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D.B. LUND
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APPLICATIONS OF "ACTIVE PACKAGING" FOR IMPROVEMENT OF SHELF-LIFE AND NUTRITIONAL QUALITY OF FRESH AND EXTENDED SHELF-LIFE FOODS[1]

T. P. LABUZA and W. M. BREENE

Department of Food Science and Nutrition
University of Minnesota
St. Paul, MN 55108

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INTRODUCTION

General Description

Active packaging systems when coupled with controlled atmospheric packaging (CAP) or modified atmospheric packaging (MAP) is a technology developing a new thrust because of the advances in packaging, material science, biotechnology and new consumer demands (Anon 1986a). This technology involves an interaction between the package film itself with the internal gas atmosphere and the food. The intent is to extend the shelf-life of foods while at the same time maintaining nutritional quality and ensuring safety. This is seen as significant, particularly for refrigerated fresh foods which have a short shelf-life and for which demand is increasing. It would be desirable to extend the shelf-life of these foods to 3–6 weeks.

New consumer trends are dramatically increasing the demand for extended shelf-life refrigerated foods. It has been reported that by the year 2000 CAP/MAP or sometimes called "chilled" foods will exceed the totals for aseptic and retort pouch packaging (Anthony 1986). In the U.S. these foods, when in the form of a complete meal, are being called ESL's or extended shelf-life refrigerated foods. Sneller (1986) estimated that there are already 250 million pounds of foods per year packed under CAP and that the volume will grow to yield a sales potential of $2 billion annually for film. Today only 1 million lb of plastic goes into this technology and the amount can triple. Over 74% of the top 100 food companies feel that this is the next major growth area. One key to the technology will be the controlled permeation of O_2 and CO_2 as well as the

[1]Presented at the Icelandic Conference on Nutritional Impact of Food Processing 1987, Reykjavik, Iceland.

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scavenging or controlled release of other compounds which could have a preservative effect on the food. It is apparent that a combination of several existing technologies, used in a new way, and combined with biotechnology where applicable, could lead to significant new products that would be major innovations in food packaging. Single or multiple effects could be combined so that the package would serve a number of shelf-life extension applications for fresh and extended shelf-life foods. This paper will review the present needs, the potential new technologies and the basis for the desired end point of each potential new application. In particular, it will review the specific needs of the various segments of the food industry for shelf-life extension and what the best technology for each of these needs would be.

In general terms, the desire for shelf-life extension has been fostered by the consumer, who now expresses a greater demand for fresh quality produce (especially salad vegetables) and for good quality fresh fish. These needs are based on nutritional concerns such as the reduced intake of fats from meats, more fresh cruciferous vegetables because of their supposedly anticancer effect and more EPA (eicosapentanoic acid) which can be obtained from cold water ocean fish like mackerel and salmon. The mobile singles, active couples and elderly want partially prepared, refrigerated, fresh meals from the supermarket that can be held for over a week in the refrigerator and can be easily cooked in the home (especially in the microwave oven). Supermarkets are interested in the area of refrigerated meals as they see this as a way to expand their deli section and increase their own profitability by making value added products and selling them directly. It should be noted that with any new technology, some resistance will occur.

Technologies Involved

Several basic techniques have the potential of being combined in a packaging film surface to achieve shelf-life extension and improved nutrition of high moisture fresh foods. These include the following physical/chemical effects:

a. Oxygen scavenging from the package atmosphere.
   (1) enzyme systems (e.g., glucose oxidase-glucose or alcohol oxidase-ethanol vapor)
   (2) chemical systems (e.g., controlled oxidation of reduced iron, photocatalysis with a dye, or catalytic conversion of oxygen to water vapor by platinum in the presence of hydrogen gas).

   Lowering of the oxygen partial pressure in the package results in a decreased rate of metabolism in fresh foods thereby increasing shelf-life except in cases where anaerobic bacteria may grow or where anaerobic respiration may occur. Molds and aerobic bacteria do not grow

under low oxygen conditions. Meat pigments will remain purple if kept under low oxygen conditions or red under high oxygen conditions.

b. Carbon dioxide control by generation, absorption and/or permeation. One method of controlling respiration is controlling the CO_2 concentration at a critical level which depends on the food being preserved. Relatively low CO_2 levels (<0–15%) slow respiration of fresh produce. A higher level (>20%) acts as an inhibitor of surface microbial spoilage for most foods. Most films have 3 to 5 times greater permeability to carbon dioxide as compared to oxygen making it difficult to independently control the CO_2 concentration by the film alone.
c. Ethylene control by absorption onto some oxidizing agent or organometallic substrate. Climacteric fruits (to be explained later) release ethylene during metabolism. This compound acts as a growth hormone stimulating the onset of ripening and senescence. Once ripened, fruits quickly spoil. Keeping ethylene under control can lengthen shelf-life.
d. Controlled release of antimicrobial preservatives onto the surface of the food by diffusion and evaporation from the film, from microcapsules imbedded in the film itself, or by chemical or enzymatic reaction (e.g., between glucose oxidase and glucose which release acid and peroxides). The preservatives such as acids, peroxide, or sorbate would act to prevent growth of surface spoilage bacteria, yeast, molds and pathogens.
e. Controlled release of ethanol into the package atmosphere. The ethanol condenses onto the food surface and acts as a microbial inhibitor.
f. Controlled release of chemical agents that slow loss of shelf-life by non-microbiological means. This would include release of antioxidants such as BHA or BHT, which is already commercially practiced with some cereals.
g. Slow adsorption of water from the food surface to lower water activity thereby reducing the rate of microbial growth.
h. Temperature control: A consumer package that would maintain temperature, either hot or cold so as to prevent growth of pathogenic or spoilage organisms during distribution and transport to the home.
i. Time-temperature integrator tags that can be used on the package surface to establish the amount of shelf-life left in a food product and thereby insure proper turnover and high nutritional quality. Another application would be a tag that indicates abuse so that a spoiled or unsafe product would not be used.

