratio of the surface area of the inner package:overwrap was approximately .60:1 in the case of the dried milk and .85:1 in the case of the cereal product. However, with commercial applications, the total surface area of the smaller packages would be greater than the area of the overwrap. Consider as an example a hypothetical system consisting of a cylindrical package 8 cm in diameter and 10 cm in height with a surface area of 351 cm^2 . If arranged 4x4x1 on a pallet, these sixteen cylinders would have a total surface area of 5616 cm^2 , but the surface area of the material needed to overwrap these containers is only 3328 cm^2 , or an inner package:overwrap area ratio of approximately 1.7:1. As more layers to be overwrapped are added (e.g. a 4x4x3 configuration), the ratio will increase since the area of the inner packages will increase at a faster rate than the area of the overwrap. Therefore, even though slightly increased levels of moisture permeation are experienced when overwrapping a relatively poor barrier with a good one, these ratios and the relative cost of the two films may result in a total system savings which might justify some reduction in shelf life due to moisture uptake.

In comparing the experimental and calculated values for moisture content vs. time (Tables 11-14), it can be seen that the calculated results are in good agreement with those determined experimentally. The difference between these values for each product and condition at the end of the test period can be found in Table 10. To further

	Moisture Data
	Final
01	Experimental
ble	and
Ta	Calculated
	Between
	Difference
	%

(Mcalc - Mexp)	Mexp

			Package	Film Combi	ination		
Product/Condition	PS/PE	PS/S	PE/PS	PE/PE	PE/S	S/PS	S/PE
Now Fat Duri Mill / 7505 - 500							
NULL FAL UTY MILK//201; SUK KHI	1.49	8.00	4.60	7.71	5.98	7.06	11.14
Drv Cereal/750F: 50% RH1	0 0	טר ער	10 60	, v ,			
	+	14.17	10.03	0.43	12.50	4.86	12.99
Non Fat Drv Milk/1000F· R5% PH2	7 7 E	2 N C	20.0	ί Γ			
	0/./	06.0	9.07	06.21	4.50	10.46	9.84
Nrv Carcal/10005. 05% Du2			C T T	() () () ()		1	
UJ CCICAI/TOCI , 03% MT	4.32	10.90	4./8	11.30	11.75	9.72	10.41

l After 42 days 2 After 4 days

Table 11

Moisture Content (d.b.%) vs Time

				No	n-Fat [Dry Milk	:: 75°F,	50% R.	Ŧ					
	PS/PE		PS/S		PE/PS		PE/PE		PE/S		S/PS		S/PE	
Time, days	Exp.1	<u>Calc²</u>	Exp.	Calc	Exp.	Calc	Exp.	Calc	Exp.	Calc	Exp.	<u>Calc</u>	Exp.	<u>Calc</u>
ю	3.30	3.33	2.91	2.94	3.58	3.57	3.16	3.18	2.91	2.84	3.01	3.00	2.96	2.98
9	3.58	3.72	2.96	3.02	4.00	4.24	3.38	3.47	2.97	3.01	3.14	3.13	3.04	3.08
6	3.85	4.18	3.02	3.09	4.37	4.69	3.57	3.72	3.02	3.08	3.23	3.25	3.10	3.17
12	4.16	4.48	3.08	3.16	4.78	5.09	3.80	3.95	3.08	3.14	3.35	3.36	3.19	3.27
15	4.41	4.75	3.12	3.23	5.11	5.44	3.98	4.29	3.13	3.21	3.45	3.47	3.26	3.37
18	4.65	5.00	3.17	3.30	5.40	5.76	4.16	4.48	3.17	3.27	3.53	3.57	3.32	3.46
21	4.87	5.24	3.21	3.37	5.67	6.04	4.33	4.67	3.21	3.33	3.61	3.67	3.38	3.54
24	5.20	5.45	3.37	3.43	6.04	6.28	4.62	4.84	3.38	3.39	3.79	3.77	3.54	3.62
27	5.25	5.66	3.28	3.49	6.11	6.50	4.63	5.01	3.29	3.45	3.74	3.86	3.49	3.70
30	5.42	5.84	3.32	3.55	6.31	6.70	4.78	5.17	3.33	3.50	3.84	3.95	3.54	3.78
33	5.58	6.01	3.37	3.61	5.50	6.87	4.93	5.32	3.38	3.56	3.90	4.03	3.60	3.85
36	5.73	6.17	3.40	3.67	6.66	7.02	5.07	5.46	3.43	3.62	3.98	4.24	3.66	3.92
39	5.79	6.32	3.37	3.72	6.71	7.16	5.10	5.60	3.37	3.67	3.95	4.32	3.62	3.99
42	6.01	6.46	3.50	3.78	6.95	7.27	5.32	5.73	3.51	3.72	4.11	4.40	3.77	4.19
10btained ex 20btained by	xperiment / calcula	cally ation												

