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Determination of Packaging Barrier Requirements By
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# DETERMINATION OF PACKAGING BARRIER REQUIREMENTS BY A MODEL APPROACH FOR A BEAN FLOUR PRODUCT

By

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## ABSTRACT

### DETERMINATION OF PACKAGING BARRIER REQUIREMENTS BY A MODEL APPROACH FOR A BEAN FLOUR PRODUCT

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Food products can become unacceptable to the consumer for a number of reasons. One particular food product reaction producing unacceptability is non-enzymatic browning, which can result in discernible color changes to the food. One of the essential reasons non-enzymatic browning occurs, besides high temperature storage, is the adsorption of moisture from the atmosphere. To prevent such moisture adsorption, food products susceptible to non-enzymatic browning must be packaged in materials which eliminate excess water vapor transfer from the atmosphere into the product. The most common method used by the food industry for determining packaging barrier requirements is accelerated testing procedures which are time consuming and can produce inaccurate results. As an alternative approach for determining packaging barrier requirements, this current research utilizes a mathematical model to predict packaging permeability requirements for a bean flour product.

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# INTRODUCTION

Packaging is of great concern to the food industry and one of the most important concerns is the protective barrier packaging materials provide to the food product. The barrier properties of a packaging material to oxygen (or other gases), and water vapor, will directly affect the storage life of a food product. Therefore, the packaging technologist, in order to determine the most feasible packaging barrier material for optimum protection of the food product, must become familiar with barrier properties of packaging materials as well as protective requirements of the food.

Flour type products and other foods containing reducing sugars and amino groups are susceptible to a series of chemical reactions known as non-enzymatic browning. These reactions can result in adverse color changes (browning) to the food, producing an unacceptable product to the consumer. The product browning rate is accelerated by adsorption of atmospheric moisture on the food surface. Adsorption of moisture can also produce caking of the dehydrated food, resulting in unacceptable product. However, the scope of this thesis will examine non-enzymatic browning as the mode of unacceptability. Thus the packaging material's barrier properties to water vapor transfer is the main concern in preventing non-enzymatic browning to the bean flour product used in this study.

The determination of packaging material specifications offering optimum protection against water vapor transfer can be a challenging endeavor to the packaging technologist. Considerations that have to be taken into account are storage or shelf life desired, storage temperature and humidity, moisture adsorption properties of the food, moisture content where discernible browning occurs, and the ratio of packaging material surface to product volume.

Storage, or shelf life, designates the distribution time period from the point of packaging to the point of consumption by the consumer. This time period is commonly 12-18 months for dehydrated food products. This means if the desired storage life is one year, the product must remain acceptable to the consumer for that one year time period. Storage life is a very important variable for selection of packaging materials for food products. Obviously, the longer the time period desired, the greater the need is for packaging materials with good water vapor barriers.

Also playing a major role in the selection of a packaging material's water vapor transfer properties is the temperature and humidity of the storage-distribution channel during the storage life time period. Higher temperatures and humidities will accelerate the non-enzymatic browning reactions, thus requiring packaging materials with better water vapor barriers.

The moisture content where discernible browning occurs can be determined through the use of visual panel tests. This moisture value is related to the moisture adsorption properties of the food. The adsorption properties are determined by a moisture isotherm curve. This curve is best described as a graph of the moisture content of the food plotted on the Y-axis, correlating to an equilibrium relative humidity surrounding the food plotted on the X-axis. The amount of moisture is that which is held after equilibrium has been reached at a constant temperature.

The ratio of package material surface area to product volume also affects the water vapor barrier requirements of packaging materials. As this ratio increases so does the barrier requirements to protect the product.

The current method used in the food industry for determining packaging material barrier requirements is accelerated testing procedures. This involves packing the product in alternate packaging materials with varying water vapor transfer properties, and storing the product/package in high temperature, high humidity conditions (100°F, 90% RH). Then based on previous accelerated testing experience, a time correlation would be made with actual product/package environmental conditions desired. A typical food industry example is four weeks in accelerated conditions equal to six months at the desired room temperature conditions (72°F, 50% RH).

Accelerated testing can be time consuming when setting up the test, and can also produce inaccurate results. High temperature, high humidity conditions have a significant effect on product stability especially with food products prone to non-enzymatic browning. Even though moisture adsorption at higher temperatures is lower than observed at lower temperatures, the dominant catalyst for the non-enzymatic reaction is high temperature conditions. In most cases water-vapor transfer through packaging materials is greater at higher temperatures than at lower temperatures due to the fact that the permeability constant will usually increase exponentially with temperature. High humidity also results in significant alterations in product/package reactions and will not display a linear correlation with results at lower humidities. Because room and accelerated environments do not produce similar effects, it appears that accelerated testing procedures produce inaccurate results, which in many cases creates over- or underpackaging of the product.

The packaging barrier requirements of the product are usually not known before the accelerated test is set up; therefore, the product is packed in materials with varying barrier properties to water-vapor transfer. This often results in a guessing game which can lead to a the product being test packed in several different material specifications, taking up many hours of a packaging technician's time.

A bean flour product, which is prone to non-enzymatic browning, was packaged in a 2-mil thickness polyethylene and a PVDC/nylon/polyethylene co-extruded film. The product/package samples were then stored in accelerated conditions (100°F, 90% RH) for four weeks and room temperature conditions (72°F, 50% RH) for six months to analyze if a correlation exists between the two environments when determining packaging barrier requirements.

A model system approach was then examined utilizing a calculation to determine the packaging barrier to water-vapor transfer required to prevent discernible non-enzymatic browning of the bean flour product for the desired storage life time period of six months at room temperature. The model approach takes into consideration the moisture adsorption properties of the food, weight of the product, surface area of packaging materials, desired shelf life, product moisture content where discernible browning first occurs, and the initial product moisture content.

The objectives of this thesis are:

(1) To prove that accelerated procedures for determination of packaging barrier requirements at room temperature conditions are not accurate for food products susceptible to non-enzymatic browning.

(2) To demonstrate that the model approach can determine the product's moisture content where discernible non-enzymatic browning occurs, which can then be used to predict the packaging barrier requirements.

# LITERATURE REVIEW

Selection of packaging materials that provide economic protection to the food product is an important concern to the food industry. The tradition used in the industry today for material selection is accelerated testing procedures. However, recent literature (Clifford et al., 1977; Waletzko and Labuza, 1976) has demonstrated that accelerated testing can be time consuming and inaccurate for predicting packaging requirements at lower temperatures.

Much attention has been paid recently to the use of model systems, which utilize a calculation for determination of packaging barrier requirments. Some of the reasons for using the model system approach have been described by Gyeszly (1980). They include: "(1) the trend toward using fewer food preservatives increases the responsibility of packaging in product stability and safety; (2) the continuous increase in prices for raw materials and energy makes over- and under-packing much more uneconomical and undesirable; (3) use of simulation model makes it possible to prepare a shelf life to packaging cost relationship, giving marketing an opportunity to review shelf life requirements; (4) the competitive nature of the industry encourages shorter development times."