Other active packaging technologies could include surface treatment of the film to change gas permeability, especially carbon dioxide permeability; light absorbers, especially for UV light to slow oxidation; films that release a mineral that might preserve color (e.g., zinc or magnesium to maintain chlorophyll in canned foods); or odor absorbers to pull undesirable odors out of the package atmosphere as they are formed.

These "active packaging" technologies can be combined with other technologies to further enhance shelf-life, e.g., irradiation, microwave heating, UV, or infra-red pasteurization and aseptic heat processing. Underlying all of this will be a concern that changes in the package gas atmosphere or the chemistry of the surface have not affected the safety of the food with respect to growth of microbial pathogens and that the loss of nutritional quality is prevented.

A REVIEW OF THE NEEDS IN POTENTIAL FOOD CATEGORIES FOR SHELF-LIFE EXTENSION

Fresh Produce

Market. The recent trend in fitness has led to an increased demand for fresh fruits and vegetables, especially cruciferous ones (broccoli and cauliflower) and exotic ones like papaya, mangoes and kiwi (Johnson 1986). Per-capita consumption of fresh produce has grown by 12% in the U.S. in the last 10 years, while that of the frozen category has grown only 10%. Consumption of canned fruits and vegetables has dropped by 20% in this period. The fresh produce section in most supermarkets has nearly doubled in size over the last decade. The volume of fresh fruits and vegetables including mushrooms will exceed 180 billion pounds in 1988. The main problem, however, has been to get the produce into the store in high quality with minimal nutritional loss, keep it that way in the store, and have some way to help the consumer keep it in high quality enroute and in the home. Many university and USDA supported studies suggest that produce waste in the United States exceeds 15–20% from field to home (Bourne 1977). Johnson (1986) reported that retailers may be throwing away as much as 15% of fresh produce, because the customers will not buy decayed product. The larger demand for excellent quality only exacerbates the problem. A series of papers addressing quality and shelf-life of minimally processed fruits and vegetables was recently published (Shewfelt 1987; Rolle and Chism 1987; Klein 1987; Brackett 1987; Barmore 1987).

Mechanisms of Decay. The main causes of loss of quality and nutritional value of fresh produce are several fold and are all interconnected. Kader (1985a) has provided an excellent guide to information on postharvest biology and technology. Once harvested, a fruit or vegetable no longer has any new nutrients coming into it from the root system. It must thus rely on the endogenous nutrients along with oxygen to continue its respiratory processes. Since enzymes are not inactivated such as occurs in canning, or partially inactivated as in freezing or drying, the fresh, respiring produce may improve in quality in the short term, but eventually will deteriorate and decay. If picked before optimum ripeness, some fruits and vegetables (called climacteric), may improve in eating and nutritional quality and then begin to degrade. Examples of climacteric fruits are

pears, apples, melons, peaches, bananas, and tomatoes. Uniform terminology to describe the sequence of events occurring between initiation of a plant or plant part and its death has been proposed (Watada *et al.* 1984).

A climacteric fruit or vegetable ripens as the levels of certain internal hormones build up in the tissues. A key hormone is the hydrocarbon gas ethylene. Bufler and Streif (1986) pointed out that endogenous ethylene synthesis occurs in plant tissue via conversion of methionine to S-adenosyl methionine which is then converted to 1-aminocyclopropene-1-carboxylic acid (ACC) by ACC synthetase and that oxygen is a substrate in the ensuing conversion of ACC to ethylene by ethylene forming enzyme (EFE). However, ACC can also be conjugated in plant tissue to N-malonyl-ACC which is metabolically inert. According to Knee *et al.* (1987), while rapid ethylene synthesis accompanies the ripening of climacteric fruits, it appears to precede the respiratory rise only in certain varieties of melon. In other fruits, including apples, carbon dioxide and ethylene production increase simultaneously. If the level of ethylene is allowed to accumulate inside the package gas atmosphere, the product will quickly ripen. The optimum would be to control the respiratory process so that ripening occurs once the climacteric fruit reaches the home. Diminution of ethylene by scavenging, chemical reaction, or allowing it to dissipate through the packaging material will slow ripening.