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| Table <b>12</b> |  |
|-----------------|--|
| • •             |  |

Moisture Content (d.b. ) vs Time

|            |       |                         |        | Dry   | Ûereal | Product | : 75`F, | 50°. R. | T            |      |      |      |      |      |
|------------|-------|-------------------------|--------|-------|--------|---------|---------|---------|--------------|------|------|------|------|------|
|            | PS/PE |                         | PS/S   |       | FL/PS  |         | FE.PE   |         | <u>PF /S</u> |      | /PS  |      | S/PE |      |
| Time, Days | Exp.1 | <u>calc<sup>2</sup></u> | Exp.   | Calc  | Exp.   | Calc    | Exp.    | Calc    | Exp_         | Calc | Exp. | Calc | Exp. | Calc |
| ю          | 2.49  | 2.65                    | 1.90   | 1.93  | 2.67   | 2.76    | 2.23    | 2.31    |              | 1.92 | 1.95 | 1.96 | 1.89 | 1.94 |
| 9          | 3.05  | 3.34                    | 2.01   | 2.08  | 3.31   | 3.51    | 2.62    | 2.78    | 2.00         | 2.05 | 2.13 | 2.13 | 2.01 | 2.09 |
| 6          | 3.50  | 3.88                    | 2.11   | 2.22  | 3.34   | 4.08    | 2.94    | 3.18    | 2.10         | 2.18 | 2.27 | 2.29 | 2.12 | 2.23 |
| 12         | 3.93  | 4.31                    | 2.22   | 2.35  | 4.34   | 4.51    | 3.26    | 3.53    | 2.20         | 2.30 | 2.41 | 2.45 | 2.23 | 2.36 |
| 15         | 4.24  | 4.64                    | 2.30   | 2.49  | 4.67   | 4.84    | 3.50    | 3.84    | 2.27         | 2.42 | 2.50 | 2.60 | 2.30 | 2.50 |
| 18         | 4.52  | 4.90                    | 2.33   | 2.61  | 4.92   | 5.09    | 3.74    | 4.11    | 2.36         | 2.54 | 2.65 | 2.74 | 2.41 | 2.62 |
| 21         | 4.75  | 5.12                    | 2.49   | 2.73  | 5.09   | 5.28    | 3.93    | 4.34    | 2.41         | 2.65 | 2.75 | 2.87 | 2.49 | 2.75 |
| 24         | 4.98  | 5.28                    | 2.55   | 2.85  | 5.22   | 5.42    | 4.15    | 4.54    | 2.50         | 2.75 | 2.86 | 3.00 | 2.56 | 2.86 |
| 27         | 5.12  | 5.41                    | 2.64   | r. 9. | 5.29   | 5.53    | 4.35    | 4.71    | 2.59         | 2.86 | 2.99 | 3.13 | 2.68 | 2.98 |
| 30         | 5.17  | 5.51                    | 2.70   | 3.07  | 5.27   | 5.62    | 4.50    | 4.87    | 2.66         | 2.96 | 3.08 | 3.25 | 2.74 | 3.08 |
| 33         | 5.18  | 5.59                    | 2.78   | 3.17  | 5.24   | 5.69    | 4.64    | 5.00    | 2.82         | 3.06 | 3.18 | 3.36 | 2.82 | 3.19 |
| 36         | 5.20  | 5.65                    | (1<br> | 3.27  | 5.23   | 5.74    | 4.78    | 5.11    | 2.83         | 3.15 | 3.31 | 3.47 | 2.93 | 3.29 |
| 39         | 5.21  | 5.70                    | 2.96   | 3.37  | 5.23   | 5.77    | 4.89    | 5.22    | 2.89         | 3.24 | 3.41 | 3.57 | 3.01 | 3.39 |
| 42         | 5.23  | 5.75                    | 3.03   | 3.46  | 5.24   | 5.80    | 4.98    | 5.30    | 2.96         | 3.33 | 3.50 | 3.67 | 3.08 | 3.48 |
|            |       |                         |        |       |        |         |         |         |              |      |      |      |      |      |