Model system work has been done in the past regarding methodology for determination of packaging requirements (Quast and Karel, 1972; Quast and Karel, 1973). Mizrahi et al. (1970 a and b) examined the use of model systems for packaging of dehydrated cabbage for prevention of non-enzymatic browning. Quast et al. (1972) investigated mathematical models for packaging predictions involving potato chip stability degradation by two interacting mechanisms. Clifford et al. (1977) used the model theory for cereal packaging predictions. Mizrahi and Karel (1977) re-evaluated kinetic models involved in package requirements for loss of ascorbic acid in tomato powder and the extent of browning in dehydrated cabbage. Labuza et al. (1972) reviewed some of the model methodology that could be used to predict packaging for food products prone to lipid oxidation and non-enzymatic browning. In this article he discussed the use of the model approach for prediction of packaging to prevent non-enzymatic browning of dehydrated milk products. According to the author's knowledge, however, no work has been done which compares accelerated testing procedures to that of the model system for determination of packaging barrier requirements for food products prone to non-enzymatic browning.

Dehydrated food products can become unacceptable to the consumer due to several mechanisms depending on the type of product. Typical dehydrated food reactions are non-enzymatic browning, protein degradation, loss of desired product texture, caking leading to insolubility, vitamin degradation, and lipid oxidation (Labuza, 1977; Salwin, 1963; Rockland, 1969). All the above mechanisms can in one way or another be affected by packaging barrier properties.

The deteriorative mechanism being used in this research is non-enzymatic browning of a bean flour product. To understand how this reaction is affected by packaging, perhaps it is best to first examine the reactants and the factors associated with this mechanism. Non-enzymatic browning, otherwise known as the Maillard reaction, occurs via a series of complex, defined reactions in which the initial reactants are usually reducing sugars and the amino groups of amino acids or proteins (Troller and Christian, 1978; Schwimmer, 1980).

Factors which can reduce or eliminate this type of browning reaction are low storage temperature, prevention of product moisture gain through use of adequate packaging materials, chemical inhibitors (e.g. $SO_4$, $HSO_3$), removal of reactants (e.g. glucose, amines), and reduction of product pH, (Fennema, 1976). Oxygen does not affect this reaction.

This food reaction can result in adverse color production (darkening) of the food, off flavors and odors (stale flavor, musty burnt odor), $CO_2$ production, liberation of water, lowered product solubility, decrease in product pH, and loss in the biological value of proteins (Fennema, 1976).

Previous research with dehydrated food products shows maximum non-enzymatic browning usually occurring in the 9-11% moisture range (Heiss and Eichner, 1971a). However, it is not necessarily the absolute moisture content that is decisive in producing this reaction; rather it is the water availability or water activity (Aw) which controls browning and other similar reactions such as vitamin degradation and lipid oxidation (Caurie, 1971; Guadagni et al., 1975; Labuza, 1968).

Research has been published examining relative reaction rates of non-enzymatic browning as a function of water activity (Heiss and Eichner, 1971b; Oswin, 1976; Makinde et al., 1976; Duckworth, 1976; Labuza et al., 1970). Troller and Christian (1978) found maximum rates of browning occurring at Aw's of .65-.70 and then decreasing rates were noticed as Aw went above .70. This phenomenon occurred at $37^{\circ}$, $70^{\circ}$, and $90^{\circ}C$. However, they mentioned that due to the many complex interactions involved with non-enzymatic browning, Aw optima of .3-.8 can be expected.

## MATERIALS AND METHODS

### (A) Theoretical Model System Approach

The model calculation used in this paper for prediction of packaging barrier requirements was developed at M.I.T. (Labuza et al., 1972). The concept assumes a moisture gain through a semi-permeable film. A semi-permeable film transports water across it according to the following equation:

$$\frac{dw}{dt} = \frac{k}{x} A \quad (Pout - Pin)$$

where:

| | | |
|---|---|---|
| w | = | weight of water transported (grams), |
| t | = | time (hours), |
| k | = | permeability of the film, weight/area · time · Δ mmHg |
| x | = | film thickness (mil), |
| A | = | area of film ($m^2$), |
| Pout | = | vapor pressure of water outside film (mmHg), |
| Pin | = | vapor pressure of water inside film (mmHg). |

The limiting assumptions of this model are:

(1) It is assumed that the system is in equilibrium and the temperature is held constant.

(2) The isotherm curve is extrapolated into a straight line. If a straight line equation cannot be used

for a particular model, other kinetic equations can be utilized (Labuza, et al., 1972).

(3) Package headspace considerations are not signigicant when small product quantities are examined, but could be significant when bulk product quantities are packaged. Therefore, this work will not include headspace considerations. (Quast et al., 1972)

(4) Permeability constant is independent of the film's thickness and water vapor partial pressure difference between the two sides of the film.

(5) Thickness of the films was assumed constant; the films did not swell due to the exposure of high relative humidity or moisture content.

(6) Water vapor was performing as an ideal gas.

(7) The method used to rate the extent of product browning was a Hunter Colorimeter L value. Other Hunter values such as a (green-red) and b (yellow-blue) could be used for darker products, however, for the white colored bean flour the L value (white-black) was found to be the most appropriate way to rate the extent of product browning.

When a film is used to package a dehydrated food, all the variables are known except for vapor pressure inside the package (Pin) and the vapor pressure outside the package (Pout). Vapor pressure outside the package is proportional to the relative humidity and temperature of the storage atmosphere. The vapor pressure inside the package is determined by the moisture content of the food and the moisture sorption isotherm, which is a property of the food system.

One of the objectives of the model is to predict the equilibrium vapor pressure from the moisture content for purposes of solving the original equation. This can be done by approximating the isotherm to be a straight line.

$$m = ba + c$$

where:

$m$ = moisture content

$b$ = slope

$a$ = water activity

$c$ = y intercept

In order to solve the original equation, the isotherm equation is rearranged and substituted into the original equation. The substitutions are displayed in Labuza et al., 1972.

Integrating this equation between $m_i$ (initial moisture) and m, and between 0 and $t_c$, results in the following:

$$\ln \left[\frac{m_e - m_i}{m_e - m}\right] = k \ \frac{A}{w_s} \ \frac{Po}{b} \ t_c$$

where:

$w_s$ = weight of dry solids enclosed

$m_i$ = initial moisture content

$m_e$ = equilibrium moisture content food will reach if stored under external conditions without pouch

$m$ = moisture content at time t

$Po$ = saturation vapor pressure of water at given constant temperature (mm Hg)

other variables as previously defined.

If $\ln \left[\frac{m_e - m_i}{m_e - m}\right]$

is plotted on the y-axis and $t_c$ on the x-axis, a straight line is obtained.

If a critical moisture content $m_c$ is defined, above which our product becomes unacceptable, and $t_c$ is the length of time for product storage, then a straight line between two points can be plotted which results in the slope of the line = $k \frac{A}{W_s} \frac{Po}{b}$. Since all these variables except k are known, the k value necessary to acceptably store the product for this length of time can be calculated. A film can then be chosen with this specification to water vapor permeability by solving for k in the following equation:

$$k = \frac{\ln \left[ \frac{m_e - m_i}{m_e - m_c} \right]}{\frac{A}{W_s} \cdot \frac{Po}{b} \cdot t_c}$$

Alternatively, if there is a film of known k value, the shelf life this film will give us can be predicted using the same type of analysis.

$$t_c = \frac{\ln \left[ \frac{m_e - m_i}{m_e - m_c} \right]}{k \cdot \frac{A}{W_s} \cdot \frac{Po}{b}}$$

(B) Experimental Procedure

The product selected for this study is a white colored flour made from navy beans. Fifty-pound bags of navy beans were cleaned and oven dried in a Michigan State University food science laboratory. The dried beans were milled into a white flour and then packed into polyethylene and co-extrusion pouch materials in 100-gram quantities. The bean flour had an initial water activity of .21 and a density of .5 grams/cc. Analytical and physical data published on navy bean flour products show the following composition properties: 40.3% starch yield, .06% nitrogen, .60% fat, .14% ash, .15% acid detergent fiber, and 83.8% water binding capacity (Naivikul et al., 1979). The bean flour reconstitutes easily with water and can be used in products such as soups, party dips, refried beans, meat loafs, cakes, breads, and other widely consumed foods (White, 1972).