Watada (1986) has recently reviewed the effects of ethylene on produce. Supplemental exogenous ethylene presently is used to induce ripening of avocado, bananas, mangoes, tomatoes, and honeydew melons. It is also used to degreen citrus fruits except limes. Oranges that develop early in the season are ripe when the skin is still green, especially those grown in California. The choice is either to dye the skin orange or treat with ethylene. Ethylene is also used to induce softening of freestone peaches and pears prior to processing. Although 1–10 ppm ethylene is sufficient to induce ripening, levels of 100–1,000 ppm are used to speed the process. It usually takes 12–48 h depending on the product and is carried out at 20–25°C and 90%–95% RH. Levels of carbon dioxide above 4% reduce the activity of ethylene, thus CO_2 must be removed or controlled during storage. Because ethylene is a highly combustible hydrocarbon gas it can explode in mixtures with air at concentrations between 3 and 32%. Safety precautions in the use of ethylene have been outlined by Reid (1985).

The process of decay involves several steps. All the enzymes present in the product before harvest are still active. The key enzyme systems are in the Embden-Myerhoff pathway and citric acid (Krebs) cycle. These are the main processes by which starches are converted to sugars which are then slowly used up as an energy source through oxidation by oxygen, with water and carbon dioxide as the main products of energy metabolism and flavor compounds as secondary metabolites. This process is called aerobic glycolysis. This aging or senescence eventually causes loss of sweetness, loss of some of the important flavors, and loss of key nutrients. As this occurs, the quality of the product

decreases once past the peak of the climacteric. If not protected from moisture loss, the product will also lose water from the cells which not only speeds up the aging process but also results in loss of turgor (Baird and Webster 1978; Grierson and Wardowski 1978).

Initially, the key end product of aerobic glycolysis is carbon dioxide, but as the source of carbohydrate for metabolism is depleted, other constituents are acted upon such as proteins and fats and new products such as acids and alcohols can accumulate. This causes off-flavors to develop. In addition, if the level of oxygen available in the package gets too low, the product will go from aerobic glycolysis into anaerobic glycolysis. This means incomplete oxidation with accumulation of acids, aldehydes, ketones and alcohols within the tissues. The accumulation of carbon dioxide in the package will also accelerate anaerobic glycolysis. This leads to loss of tissue integrity as cell membranes become damaged by accumulation of acids. The loss of integrity then allows cell contents to spill into the tissue fluid and react, producing off flavors, discoloration, and further loss of tissue integrity. Cells near the surface lose their ability to fight off infection by the microbes present and thus invasion by molds, yeast or bacteria occurs. This further accelerates spoilage.

Metabolic activity as a function of oxygen pressure is represented in Fig. 1. As can be seen in Fig. 1, if the oxygen pressure gets too low, anaerobic glycolysis occurs. This increases generation of carbon dioxide and fresh produce spoils

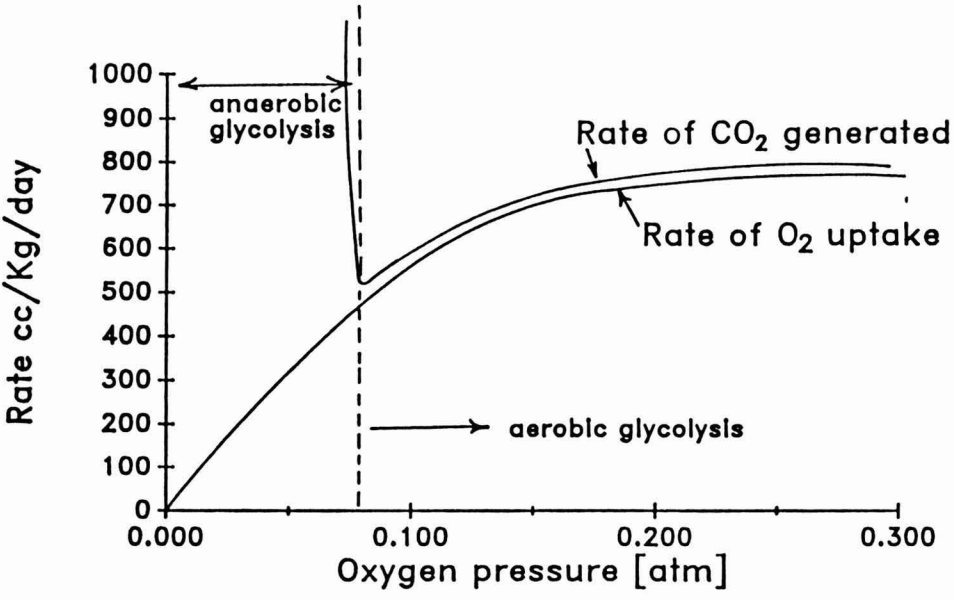

FIG. 1. RESPIRATION RATE OF A FRESH FRUIT OR VEGETABLE AS A FUNCTION OF OXYGEN PRESSURE

more rapidly. Each fruit or vegetable has a specific O_2 and CO_2 level at which this begins to occur. The Linde Corp. did extensive work in this area in the 1960's but none of it was published. Kader (1986) suggested that we do not understand very well the mechanisms for this action. His review related the biochemical basis for the action to changes in color, flavor, texture and nutritional composition.