10btained Experimentally 20btained by Calculation







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|            |       |                   |             | MoT  | isture ( | Content  | (g.p.S)  | ) vs Tin | he   |      |      |      |      |       |
|------------|-------|-------------------|-------------|------|----------|----------|----------|----------|------|------|------|------|------|-------|
|            |       |                   |             | Nor  | r Fat Di | ry Milk: | : 100°F, | 85% R.   | н.   |      | 1    |      |      |       |
|            | PS/PE |                   | <u>bš/S</u> |      | PE/PS    |          | PE/PE    |          | PE/S |      |      |      | S/PE |       |
| Time, days | Exp.1 | Calc <sup>2</sup> | Exp.        | Calc | Exp.     | Calc     | Exp.     | Calc     | Exp. | Calc | Exp. | Calc | Exp. | Ca 1c |
| 1          | 4.16  | 4.25              | 3.24        | 3.25 | 4.58     | 4.79     | 3.70     | 3.89     | 3.17 | 3.23 | 3.34 | 3.45 | 3.25 | 3.35  |
| 2          | 4.72  | 5.32              | 3.40        | 3.53 | 2.24     | 6.18     | 4.1:     | 4.70     | 3.35 | ,48  | 3.56 | 3.89 | 3.43 | 3.71  |
| ĸ          | 5.38  | 6.21              | 3.55        | 3.79 | 6.06     | 7.24     | 4.54     | 5.42     | 3.49 | 3.73 | 3.78 | 4.30 | 3.60 | 4.05  |
| 4          | 6.42  | 6.96              | 3.88        | 4.04 | 7.32     | 8.05     | 5.29     | 6.05     | 3.78 | 3 96 | 4.20 | 4.69 | 3.94 | 4.37  |
| 2          | 7.46  | 7.58              | 4.24        | 4.23 | 8.51     | 8.68     | 6o       | 6.60     | 4.13 | 4.19 | 4.68 | 5.06 | 4.34 | 4.68  |
|            |       |                   |             |      |          | Table    | 14       |          |      |      |      |      |      |       |
|            |       |                   |             | Mo   | isture ( | Content  | (d.b.)   | nil sv ( | é    |      |      |      |      |       |
|            |       |                   |             | Dry  | Cereal   | Product  | :: 100`F | , 85° F  | с.н. |      |      |      |      |       |
|            | PS/PE |                   | PS/S        |      | PE/PS    |          | PE/PE    |          | JE∕S |      | S/PS |      | S/PE |       |
| Time, days | Exp.1 | Calc <sup>2</sup> | Exp.        | Calc | Exp.     | Calc     | Exp.     | Calc     | Exp. | Calc | Exp. | Calc | Exp. | Calc  |
| 1          | 3.81  | 3.93              | 2.25        | 2.33 | 4.10     | 4.12     | 3.03     | 3.22     | 2.19 | 2.27 | 2.32 | 2.43 | 2.22 | 2.35  |
| 2          | 4.53  | 5.29              | 2.51        | 2.82 | 4.66     | 5.53     | 3.60     | 4.31     | 2.40 | 2.71 | 2.62 | 2.98 | 2.49 | 2.82  |
| ę          | 5.25  | 6.15              | 2.80        | 2.27 | 5.34     | 6.38     | 4.23     | 5.13     | 2.66 | 3.12 | 3.00 | 3.47 | 2.81 | 3.25  |
| 4          | 6.42  | 6.71              | 3.27        | 3.67 | 6.57     | 6.90     | 5.10     | 5.75     | 3.08 | 3.49 | 3.53 | 3.91 | 3.27 | 3.65  |
| 5          | 7.55  | 7.06              | 3.77        | 4.04 | 7.79     | 7.21     | 5.91     | 6.22     | 3.55 | 3.83 | 4.13 | 4.31 | 3.8I | 4.01  |

Table 13

52

10btained experimentally 20btaired by calculation

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verify the accuracy of the calculation, a product/package combination was selected at random from those used in the study and two separate calculation programs were run. One of these considered all possible parameter errors which would have a maximizing effect upon moisture content and another in which all minimizing errors were considered. Table 15 shows these parameters and their estimated variation from actual values used in the calculation.