Model calculations used in this study take into consideration properties of the product and the environment to predict the packaging barrier requirements. The sorption isotherm, initial moisture content, moisture content where noticeable non-enzymatic browning occurs, packaging material surface area, and product weight per package are required for determination of the water vapor permeability rate (k) of the packaging material.

The bean flour sorption isotherm was determined by placing samples of known initial moisture content in contact with a range of constant relative humidities at three constant temperatures and measuring the weight gain or loss. The use of saturated salt solutions can create constant humidities in an enclosed atmosphere. The humidity condition is produced by a certain salt's affinity for water. This controls the water vapor pressure in the environment surrounding the salt material. Therefore, by selecting appropriate salt compounds a range of humidity environments can be produced (Packaging Institute, 1952; Rockland, 1960).

This research examined five enclosed humidity environments ranging from 11% RH to 76% RH. Five-gram samples of the bean flour product were weighed regularly on an analytical balance until the samples neither gained or lost weight. This is an indication that the product samples had reached the moisture equilibrium state. The equilibrium moisture content was expressed in units of gram moisture/100-gram dry sample. This data can then be used to develop the sorption isotherm curve which is the average equilibrium moisture content of two repeat samples plotted against the relative humidity environment the samples were stored in. The results of the equilibrium contents at three temperatures are located in Table 1, and sorption isotherm curves are located in Figure 1.

The vacuum oven method was used to determine the initial moisture content of the product. The term "moisture content" refers to the amount of moisture being held in a food product at a point in time after the product is produced. Determination of a product's moisture content is usually done by removal of the water from the product through high temperatures and then the weight change measured.

The following procedure was used for moisture determination of the bean flour product. Four samples of the product in five-gram quantities were placed in a vacuum oven at 65°C for four hours. The average loss of weight due to moisture

Table 1. Test conditions, salt solutions, and moisture contents for sorption isotherm curves.

| Temperature | Salt Solution | Relative Humidity (%) | Equilibrium Moisture Content $\frac{\text{g. moisture}}{\text{100 g. dry prod.}}$ |
|---|---|---|---|
| 100°F | LiCl | 11.1 | 4.01 |
| | $MgCl_2$ | 32.2 | 6.30 |
| | $KNO_2$ | 46.9 | 8.31 |
| | $NaNO_2$ | 62.9 | 11.20 |
| | NaCl | 75.2 | 15.43 |
| 72°F | LiCl | 11.1 | 4.40 |
| | $MgCl_2$ | 32.8 | 6.85 |
| | $KNO_2$ | 48.2 | 9.80 |
| | $NaNO_2$ | 64.5 | 13.31 |
| | NaCl | 75.4 | 18.52 |
| 47°F | LiCl | 11.1 | 5.11 |
| | $MgCl_2$ | 33.3 | 7.43 |
| | $KNO_2$ | 49.6 | 10.41 |
| | $NaNO_2$ | 66.2 | 15.22 |
| | NaCl | 75.6 | 19.03 |

Initial moisture content of bean flour = 3.6 $\frac{\text{g. moisture}}{\text{100 g. dry prod.}}$

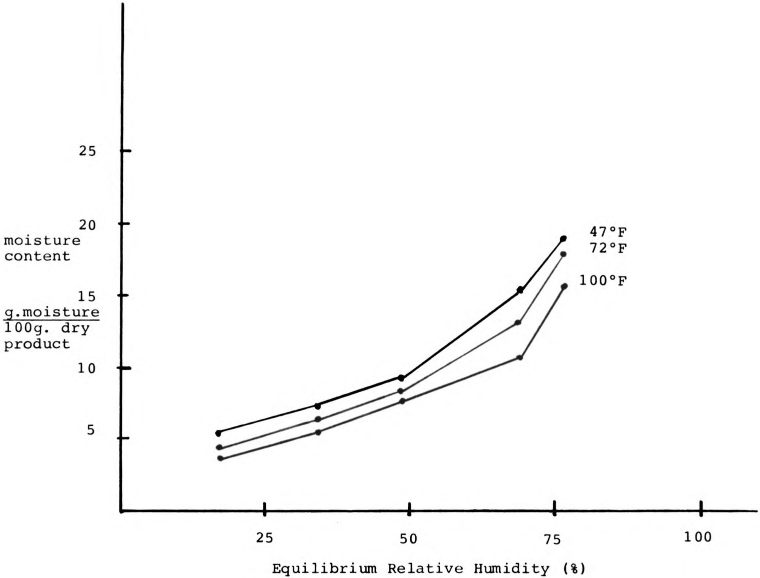


Figure 1. Bean flour moisture isotherm.

loss was calculated for the four samples. This allowed us to then determine the dry basis moisture content which is expressed in units of gram moisture/100 gram dry product. The results are located in Table 1.

The determination of the moisture content where non-enzymatic browning becomes noticeable is the most critical phase of the research. Unacceptable product in this work was designated as a point in time during storage where a panel of ten judges was able to observe a discernible difference in product color between freshly produced bean flour and stored bean flour.

The moisture content where darkening occurred was determined by storing the product in five enclosed humidity environments ranging from 11% RH to 76% RH at three different temperatures (47°F, 72°F, 100°F). The product samples were weighed periodically until they neither gained nor lost weight, indicating the equilibrium moisture content of the product had been reached. Six samples, five grams each, were then removed from the humidity environments and presented to a panel of ten randomly selected judges who determined, through the use of visual triangle tests, the moisture content where a discernible difference was noticed in product color.

The triangle test is commonly used in the food industry for determining differences in product characteristics (odor, color, flavor). It involves presenting to a taste panel judge three product samples where two samples are control and one sample is product which has been altered in some way. The judge is then asked to select the odd sample according to flavor, odor, color, or whatever differences are being examined. The samples should be switched halfway through the test where the odd sample is the control and the other two samples are the altered product.

This study examined color differences or darkening of product stored at different relative humidities versus freshly produced product color (control). Each of the ten judges was presented three- to five-gram samples of the bean flour in petri dishes covered with plastic film. Two samples were from product stored in one of the five humidity environments, and the other sample was freshly produced product stored in controlled atmosphere (35°F, 40% RH) where no browning occurs. By asking the judges to select the odd sample, a determination could be made of the relative humidity where discernible product browning first occurred. This concept is illustrated in Figure 2.