Cell damage can also occur due to exposure to too low a temperature. Freezing is known to damage all produce extensively. Some produce are also susceptible to what is termed "chill injury" at temperatures above freezing, generally in the range of 5–15°C, depending on the product. Raison and Lyons (1986) proposed uniform terminology for describing chilling injury. Kader (1985b) categorized fruits and vegetables with regard to their susceptibility to chilling injury as well as their respiration rates, ethylene evolution rates and whether fruits are climacteric or nonclimacteric. Low temperature storage may cause membrane damage which can lead to increased uncontrolled biochemical reactions. The brown spotting of limes below 2°C, and the loss of flavor development of tomatoes below 9°C are examples of this type of damage.

At the same time that this complex series of events is taking place, there is also the potential for growth of microbes on the surface of the food. The extent of growth and types of microorganisms that can grow are dependent on the product itself (i.e., type of nutrients present) and external factors. Surface bruising damages cells and releases nutrients onto the surface but also allows for production of brown pigments by polyphenol oxidase—these pigments have some antimicrobial effect. Other factors include pH of the surface, temperature, relative humidity (a higher % RH encourages growth of spoilage microbes, especially molds, but a low % RH causes loss of cell water leading to wilting and loss of crispness), oxygen level (different microbial species will grow depending on the redox potential of the surface), and microbial load which depends on handling and the degree of washing, soaking, or other cleaning treatments. The damage to surface tissue that accompanies chilling injury enhances the invasion of spoilage organisms. Growth of the organisms can result in production of uncharacteristic odors and flavors, slime on the surface, and invasion of the interior of the product accelerating further decay. Excellent descriptions of physiological and microbial disorders in fruits, illustrated by color photographs, along with their causes and possible preventative measures have been published (Hall and Scott 1977; Porritt *et al.* 1982; Sommer 1985a).

There is also the potential for the growth of pathogens, organisms which can cause human disease, especially gastrointestinal upset. These organisms can come from mishandling, contamination with fecal matter (as in some countries where night soil-human feces is used as fertilizer, contaminating the produce with fecal coliforms), and from suppression of growth of the normal spoilage organisms thereby allowing pathogens to outgrow and predominate. Generally,

pathogens are not a significant problem with fruits and vegetables in developed countries since they are more likely transmitted by meats, fish, and poultry. However, a low oxygen level may allow the growth of anaerobic spore forming bacterial pathogens such as *Clostridium botulinum* which resides in soil and would be found on any vegetable grown on or in the ground. In fact, because of the way mushrooms are cultivated on horse manure they could present a health hazard at low oxygen levels and warm temperatures (>5°C). Inhibition of surface decay would also make it more difficult for the consumer to assess the true end of high quality shelf-life for fresh produce and they might try to eat a product that is spoiled (Bell 1986). Thus, some form of shelf-life time temperature integrator or a chilling system for the individual package might be needed as well.

Shelf-Life Data. Shewfelt (1986), Kader (1986) and Watada (1986) have recently reviewed the area of shelf-life extension for freshly harvested fruits and vegetables. Shewfelt's (1986) article contains over 160 references dating from the 1960s which shows the high interest in this area. No attempt was made to further review this area. With respect to nutrient loss, Labuza (1982) has presented a compilation of the data found in the literature for refrigerated foods. At that time there were few data available for extended shelf-life products. Kader (1986) estimated that there have been over 4000 reports on CA/MA storage but few have dealt with the biochemical mechanisms and the changes in sensory properties and nutritional value that occurs. Weichmann (1986) reviewed the effects of CA storage on sensory and nutritional quality of fruits and vegetables. He and Klein (1987) agreed that knowledge of CA storage effects on vitamin content is sparse and is available primarily for ascorbic acid and carotene. Generally, lower oxygen levels favor ascorbic acid retention while the reverse is true for carbon dioxide. However, storage temperature and the ratio of oxygen to carbon dioxide also appear to be important in governing the fate of ascorbic acid. Species, cultivar, maturity and other effects are likely. Weichmann (1986) reported that carotene in CA stored carrots appears to be most stable at low oxygen levels and at 7.5 to 10% carbon dioxide.

The key concept for improvement of quality of fresh produce is the understanding of postharvest physiology in much more depth than broadly characterized above. Once this is understood, then technologies can be applied to control the decay. Of key importance is the defining of the end point of high quality life for each fruit or vegetable, i.e., the kind and amount of quality factors or nutrients that can be lost before the product is deemed unacceptable. It should be realized that this will differ for each product but in general will include assessment of texture, flavor (e.g., sweetness or tartness), odor, color and nutritional quality as a function of time under different storage conditions. In the U.S., the Food and Drug Administration (FDA) uses 10% of the RDA of a