As can be seen from the results found in Table 16 and Fig. 22, the values obtained for final moisture content were well within the possible range of values when the effects of maximizing and minimizing errors were considered. It was also found that the calculated values were in all cases slightly greater than the experimental ones, indicating that some factor of error is present in the data used in the calculation. The calculated results also show agreement with experimental results which indicate that superior moisture protection is afforded when the better of two barrier materials is in the inner package.

One purpose of this study was to investigate the validity of the accelerated (high temperature, high humidity) test for packaged products which is commonly used in industry. The basis of this test is to determine some ratio relating a product's shelf life at accelerated conditions to shelf life at ambient conditions, perhaps stating that 16 weeks at accelerated conditions equals 100 weeks at normal room conditions. This 16:100 ratio is then used as a basis for predicting the shelf life of packaged products traveling through the distribution system. The error of this method lies in the fact that this ratio is not constant but changes as the product gains moisture. In comparing



| Table 15                                      |
|-----------------------------------------------|
| Estimated Range of Variability of Values      |
| Affecting the Calculation of Moisture Content |

| Variable Factor                    | Estimated Range<br>of Variability |
|------------------------------------|-----------------------------------|
| Permeance of Films                 | ±10%                              |
| Intercept of Isotherm Slope        | ±15%                              |
| Slope of Isotherm                  | ±15%                              |
| Area of Packages                   | ±10%                              |
| Headspace of Packages              | ±20%                              |
| Fill Weight of Packages            | ±15%                              |
| Internal Humidity of Inner Package | ±15%                              |
| Initial Product Moisture Content   | ±10%                              |
|                                    |                                   |

| Comparison of Experimental and Calculated Moisture Contents Using<br>Maximizing and Minimizing Errors in Calculation Parameters<br>for Saran/Polystyrene System |             |      |              |      |  |  |  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|------|--------------|------|--|--|--|
| Time, days                                                                                                                                                      | <u>Min.</u> | Exp. | <u>Calc.</u> | Max. |  |  |  |
| 3                                                                                                                                                               | 1.79        | 1.95 | 1.96         | 2.17 |  |  |  |
| 6                                                                                                                                                               | 1.94        | 2.13 | 2.13         | 2.35 |  |  |  |
| 9                                                                                                                                                               | 2.09        | 2.27 | 2.29         | 2.53 |  |  |  |
| 12                                                                                                                                                              | 2.23        | 2.41 | 2.45         | 2.70 |  |  |  |
| 15                                                                                                                                                              | 2.36        | 2.50 | 2.60         | 2.86 |  |  |  |
| 18                                                                                                                                                              | 2.49        | 2.65 | 2.74         | 3.01 |  |  |  |
| 21                                                                                                                                                              | 2.61        | 2.75 | 2.87         | 3.16 |  |  |  |
| 24                                                                                                                                                              | 2.73        | 2.86 | 3.00         | 3.31 |  |  |  |
| 27                                                                                                                                                              | 2.84        | 2.99 | 3.13         | 3.44 |  |  |  |
| 31                                                                                                                                                              | 2.94        | 3.08 | 3.25         | 3.57 |  |  |  |
| 33                                                                                                                                                              | 3.04        | 3.18 | 3.36         | 3.70 |  |  |  |
| 36                                                                                                                                                              | 3.14        | 3.31 | 3.47         | 3.82 |  |  |  |
| 39                                                                                                                                                              | 3.23        | 3.41 | 3.57         | 3.94 |  |  |  |
| 42                                                                                                                                                              | 3.31        | 3.50 | 3.67         | 4.05 |  |  |  |
|                                                                                                                                                                 |             |      |              |      |  |  |  |

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Table 16





the S/PS film combination of the dry cereal product at room conditions with those at accelerated levels (Table 17), one can see this change in ratio as the product moisture content increases. The table shows that the time required for product moisture content to reach 2.6% is 2 days under accelerated conditions while the time required to reach this same moisture level at room conditions is 18 days or at (Room)/t(Acc.) ratio of 9.0. This ratio remains at 9.0 while moisture increases to 3% but as the product attains a moisture content of 3.5%, the ratio increases to 10.5. Table 17 also illustrates that the ratio will change depending upon the package. If the PE/PE sample for the nonfat dry milk is examined, it can be seen that not only do the ratios differ within the combination but that they also differ from the ratios of the S/PS sample. The table further illustrates that the ratio is also influenced by product since the ratios of t(Room)/t(Acc.) for a S/PS film combination are different for the cereal and the milk powder. Although those differences seem obvious, they are often unaccounted for in industry where a given ratio of t(Room)/t(Acc.) may be indiscriminately used on all product/package combinations.