The question that needs to be answered at this point is how many correct responses by the ten-member judging panel constitute discernible product browning. A chart published in a Merck Technical Bulletin (1963) examines the number of correct responses as a function of the total number of panel judges used and then classifies the correct response number as either 1% or 5% significance. The 1% significance level was used for this work because it produces greater accuracy for proving the hypothesis of this work. Another definition

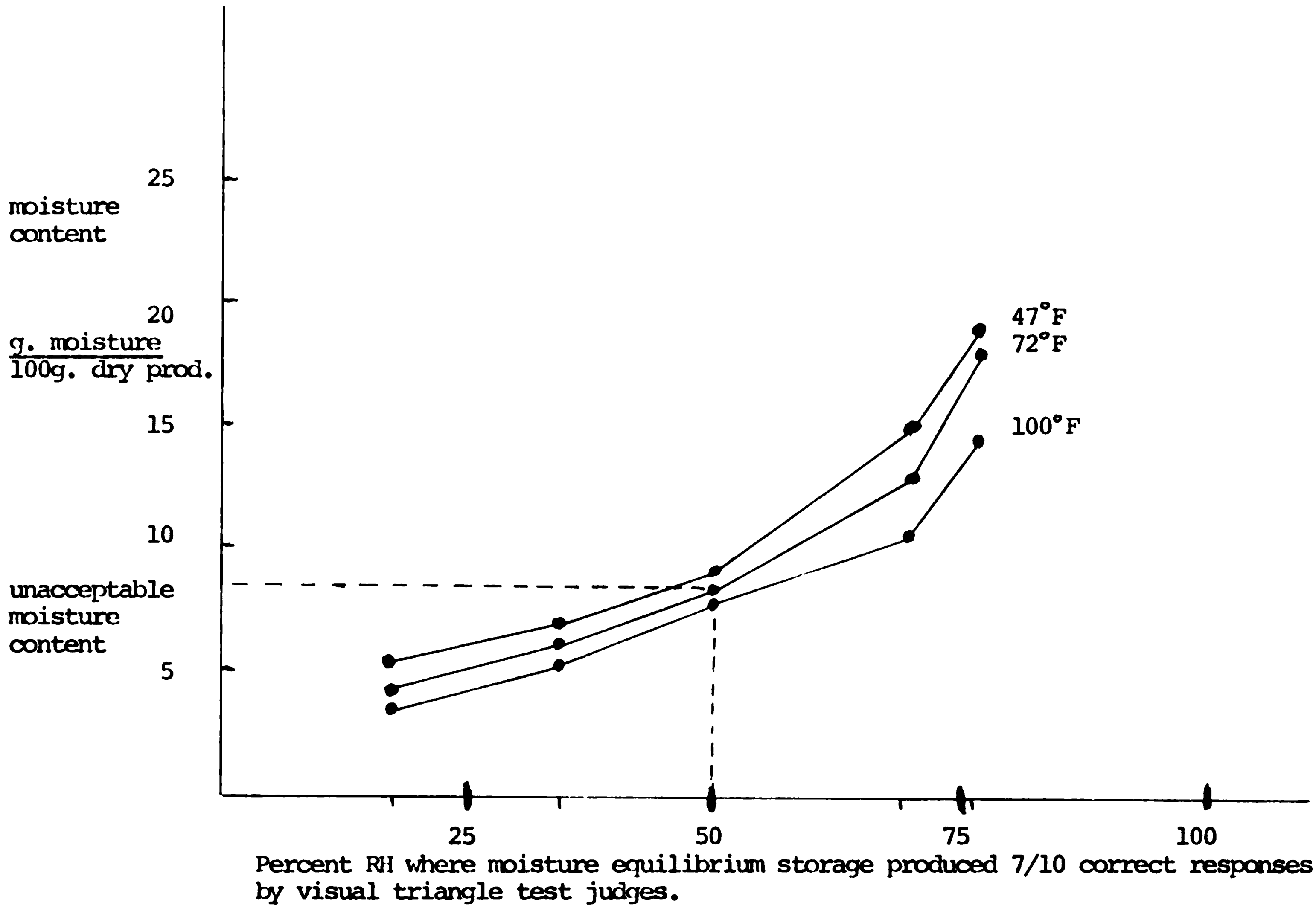


Figure 2. RH storage versus unacceptable moisture content concept.

of the 1% significance level is a 99% confidence level. In other words if the panel testing were repeated 100 times the results would be the same 99 times out of the 100 repeated tests. This level of significance requires seven correct responses out of ten panel judges in order for the product to be considered discernibly different from the control.

The above procedure gives us a method to determine the moisture content where perceptible product browning first occurs. However, a way to rank or identify the degree of non-enzymatic browning of the product needs to be determined. This will enable us to attach a number or objective indicator to the moisture content where noticeable browning occurs.

A simple method used in this research to identify the extent of browning involved the use of a D25-2 Hunter Lab Colorimeter instrument. This instrument produces digital readouts which examine different color scales ranging from black to white, red to green, and yellow to blue. The particular color scale used for this research was the L value which rates product color from white (L=100) to black (L=0).

The results of the Hunter browning data along with the corresponding triangle test results for each relative humidity environment are located in Table 2. Figure 3 represents a plot of relative humidity storage versus product L values.

In summary, the following steps were taken for determination of the moisture content where non-enzymatic browning occurs:

Table 2. Visual triangle test results and browning values.

| Temperature | Relative Humidity (%) | Visual triangle test results -correct responses of 10 judges | Browning Value (L) |
|---|---|---|---|
| 100°F | 11.1 | 3/10 | 84.2 |
| | 32.2 | 7/10* | 83.5 |
| | 46.9 | 9/10 | 82.8 |
| | 62.9 | 7/10* | 82.4 |
| | 75.2 | 10/10 | 80.1 |
| 72°F | 11.1 | 2/10 | 84.9 |
| | 32.8 | 5/10 | 84.2 |
| | 48.2 | 7/10* | 84.1 |
| | 64.5 | 9/10 | 84.1 |
| | 75.4 | 10/10 | 81.9 |
| 47°F | 11.1 | 1/10 | 84.8 |
| | 33.3 | 4/10 | 84.9 |
| | 49.6 | 1/10 | 84.4 |
| | 66.2 | 3/10 | 84.5 |
| | 75.6 | 5/10 | 84.4 |

Initial browning value of bean flour: L, 85.3

* Seven correct responses out of ten judges signifies the point where browning of the product becomes noticeable and will represent the point of product unacceptability in this research paper. 84.1 is the L value where discernible browning first occurs.