TABLE 1.
OPTIMAL STORAGE CONDITIONS FOR VEGETABLES

Commodity	Storage Temperature °C	Relative Humidity %	Approximate Storage Life
Artichokes - Globe	0	95	2 to 4 weeks
Asparagus	0-2	95	2 to 3 weeks
Beetroot (topped)	0	95-100	3 to 5 months
Broccoli	0	95	10 to 14 days
Brussels Sprouts	0	95	3 to 5 weeks
Cabbage, late	0	90-95	3 to 5 months
Carrots			
Topped - immature	0	90-95	4 to 6 months
Topped - mature	0	90-95	4 to 5 months
Cauliflower	0	95	2 to 4 weeks
Celery	0	95	2 to 3 months
Corn (sweet)	0	95	4 to 8 days
Cucumbers	7-10	90-95	10 to 14 days
Eggplant	7-10	90	5 to 7 days
Garlic, dry	0	65-70	6 to 7 months
Leeks, green	0	90-95	1 to 3 months
Lettuce, head	0	95	2 to 3 weeks
Mushrooms	0	90	3 to 4 days
Onions			
green	0	90-95	3 to 4 days
Dry and onion sets	0	65-70	1 to 8 months
Parsley	0	90-95	1 to 2 months
Parsnips	0	90-95	2 to 6 months
Peppers - sweet	7-10	90-95	2 to 3 weeks
Potatoes			
Early	10-13	90	-
Late Crop	3-10	90-95	5 to 12 months
Sweet	13-16	85-90	4 to 6 months
Pumpkins	10-13	70-75	2 to 3 months
Radishes			
Spring	0	95	3 to 4 weeks
Winter	0	95-100	2 to 4 months
Rhubarb	0	95	2 to 4 weeks
Spinach	0	95	10 to 14 days
Squash			
Acorn	7-10	70-75	5 to 8 weeks
Summer	0-10	85-95	5 to 14 days
Winter	10-13	70-75	4 to 6 months
Tomatoes			
mature green	13-21	85-90	1 to 3 weeks
firm, ripe	7-10	85-90	4 to 7 days

nutrient as the level equivalent to a significant source and 2% as the minimum amount to trigger nutritional labeling. Such factors as stage of maturity, cultivar, cultural practices and growing conditions can easily cause the important nutrients in fruits and vegetables to vary by a factor of two (Breene 1983). In order to establish the technical specifications for the proposed technology, data will need to be collected for each of these categories as a function of the physiological condition of the product and as a function of temperature, relative humidity, gas atmosphere composition, and light.

Some very general data for shelf-life of vegetables is shown in Table 1 and for fruits in Table 2 revised from USDA Handbook No. #66, (Lutz and Hardenburg 1968; Hardenburg *et al.* 1986). The data did not specify the major mode of deterioration for loss of eating quality. It can be seen that for each product there is a range of shelf-life depending on the temperature and that some products have a shelf-life of less than 2 weeks. Several vegetables with short shelf-life (<3–4 weeks) are increasing in consumption in the U.S. because of perceived health benefits or because they represent a more nutrition conscious culture. These include artichokes, asparagus, broccoli, cauliflower, corn, cucumbers, lettuce (all varieties), mushrooms, sweet peppers and tomatoes. Those fruits with a short shelf-life include apricots, strawberries, raspberries, blueberries, cantaloupe, cherries, kiwi, peaches, and tangerines.

In general, the more rapid the respiration rate, i.e., utilization of oxygen for metabolism of a product, the more rapidly the commodity is deteriorating. Thorne and Meffert (1978) have published crude data for the shelf-life of different fruits and vegetables using the simple kinetic model where:

$$\ln(\text{time}) = A + BT \quad (1)$$

A, B are constants

T is temperature

Although Eq. 1 is possibly not the more correct Arrhenius inverse absolute temperature model, the equation can be used to develop typical shelf-life plots to see the effect of temperature on shelf-life. End points in this case were derived from sensory evaluation and the constants are reported in Table 3 (Thorne and Meffert 1978). Labuza (1982) also summarized data for shelf-life of fresh fruits and vegetables by using shelf-life plots and by calculating the Arrhenius activation energy. This was done for an Office of Technology Assessment (US Congress) assessment on shelf-life of foods. These data can be used as benchmarks for the assessment of any technology used to improve shelf-life at a given storage temperature. Figure 2 shows a typical shelf-life plot for strawberries and asparagus.

In general, a major factor for controlling shelf-life is temperature control all through the distribution chain. The Q_{10} value represents the increase in rate of decay for each 10°C increase in temperature above the optimum for storage