## Errors Affecting Experimental Results

In conducting this investigation, certain errors are introduced which may result in a discrepancy between the actual values and those obtained experimentally. One possible source of error lies in the determination of the initial moisture content of the product. This value is of great importance since it forms the basis for the construction of the sorption isotherms and the calculation of moisture content vs. time. Therefore, any error in this determination can result in miscalculation of any subsequent computation calculations of moisture con-





| Product | <u>Film</u> | Moisture<br>Content % | Time of<br>Acc.Cond.(days) | Time of<br>Room Cond.(days) | Ratio( <u>t Room</u> ) |
|---------|-------------|-----------------------|----------------------------|-----------------------------|------------------------|
| Cereal  | S/PS        | 2.6                   | 2                          | 18                          | 9.0                    |
| Cereal  | S/PS        | 3.0                   | 3                          | 27                          | 9.0                    |
| Cereal  | S/PS        | 3.5                   | 4                          | 42                          | 10.5                   |
| NFDM    | S/PS        | 3.5                   | 2                          | 15                          | 7.5                    |
| NFDM    | S/PS        | 3.8                   | 3                          | 24                          | 8.0                    |
| NFDM    | S/PS        | 4.2                   | 4                          | 36                          | 9.0                    |
| NFDM    | PE/PE       | 4.1                   | 2                          | 18                          | 9.0                    |
| NFDM    | PE/PE       | 4.5                   | 3                          | 22                          | 7.3                    |
| NFDM    | PE/PE       | 5.3                   | 4                          | 33                          | 8.3                    |
| Cereal  | PS/S        | 2.3                   | 1                          | 15                          | 15                     |
| Cereal  | PS/S        | 2.5                   | 2                          | 24                          | 12                     |
| Cereal  | PS/S        | 2.8                   | 3                          | 33                          | 11                     |
|         |             |                       |                            |                             |                        |

Table 17 Comparison of Ratio of Time at Room Conditions vs. Time at Accelerated Conditions

tent. When drying food products using the vacuum oven technique, there is a possibility that some volatile components may be lost from the sample and reported as weight loss due to moisture. Similarly, carbohydrate fractions of the products may be subject to heat induced carmelization and charring which can also result in erroneous values for initial moisture levels.

A further possibility for initial moisture error is due to the fact that some of the small inner pouches were filled, sealed and stored for up to 24 hours in closed buckets containing desiccant in order that all could be put in the proper overwrap pouch and subjected to testing conditions at the same time.

The construction of the sorption isotherms for the products at the two temperature conditions used in the test is also a source of error. Recommendations for the preparation of various salt solutions were carefully followed and sufficient time was allowed for the product to reach equilibrium with its respective humidity environment as directed. The main source of error arises from the fact that temperature fluctuations of as little as 2<sup>o</sup>F can result in a 5% change in relative humidity.

It should also be mentioned that in many cases, literature sources do not agree upon a humidity exhibited by a given salt solution at a specific temperature. There is also the possibility that a humidity gradient existed in the buckets since no means of circulating the air in the containers was available. Periodic weighing of the samples required opening and closing the buckets which may have caused disruption of equilibrium conditions which could result in the actual humidity levels being different than those assumed for use in the construction of the isotherm. Finally, normal bumping and scuffing of the pouches incurred in handling and weighing may have resulted in undetectable damage which would in turn lead to increased weight gain, although all packages finishing the test were assumed to be "perfect" (that is, no leakers).

## Errors Affecting Calculated Results

Perhaps the greatest possibility for error in the calculation of moisture content vs. time is that resulting from inaccuracies of the sorption isotherms of the products. Errors in initial moisture content and actual humidities exhibited by the salt solutions can greatly affect the construction of the isotherm. Since the equation of the line describing this curve (Equation 2) is used to calculate moisture content from internal relative humidity, an error in the isotherm will in turn result in an incorrect calculated moisture content. Errors in initial moisture content of the product will also affect the determination of the internal relative humidity of the package which is also required in Equation 2 for the calculation of moisture levels at each time step.

Another area in which discrepancies are possible is in the fitting of a straight line to the isotherms of each product and the subsequent determination of the slope and intercept of that line. In certain cases, the "best" fitting line may be inadequate for accurately describing the line. This was the case when trying to find a slope and intercept value for the nonfat dry milk isotherm at 75°F (Fig. 3). As can be seen, the line has a point of inflection at approximately 25% relative humidity, after which the slope increases and the intercept decreases relative to those values below 25%. In an example such as this, there may not be a single straight line which accurately describes the curve.