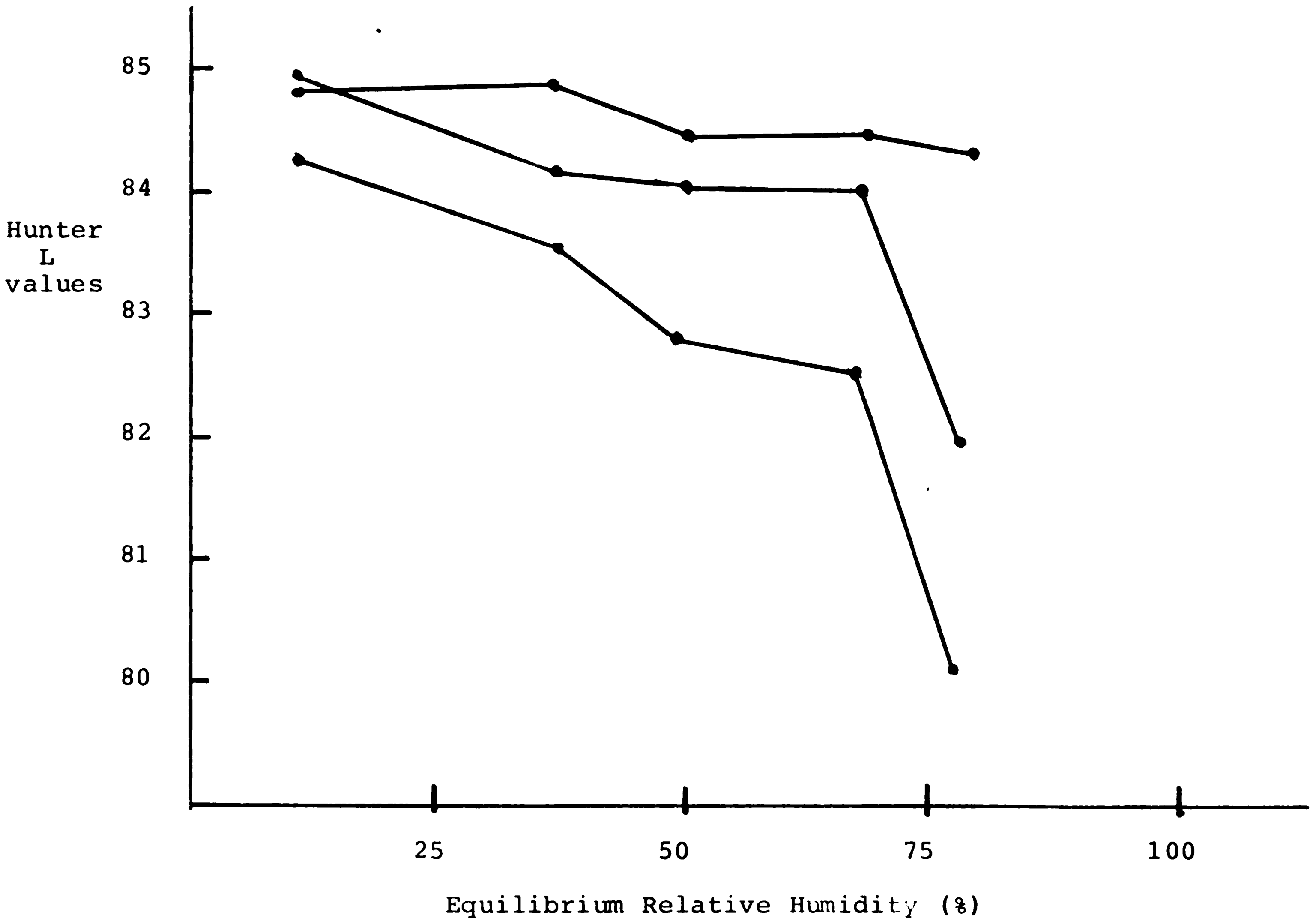


Figure 3. Browning L values at % RH storage environments of bean flour.

(1) Five-gram product samples were stored in enclosed relative humidity environments until product reached the equilibrium moisture state.

(2) Visual triangle tests were set up using ten panel judges. Each judge examined three numbered samples and picked the odd-colored sample. A triange test was set up for each of the five humidity environments for three temperatures. Therefore, judges were asked to examine 15 visual tests where they marked down on a sample ballot the odd-colored sample for each of the 15 tests.

(3) The number of correct responses was compared to the Merck Technical Bulletin which gave the number of correct responses required to show the product was unacceptable at a certain relative humidity.

(4) Then by referring to the moisture isotherm curve we could compare the relative humidity environment where browning first occurred to the equilibrium moisture content. This gives the moisture content for each of the three storage temperatures where discernible product browning first occurred.

(5) The extent of browning at each critical moisture level was quantified through the use of a Hunter lab color and color difference meter.

The other two requirements for the model system calculation are pouch surface area and product weight. These are easily obtainable items. The product weight for this research was 100 grams, and pouch surface area was calculated by multiplying the web width by the pouch cutoff. This is located in Table 3.

All the data which can be inserted into the model calculation for determination of the packaging barrier requirements to prevent noticeable non-enzymatic browning to the bean flour product for the desired shelf life (six months) has now been developed. However, to prove the validity of this model calculation the k value will first be determined

Table 3. Storage results of product/package testing. (Package material surface area - .0232 $m^2$).

100°F - 90% RH accelerated testing (four weeks)

| Material Specifications | Moisture content $\frac{g.\ H_2O}{100\ g.\ dry\ prod.}$ | | | | (L value) | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 week | 2 weeks | 3 weeks | 4 weeks | 1 week | 2 weeks | 3 weeks | 4 weeks |
| (A) 2 mil polyethylene | 4.44 | 6.95 | 7.53 | 10.01 | 84.3 | 83.2* | 83.2 | 82.5 |
| (B) Polyethylene/ nylon/PVDC | 4.16 | 4.98 | 6.95 | 7.67 | 85.2 | 84.3 | 84.0* | 83.3 |

72°F - 50% RH room temperature storage (six months)

| Material Specifications | Moisture content $\frac{g.\ H_2O}{100\ g.\ dry\ prod.}$ | | | | | | (L value) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 month | 2 months | 3 months | 4 months | 5 months | 6 months | 1 month | 2 months | 3 months | 4 months | 5 months | 6 months |
| (A) 2 mil polyethylene | 5.26 | 5.54 | 5.82 | 6.38 | 6.95 | 8.69 | 84.7 | 84.7 | 84.3 | 84.3 | 84.3 | 84.3 |
| (B) Polyethylene/ nylon/PVDC | 4.16 | 4.44 | 4.98 | 5.26 | 5.68 | 5.82 | 84.9 | 84.7 | 84.5 | 84.5 | 84.4 | 84.5 |

The 84.1 L value was not reached for either material specification at six months at 72°F, 50% RH.

*If 84.1 and below (L value) is the perceptible browning point, then accelerated results show discernible differences for the polyethylene barrier specification at two weeks and three weeks for film B.

and then inserted into the formula while leaving the storage time ($t_c$) as the unknown value. When this unknown value is calculated, actual product package storage can be continued to that unknown time period ($t_c$) and an analysis can be made of the correlation between the model calculation and room temperature product/package storage tests. An examination will be made of the product moisture content and the browning rate (L value) of actual product/package storage tests carried out to $t_c$. It will then be determined if these results correlate with the product moisture content and L value predicted by the model calculation.

The packaging material k value used for determining $t_c$ in this study (2-mil polyethylene) was the same film used in actual product/package storage tests. The k values of the packaging materials were determined by standard method ASTM E96-66 (1972) and conducted at 72°F, 50% RH.

The calculation to determine the k value required for the model calculation was given in the previous chapter. The k values of the two packaging films used in this study are located in Table 4.

Table 4. k value of packaging films (72°F, 50% RH).

| Material specification | k - $g(H_2O)/(m^2)$ (24 hrs.) ($\Delta$ mmHg) |
|---|---|
| (A) 2-mil polyethylene | .43 |
| (B) Polyethylene/nylon/ PVDC | .14 |

Actual Product/Package Storage
Test Procedures

The bean flour product was packed in two flexible film specifications in 100-gram quantities. The films used were

2-mil thickness low density polyethylene,

polyethylene/nylon/PVDC co-extruded film.

The 2-mil polyethylene material is lower in cost than the co-extruded film. According to industry data, the relative costs of each film specification are:

polyethylene film - \$.03/1000 $in^2$

co-extruded film - \$.09/100 $in^2$.

The pouch dimensions and sealing variables for each film are as follows:

. . . size for both specifications: (3 side seal) web width - 8¼"; cutoff - 5" (¼" seals); area exposed to product - 8" x 4½ = .0232 $m^2$.

. . . sealing variables:

polyethylene film - 20 psi; impulse time - .5 sec; cool time - 1 sec.

co-extruded film - 20 psi; impulse time - .3 sec; cool time - 1 sec.

The initial moisture of the product was determined before packaging. The procedure used was given in the previous section. Four 100-gram pouches of each film specification were stored in each of the following temperature-humidity environments:

100°F, 90% RH (accelerated storage),

72°F, 50% RH (room temperature storage).