TABLE 2.
OPTIMAL STORAGE CONDITIONS FOR FRUITS

Commodity	Storage Temperature °C	Relative Humidity %	Approximate Storage Life
Apples	-1-4	90	3 to 8 months
Apricots	0	90	1 to 2 weeks
Avocados	4-13	85-90	2 to 4 weeks
Blackberries	-0.5-0	90-95	2 to 3 days
Blueberries	-1-0	90-95	2 weeks
Cantaloupes	2-4	90-95	5 to 15 days
Cherries			
Sour	0	90-95	3 to 7 days
Sweet	-1	90-95	2 to 3 weeks
Casaba melons	7-10	85-90	4 to 6 weeks
Cranberries	2-4	90-95	2 to 4 months
Currants	-0.5-0	90-95	10 to 14 days
Dewberries	-1-0	90-95	3 days
Gooseberries	-1-0	90-95	2 to 4 weeks
Grapefruit	10-16	85-90	4 to 6 weeks
Grapes			
American	-1-0	85	2 to 8 weeks
Vinifera	-1	90-95	3 to 6 months
Guavas	7-10	90	2 to 3 weeks
Honeydew melons	7-10	85-90	3 to 4 weeks
Lemons	0-10	85-90	1 to 6 months
Nectarines	-0.5-0	90	2 to 4 weeks
Oranges	0-9	85-90	3 to 12 weeks
Peaches	-0.5-0	90	2 to 4 weeks
Pears	-1.6-0.5	90-95	2 to 7 months
Persian melons	7-10	85-90	2 to 3 weeks
Persimmons	-1	90	3 to 4 months
Plums	-1-0	90-95	2 to 4 weeks
Pomegranates	0	90	2 to 4 weeks
Prunes	-1-0	90-95	2 to 4 weeks
Quinces	-1-0	90	2 to 3 months
Raspberries	-0.5-0	90-95	2 to 3 days
Strawberries	0	90-95	5 to 7 days
Tangerines	0-3	85-90	2 to 4 weeks
Watermelons	4-10	80-85	2 to 3 weeks

(generally around 1°C). The Q_{10}s for most fruits and vegetables vary between 2 and 3 in the 0 to 25°C temperature range. Thus, a product such as asparagus which can remain in high quality for 2–3 weeks at 1°C will have only 2–4 days shelf-life when held at 22–25°C. Strawberries have a shelf-life of only 1 week at 1°C; at room temperature they will last less than 2 days. These data show the importance of temperature control in distribution. In fact, temperature control

TABLE 3.
PARAMETERS FOR EQ. (1) RELATED TO THE EFFECT OF TEMPERATURE ON SHELF-LIFE OF FRUITS AND VEGETABLES

Product	A	B	Correlation	Range
Apples	180	0.109	0.999	0 - 20
Asparagus	33	0.100	0.983	2 - 25
Carrots, unwashed	159	0.228	0.992	0 - 20
Carrots, washed	20	0.125	0.953	0 - 20
Cauliflower	38	0.150	0.986	0 - 20
Cucumber	112	0.199	0.994	13 - 20
Chicory	21	0.157	0.984	0 - 20
Endive	12	0.122	0.994	0 - 20
Lettuce	11	0.115	0.994	0 - 20
Lettuce, Iceberg	39	0.074	0.977	0 - 15
Mushrooms	5.7	0.081	0.987	1 - 20
Oranges	91	0.087	0.995	5 - 15
Pears, Packhams	219	0.175	0.994	0 - 5
Pears, Buerre Bose	219	0.175	0.994	0 - 5
Plums, Victoria	19	0.106	0.992	0 - 20
Plums, others	9	0.081	0.984	0 - 20
Purslane	5.7	0.081	0.986	0 - 20
Raspberries	5.7	0.081	0.986	0 - 20
Strawberries	5.7	0.080	0.988	0 - 20
Tomatoes, green	97	0.131	0.999	12 - 20
Tomatoes, orange	125	0.160	0.999	12 - 20
Tomatoes, red	43	0.128	0.998	8 - 20
Asparagus, frozen	4.4	0.214	0.992	-17 - -24
Beans, frozen	7.4	0.204	0.996	-15 - -22
Beans, frozen, lima	7.4	0.204	0.996	-15 - -22
Broccoli, frozen	4.4	0.213	0.992	-18 - -24
Cauliflower, frozen	2.4	0.227	0.992	-15 - -22
Peaches, frozen	5.3	0.237	0.997	-15 - -21
Peas, frozen	7.4	0.204	0.996	-15 - -22
Spinach, frozen	4.1	0.205	0.991	-15 - -20

is not practiced very well. The Q_{10} values also point out that application of other technologies that might help to lengthen shelf-life may be inappropriate if temperature control is not practiced. Some of the major U.S. food companies are getting into branded produce (Dole, Bud, Pillsbury, Kraft). Most likely they will have to insure that proper temperature control is practiced along with the other technologies that will be used to extend the shelf-life. Whether there is a synergistic effect between different technologies is not known.

Current Technology: Controlled Atmosphere (CA)—Modified Atmosphere (MA) Storage. Based on the above discussion, the food industry has developed two technologies for storage to enhance shelf-life of fresh produce:

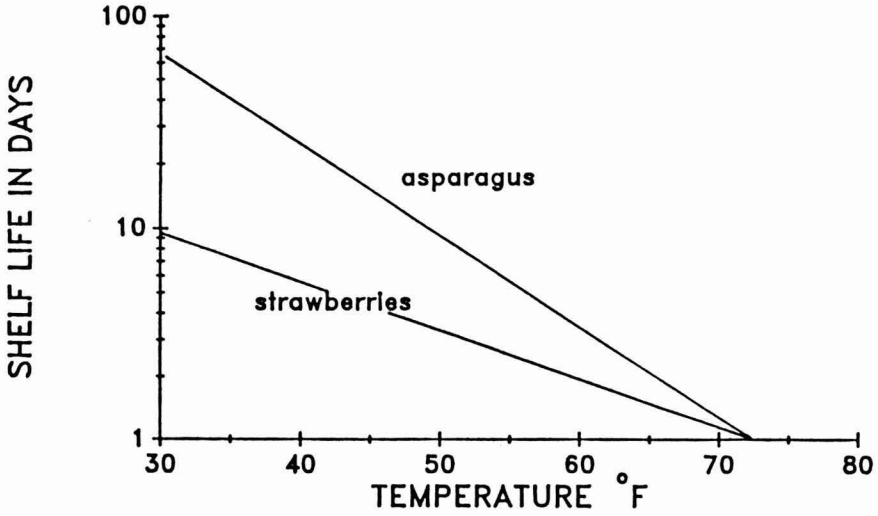

FIG. 2. SHELF LIFE OF SEVERAL FRESH FOODS AS A FUNCTION OF TEMPERATURE.

controlled atmospheric (CA) and modified atmospheric (MA). These are practiced either in completely sealed warehouses, in large shipping containers or in an individual package. Each involves a combination of lowering the oxygen level (by natural means or by vacuum or nitrogen flushing), raising or lowering the carbon dioxide level (naturally from the respiring produce or by flushing), and controlling the level of ethylene. Ethylene can be controlled by use of hypobaric storage (HBS), also called low pressure storage (LPS) (Kader 1985c; Sommer 1985b). In this case, the container atmosphere is under the pull of a vacuum which not only controls the oxygen and carbon dioxide levels but also sucks the ethylene out of the tissues and the gas space. The problem of implosion, and the required humidity control to prevent dehydration have limited this technology.

Tompkins (1965) presented an excellent review of CA storage for fruits and vegetables. Other reviews on the subject have been published by Smith (1963) and Smock (1979). Several major conferences have been held on CA storage and transport of perishable foodstuffs (Dewey *et al.* 1969; Dewey 1977; Richardson and Meheriuk 1982; Blankenship 1985). The increasing interest in this subject is borne out by the fact that these conferences have been occurring more often and the published proceedings have more than tripled in size. As early as the late 1920s it was known that the shelf-life of produce could be extended by lowering the oxygen to 2–3% from the normal 21% in air, and raising the CO_2

level up to 3–5% from the 0.03% in air. Some fruits and vegetables can stand higher or lower levels of each gas. For example, tomatoes can only withstand 5% CO_2 and some apple varieties 10%. Table 4 (Labuza 1982) summarizes some of the data for optimum storage gas composition. As noted, some fresh products do best in the absence of CO_2 while others require 10–15%. Strawberries

TABLE 4.
OPTIMAL CONTROLLED ATMOSPHERE CONDITIONS FOR FRUITS AND VEGETABLES WITH A COMPARISON OF ESTIMATED SHELF-LIFE

Commodity	Application S=Storage T=Transport	Temp. °C	Atmosphere % O_2	Atmosphere % CO_2	Benefit	Injurious Atmosphere % O_2	Injurious Atmosphere % CO_2	Marketable Life (days) Air	Marketable Life (days) CA	Marketable Life (days) Hypobaric	Commericial CA Potential
Fruits											
Apples											
McIntosh & Newtons	S	3	3	5	major	2	10	120	200	200	great
All other varieties	S	0	3	3	major	1	5	200	300	300+	great
Apricots	S	0	1-2	2-3	major			14	50	84	slight
Blueberries	S	0	10	11	slight			14	42	56	slight
Cherries, sweet	S & T	0	1-3	5-10	moderate			21	28	56	moderate
Nectarines	S	0	1-3	5	major	0.25	6	21	42	—	moderate
Peaches	S	0	1-2	5	major	0.25	6	21	56	84	moderate
Grapefruit	S	7	2-5	2-5	moderate	1		28	42	100	slight
Lemons	S	15	3-5	0-5	major		6	130	220	—	slight
Limes, Persian	S	10	5	7	moderate	1		21	42	84	moderate
Oranges, Valencia	S	1	15	0	slight	5	5	42	84	—	nil
Mangos	S	13	5	5	slight	1	6	14	21	28	moderate
Pears, Bartlett	S	0	1	5	major			60	100	200	moderate
Pears, winter	S	0	2	1	major		2	200	300	—	moderate
Plums	S	0	1-7	0-7	moderate			21	28+		nil
Raspberry	T	0	2-5	0-20	slight			3	3+	—	nil
Strawberry	S & T	0	4-10	0-20	major	1		7	7+	21	moderate
Table grapes	S	0	5	2-5	slight			120	120+	—	nil
Avocado	S	7	1	9	major	0.5		30	60	100	moderate
Banana	T	13	2	5	major	1	8	21	60	150	nil
Papaya	T	13	1-2	0	major		5	14	21	28	moderate
Pineapple	T	7	2-5	0	major			12	12+	40	moderate
Vegetables											
Artichoke	T	0	2-5		moderate	1		21	21+	—	nil
Asparagus	S & T	0-2	1-3	5-15	major	1		14	14+	28	slight
Green beans	T	7	2-5	15	major			7	21	—	moderate
Broccoli	T	0	2-5	10	moderate			14	21	—	slight
Brussel sprouts	S	0	2-14	5-10	major			21	21+	—	nil
Cabbage	S	0	1-2	5-10	major			90	180	—	slight
Cauliflower	S & T	0	2-4	2	none	1	5	14	21	—	none
Cantaloupe	T	5	2	10	moderate	1		14	14+	—	moderate
Melons	T	10	2-5		moderate			14	14+	—	moderate
Celery	T	0	1-4		slight		3	28	28+	—	nil
Sweet corn	T	0	2-4	0-10	moderate	1	10	3	8	21	major
Cucumbers	T	8	3-5		slight			14	14+	42	slight
Lettuce	T	0	2-5	0	slight		4	21	21+	42	moderate
Mushrooms	T	0	1-2	10-15	moderate	0.5		5	8	18	major
Okra	T	10		10-12	slight			7	7+	—	nil
Green onions	T	0	2-5	5-10	major			7	7+	14	nil
Green peas	S & T	0	5-10	5-7	variable			7	7+	—	slight
Sweet peppers	T	13	3-5	2-8		2	10	14	28	50	moderate
Tomatoes	S & T										
(mature green)		13	3-5	0	moderate	2	- 2	21	42	84	major
(breakers)		13	3-5	0	slight	2	2	14	28	42	moderate