The permeance of the three films used in the test are another possible point of error since they are based upon water vapor transmission rates of the materials as determined by ASTM E-96, which describes the dish method for evaluating the moisture barrier properties of flat film samples. However, the permeability of the material when it is in the finished package form may be different due to the presence of seals and folds in the material, handling damage and other unavoidable mechanical abuse. It should also be noted that film thickness can vary up to  $\pm 10\%$  of the stated thickness which can lead to further errors in permeability calculations as can the presence of pinholes left by the manufacturer.

The area of the packages also introduces some error into the calculation of moisture content. As stated earlier, all packages were handmade and although reasonable precautions were taken to ensure uniformity, there is certainly some variance of the actual surface area of each individual package and the values stated in the calculation which are based on an average. Package headspace is also a point of possible error since this parameter was estimated based upon knowledge of the package dimensions. However, it was determined by doubling and halving the headspace values used that these parameters had little effect upon the outcome of the calculation.

In terms of experimental testing conditions, it was assumed that external temperatures and humidities to which the packages were subjected were constant when in reality normal minor fluctuations occurred as indicated by recording equipment. There is also a possibility that initial internal package relative humidity may be in error since this value was determined by calculation using the slope and

intercept parameters of the isotherm and the initial product moisture content, the values of which contain certain error possibilities which were discussed above.

Another source of error in the calculation is in the value obtained for the dry weight of the product within the pouches, a value whose accuracy is in turn dependent upon the accuracy of the initial product moisture content and the fill weight of the packaged product. The packages were filled volumetrically in the case of the milk powder and by count in the case of the cereal. Since variations in density and size respectively can affect the net fill weight, some variations from the average stated value are to be expected.

We must also consider as a potential source of error the assumption that the product is in equilibrium with the moisture in the headspace at the end of the time step. This state of equilibrium can depend upon a number of factors including the headspace, product fill weight, hygroscopic nature of the product as well as the length of the time step.

As described in Equations 4 and 5, the amount of water which penetrates a film is directly related to time,  $\Delta t$ . Therefore, the shorter the time step, t, the smaller the quantity of water which penetrates the package and the greater the likelihood that this water has equilibrated with the headspace. Conversely, a longer time step would result in more water penetrating the package and a reduced possibility of equilibrium.

In selecting a time step for calculation of moisture content, we desire one that is short enough to be accurate yet long enough to be practical. For this study a value of 0.01 hour (36 sec.) was chosen since larger values resulted in negative values for  $\Delta Q_B$  as described by Equation 5 and it was decided that the hygroscopic nature of the products and the relatively small headspaces made a smaller value unnecessary. A smaller time step of .001 hour was also tried but was found to give moisture contents which differed from those obtained with the 0.01 time step only in the third decimal place. Therefore, the 0.01 hour step was found to be acceptable for this investigation. It should be noted that one can only assume equilibrium between product and headspace based upon selection of the time step since there is no practical way to verify this condition. SUMMARY

The results of this investigation show that the placement of barrier materials has an influence on the level of moisture protection given by a system comprising a series of small packages sealed within a larger one. Specifically, it was determined that lower final moisture contents were reached when the better moisture barrier film forms the inner package.

In attempting to predict moisture content by calculation based on simulation, the calculated results are in agreement with values obtained experimentally when considering possible errors which may have influenced the results of the calculation. Future studies in this area might include the use of dried food products packaged by the manufacturer to ensure uniformity of package surface area, headspace, fill weight and seal quality, thereby eliminating many of the errors inherent in a hand made system such as the one used in this study. These packages could then be used in a large scale test involving a system that more closely approximates the size of an actual pallet or unit pack of the product. It is also suggested that the system be subjected to variations in temperature and humidity so as to simulate the environmental fluctuations that may be encountered in a warehousing situation. Future investigation might also examine high or intermediate moisture foods in flexible packages to determine the ability to predict moisture loss by calculation.

This study has also determined that the accelerated method of



shelf life evaluation was not accurate for the system used here. Results indicate that the ratio relating time at room conditions to time at accelerated conditions was not as constant as it should be if the basis of the accelerated test is valid. It was also determined that this ratio also varies depending upon the product and package used.

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