Product weight gain in accelerated storage was monitored once a week for four weeks, while weight gain analysis for room temperature conditions took place once per month for six months. The weight gain examination permitted monitoring the product and determination of product moisture contents at a certain point in time during the storage period.

Actual product/package storage will show the correlation between room temperature conditions versus accelerated testing procedures, and the correlation between room temperature conditions and predictions made by the model approach. Results of actual product/package testing are located in Table 3.

(C) Sample Calculation for Determining Packaging Barrier Requirement k When Storing Product at 72°F, 50% RH

Input Values

$m_e$ - Equilibrium moisture content at 50% RH on moisture isotherm curve.

$$10.5 \ \frac{\text{g. moisture}}{\text{100 g. dry prod.}}$$

$m_c$ - Moisture content where discernible browning first occurred (determined by visual triangle tests at 72°F).

$$9.8 \ \frac{\text{g. moisture}}{\text{100 g. dry prod.}}$$

$m_i$ - Initial moisture content determined by vacuum oven method

$$3.6 \ \frac{\text{g. moisture}}{\text{100 g. dry prod.}}$$

A - Surface area of packaging materials ($.0232\ m^2$)

$W_s$ - 100 grams.

Po - Vapor pressure of pure water at 72°F, 55% RH (10.07 mmHg)

b - Slope of moisture isotherm at 72°F (.22).

$t_c$ - Storage time desired (180 days - six months).

$$\ln \left[\frac{10.5 - 3.6}{10.5 - 9.8}\right] = k \cdot \frac{.0232}{10} \cdot \frac{20.07}{.22} \cdot 180$$

$$\ln \left[\frac{6.9}{.7}\right] = k\ 3.28$$

$$\ln = 2.288$$

$$2.288 = k\ 3.28$$

$k = .69$ g ($H_2O$)/($m^2$) (24 hrs.) ($\Delta$ mmHg) required to protect the product from noticeable browning for six months' storage

(D) Proof of Model Approach

The following model calculation leaves the storage time ($t_c$) as the unknown value. The k values of the two film specifications were inserted into the calculation to determine the storage period each film will provide before the perceptible browning value (L, 84.1) is observed. The model calculation was examined at 72°F, 50% RH, so the prediction results could be compared to results obtained with actual product/package storage at 72°F, 50% RH.

Input Values

$m_e$ - Equilibrium moisture content at 50% on moisture isotherm curve.

$$10.50 \ \frac{\text{g. moisture}}{\text{100 g. dry prod.}}$$

$m_c$ - Moisture content where discernible browning first occurred (determined through visual triangle tests at 72°F).

$$9.80 \ \frac{\text{g. moisture}}{\text{100 g. dry prod.}}$$

$m_i$ - Initial moisture content.

$$3.6 \ \frac{\text{g. moisture}}{\text{100 g. dry prod.}}$$

A - Surface area of packaging material (.0232 $m^2$).

$W_s$ - 100 grams.

Po - Vapor pressure of pure water at 72°F (20.07 mmHg).

k - Permeability of film to water vapor.

2-mil polyethylene - .43 )
Polyethylene/nylon/ )
PVDC - .14 ) $g(H_2O)/(m^2)$ (24 hrs.) ($\Delta$ mmHg)

$t_c$ - Unknown storage time.

Problem 1 - Storage time obtained with polyethylene specification:

$$\ln \left[ \frac{10.5 - 3.6}{10.5 - 9.8} \right] = .43 \ \frac{.0232}{100} \cdot \frac{20.07}{.22} \cdot t_c$$

$$2.288 = .43 \cdot .0002 \cdot 91.23 \cdot t_c$$

$$t_c = \frac{2.288}{.0078}$$

$$t_c = 293 \text{ days}$$

Problem 2 - Storage time obtained with polyethylene/nylon/ PVDC specification:

$$\ln\left[\frac{10.5 - 3.6}{10.5 - 9.8}\right] = .14 \cdot \frac{.0232}{100} \cdot \frac{20.07}{.22} \cdot t_c$$

$$2.288 = .14 \cdot .0002 \cdot 91.23 \cdot t_c$$

$$t_c = \frac{2.288}{.0026}$$

$$t_c = 880 \text{ days}$$

Due to time restrictions only the polyethylene $t_c$ value was compared to actual product/package storage at 72°F, 50% RH. The following are the moisture content and browning L values of the bean flour product stored in the polyethylene material for 293 days at 72°F, 50% RH:

Moisture content: 10.43 $\frac{\text{g. } H_2O}{\text{100 g. dry prod.}}$

L value: 83.2

To offer further proof of the accuracy of the model approach, graphs were produced showing product moisture content over time with accelerated prediction methods and calculated values. Included in these graphs is the product moisture content over time with room temperature storage of the product in the polyethylene pouch material. Figures 4 and 5 illustrate these two graphs.

Figure 4 shows the accelerated moisture predictions remaining relatively close to the room temperature storage results until the 4½-month interval. After this point accelerated moisture predictions increase at a significant rate and at the six-month interval, accelerated moisture

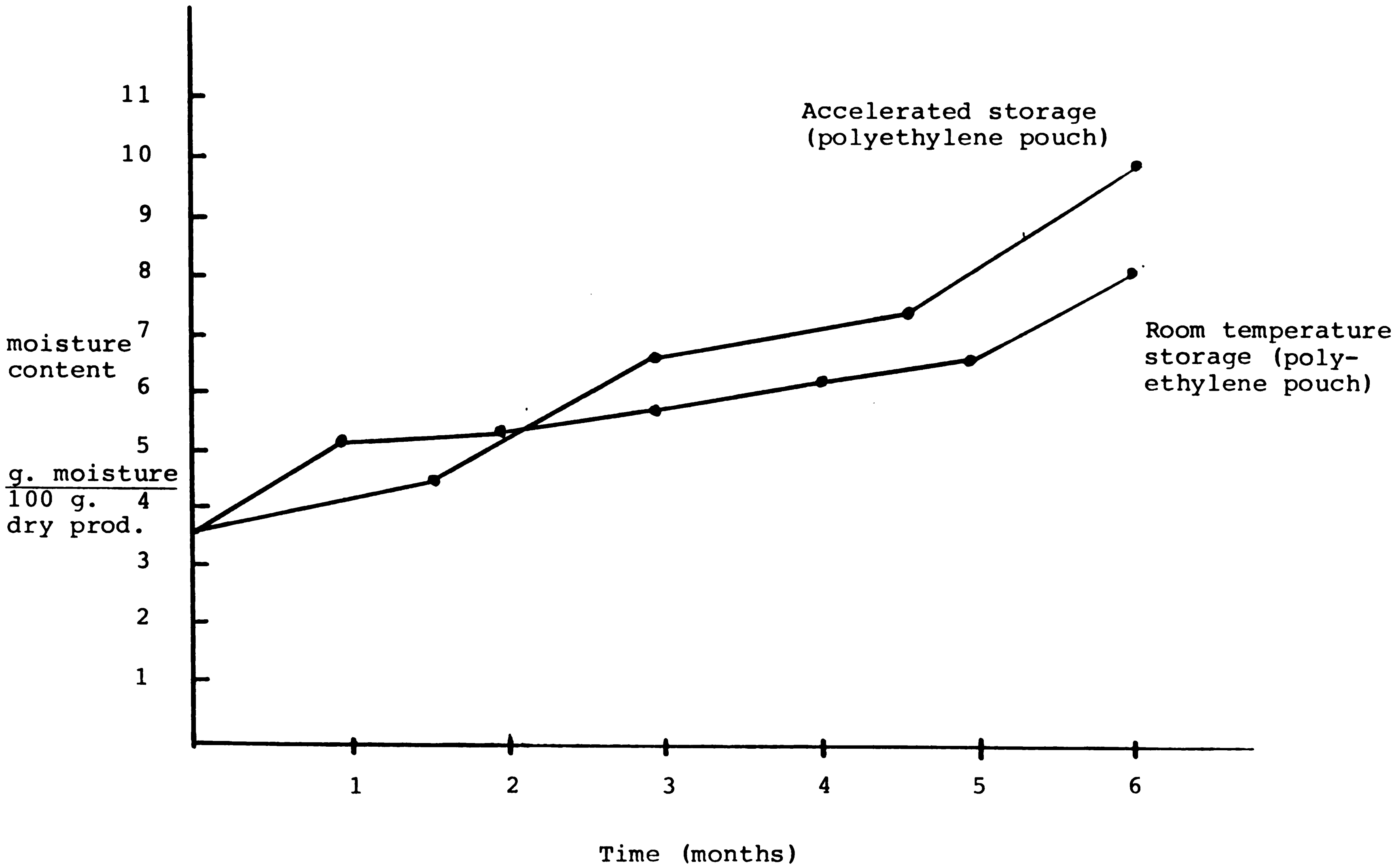


Figure 4. Accelerated moisture contents versus room temperature moisture contents of bean flour.

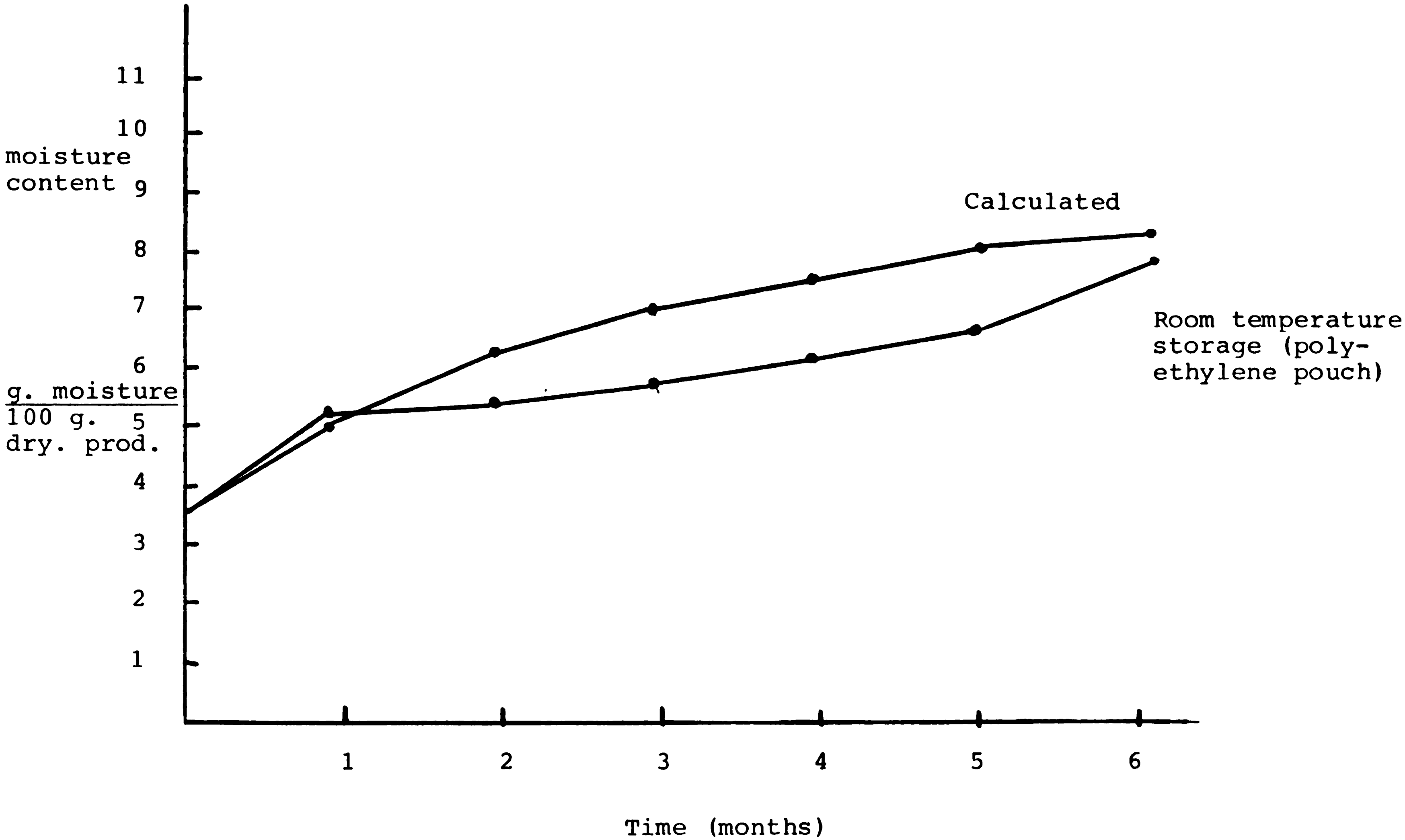


Figure 5. Calculated moisture contents versus room temperature moisture contents of bean flour.

predictions are well beyond the moisture contents of product stored at room temperature in polyethylene pouch material. This is a good example of why food products are overpackaged when using accelerated testing procedures for determining packaging barrier requirements.

Figure 5 illustrates the calculated moisture values increasing at a faster rate than room temperature values during the first three monthly intervals. However, at the four-month interval, calculated and room temperature storage, moisture contents become increasingly closer to the final six-month interval. At the six-month interval the calculated moisture content is slightly higher than the room temperature storage value. An analysis of percentage difference of actual room temperature moisture contents and accelerated moistures along with calculated moisture values are included in the discussion and conclusion chapter.

## DISCUSSION AND CONCLUSION

Current food industry practice for determining packaging barrier requirements for food products involves the use of accelerated testing procedures. A typical example is storing the product/package in accelerated conditions for 4 weeks and concluding that this equals 6 months' storage at room temperature. This correlation is based on previous storage experience with a similar product. Another typical example utilizing accelerated test procedures is the use of room temperature to accelerated storage ratios. For example, if 4 weeks accelerated equals 6 months' storage at room temperature from previous storage experience, then the following ratios can be utilized: room temperature--180 days (6 months); accelerated--29 days. This results in a ratio of 6.43. If a product becomes unacceptable at 2 weeks in accelerated conditions, then the ratio figure of 6.43 is multiplied by the 14-day unacceptability period. The result is 90 days of predicted storage at room temperature conditions.

One of the objectives of this study was to show that accelerated procedures for determination of packaging barrier requirements are not accurate. Visual triange test panels determined that the perceptible browning rate was reached at Hunter L value of 84.1 and below (Table 2).

As Table 3 points out, product packed in 2-mil polyethylene reached the discernible browning rate after 2 weeks of accelerated testing; however, it remained acceptable 6 months in room temperature conditions. Likewise, the product packed in the polyethylene/nylon/PVDC material reached the discernible browning point at 3 weeks in accelerated storage but remained acceptable 6 months in room temperature. The results of this data show the extremely poor correlation between accelerated testing results and room temperature results.

When applying the ratio concept of accelerated testing, the following predictions are evident:

polyethylene specifications - 6.43 x 14 days = 90 days;

polyethylene/nylon/PVDC - 6.43 x 21 days = 135 days.

The ratio prediction concept does not correlate with room temperature conditions at either 90- or 135-day storage.

Accelerated testing results in Table 3 show that both package material specifications resulted in discernible browning before the 4-week interval. A typical food industry conclusion would be, since neither film material produced acceptable results at 4 weeks, and 4 weeks equals the desired 6-month storage at room temperature, that the product will have to be packaged in a better barrier. This illustrates how accelerated testing procedures can result in inaccurate prediction data, which in this case would produce overpackaging of the food product.

The model approach demonstrated that the moisture content where non-enzymatic browning occurs can be determined at an earlier point in time than accelerated test procedures. This critical moisture content value can then be inserted into the model calculation which predicts the packaging material barrier requirements for the bean flour product.

Table 2 shows the method used to determine the moisture content where non-enzymatic browning becomes perceptible. This method used visual triangle test procedures with ten panel judges. The time period required to determine the discernible moisture content was in the range of 18-22 days. Depending on the packaging material used for product/package testing in accelerated storage, the time period for determining unacceptable moisture contents can take up to 4 weeks. Therefore, the model system approach for determining critical moisture contents can be a quicker method as compared to accelerated testing procedures.

Once the discernible moisture content had been obtained, a sample calculation was performed to determine the packaging material barrier rate to water vapor k needed to prevent perceptible browning to the bean flour product when stored 6 months at room temperature conditions. The result showed a maximum k value of .69 $g/m^2 \cdot 24$ hours$\cdot\Delta$ mm Hg required to keep the product acceptable. As Table 4 points out, both package materials had k values below this calculated value. Therefore, the model calculation, in this case, predicted that both package materials should provide acceptable storage for 6 months at room temperature conditions. Table 3 confirms the model calculation prediction with product/package storage at room temperature resulting in acceptable product when both package material specifications were used.

Further proof of the validity of the model approach was examined by inserting the k values of the film specifications into the model calculation while leaving storage time ($t_c$) as the unknown value. The model calculations were conducted using room temperature conditions as the environmental input values. Once the unknown ($t_c$) values were determined, product/package storage at room temperature was carried out to the unknown time value calculated by the model calculation. The ($t_c$) values determined by the model were: 2-mil polyethylene--293 days; polyethylene/nylon/PDVC--880 days.

Due to time restrictions, only the polyethylene ($t_c$) value was compared to product/package storage at 72°F, 50% RH. Room temperature storage results versus results predicted by the model approach are:

Room temperature

Moisture content: $10.43 \dfrac{\text{g. } H_2O}{\text{100 g. dry prod.}}$

Browning value (L): 83.2

Prediction model

Moisture content: $9.80 \dfrac{\text{g. } H_2O}{\text{100 g. dry prod.}}$

Browning value (L): 84.1

The correlation between actual storage results and model predicted results were examined through the use of a percentage difference value which is calculated in the following manner:

$$\frac{\text{actual storage value - model predicted value}}{\text{actual storage value}} \times 100$$

The percentage difference value for moisture values when leaving storage time ($t_c$) as the unknown value was 6.00, and the percentage difference for browning (L) values was 1.08. The percentage difference between the calculated moisture contents and actual room temperature moisture values at 6 months (Figure 5) was 1.50. Percentage differences between accelerated prediction moisture contents and actual room temperature moisture values at 6 months (Figure 4) was 15. The percentage difference values show greater accuracy with the model calculation method as compared to accelerated predictions.

Table 5 gives the calculation input values when varied ±6%, which was the percentage difference when calculating the unknown $t_c$ value. If the moisture content $m_c$ is calculated when input values are varied ±6%, the range of $m_c$ can then be determined. When the values in Table 5 were inserted into the model calculation, the range of $m_c$ resulted in values of 8.33-9.96, which shows the relative accuracy of the model results.

There are a few possible reasons for the percentage difference values with the model approach, such as errors due to:

Table 5. Model calculation input values if ± 6% error at 72°F--6 months

| Input Symbol | Input Variable | Calculated Value | - 6% | + 6% |
|---|---|---|---|---|
| $m_e$ | Equilibrium moisture at 50% RH on isotherm curve $\left(\frac{\text{g. moisture}}{\text{100 g. dry product}}\right)$ | 10.5 | 9.87 | 11.13 |
| $m_i$ | Initial moisture content $\left(\frac{\text{g. moisture}}{\text{100 g. dry product}}\right)$ | 3.6 | 3.38 | 3.82 |
| A | Surface area of packaging materials ($m^2$) | .0232 | .0218 | .0246 |
| $W_s$ | Dry product weight within pouch (grams) | 100 | 94 | 106 |
| Po | Vapor pressure of pure water at 72°F (mmHg) | 20.07 | 18.87 | 21.27 |
| b | Slope of moisture isotherm at 72°F | .22 | .207 | .233 |
| $t_c$ | Storage time (days) | 180 | 169 | 191 |
| k | Permeability of film to water vapor $g/m^2 \cdot 24\ \text{hours} \cdot \Delta\ \text{mmHg}$ | .43 | .404 | .456 |

(1) Temperature and humidity of storage conditions fluctuated from day to day, which will affect the final moisture contents and thus the browning L values.

(2) Relative humidity environments produced by saturated salt solutions may not be displaying the percentage RH desired. This can be due to improper preparation of the salt solutions or constant removal of chamber lids when weighing product samples.

(3) Determination of the moisture content when perceptible browning occurs by the model approach was conducted at five relative humidity storage environments, which may not always produce exact results. Perhaps using up to ten relative humidity environments for visual triangle tests would create a more precise moisture content value where browning occurs.

(4) Determination of the k value could have been another area of possible error. The ASTM dish method used a flat sheet of material, whereas the same packaging material used in the product/package testing was subjected to folding and handling which would cause stress cracking which increases the k value.

(5) The model approach contains the assumption that a straight line isotherm can be projected from a certain portion of the S-shaped curve. This could throw the model calculation off when the isotherm slope value (b) is determined.

As an alternative approach for determining packaging barrier requirements, this current research utilizes a mathematical model to predict packaging permeability requirements for a bean flour product. The model approach is especially useful for package development when a new product has to be introduced in a short lead time and the packaging barrier requirements need to be determined for a certain storage-distribution condition.

Current industry practice dictates the use of product/package storage studies for determining packaging barrier requirements. Since the model approach can be used to predict a packaging barrier rate (k), this k value can be used to take the guesswork out of product/package storage studies. Current industry storage studies require that the product be packaged in several materials with varying k values since the product's hygroscopic properties are not known before the studies are set up. By determining beforehand what k value is needed to keep the product stable, fewer package materials can be used for product/package storage studies.

The model approach for packaged food products can take into consideration environmental conditions that the product would be exposed to in various geographical areas of the world. Product/package acceptability for food products depends on the storage or distribution location and time of year of the location. Publications by worldwide weather organizations can be obtained to analyze temperature and humidity data. This can then be inserted into the model calculation for determination of the packaging barrier requirements when the product is being marketed in a certain location of the world at a certain time of the year.

In conclusion, the model approach method is an inexpensive, quick, and relatively accurate method for predicting the packaging barrier requirements for new or improved food products. Determination of packaging barrier requirements through modeling calculations would be especially useful to the food industry with product introductions requiring short lead times. In essence, the model approach method offers relatively accurate data for predicting packaging permeability requirements for food products. Nevertheless, follow-up on actual product shipment should be made to verify model calculation results.

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