require from 0 to 20% carbon dioxide showing the variability. In PVC film, lettuce will rot in 2 days at 20°C as the CO_2 goes above 9%; in LDPE it will brown in 3 days, while in a 10% O_2/10% CO_2 flush it will last 4 weeks at 4°C.

For McIntosh apples, the optimum conditions are 3% oxygen and 3% carbon dioxide at 3°C and 87% RH for the first month after picking and then 5% CO_2, and 3% O_2 and 87% RH afterwards. In a commercial process, the cold storage warehouse is filled with fruit after chilling, sealed and then gas generators are used to fill and then control the atmosphere. Because of the volume of fruit, this is usually only done with fruits that have long shelf-life, such as apples, because the time required to get control exceeds the shelf-life of the more sensitive products. Apples stored as described above will retain good quality for over 6 months. Some vendors have built portable units for transporting highly sensitive fruits. Union Carbide Corp. has developed the POLARSTREAM transportation system which uses LN_2 (liquid nitrogen) to flush out and cool transport vehicles for fresh produce. The main aim is cooling and there is no effort to control the oxygen/carbon dioxide ratio. Other similar systems include the Nitrol and Nhytemp systems which meter nitrogen into the vehicle storage compartment during transit (Kader 1985c). TransFRESH Corp. sells the TECTROL CA mobile technology with 25,000–30,000 bulk freight containers employed worldwide (Bell 1986). They estimate that 60% of them are for fresh produce while the rest are for meat. It is also being used by the Red Lobster® restaurant chain.

An innovative way to employ CA storage and one that can be practiced at the harvester level is the use of selectively permeable packaging films that will cause the inside atmosphere of a package to achieve the desired composition. Tompkins (1965) also noted that the package should allow for a slight loss of water, but not more than 3% of fresh weight can be lost or serious wilting occurs. Because the excess water produced by respiration in the cells can cause splitting of the skins, some means must be used to have it escape into the environment. Two excellent recent reviews of this technology have been written by Rizvi (1981) and Ben-Yehoshua (1985).

In a sealed package, the oxygen level will fall and the carbon dioxide level will rise as the product inside respires. In addition, as the O_2 level falls, there is a concomitant ingress of oxygen through the packaging film due to its permeability. The lower the inside oxygen level, the faster the permeation rate. The lower the permeability of the film, the lower will be the ultimate internal oxygen level. Table 5 lists the typical industry oxygen permeation rates for common films in various units. For most polymer films, the carbon dioxide permeation rate is generally 3 to 5 times greater than that of oxygen because of its greater solubility in the film. The values in Table 5 refer to the k/x value in the following equation for the rate of oxygen penetration into the package:

$$RO_2 = [k/x]\,[A]\,[P_{out} - P_{in}] \qquad (2)$$

TABLE 5.
OXYGEN PERMEATION RATES FOR PACKAGING FILMS*
EXPRESSED IN DIFFERENT UNITS

Film	cc per 100 in^2 day ATM	cc per m^2 day mm Hg	cc per m^2 day ATM
PP/EVOH/PP	<0.001	<0.00001	0.01-0.02
Foil laminate [mylar/Al/poly]	<0.01	<0.00001	<0.01-0.1
PVDC	1	0.02	15
Acrylonitrile polymer	1	0.02	15
Brickpak flat	2-3	0.04-0.05	30-40
PET (polyester)	4-6	0.08-0.13	60-100
PVC	10	0.2	150
Brickpak (folded and scored)	100	2	1500
HDPE	130	2.6	1980
PP	150	3.0	2280
LDPE	400-500	8-10	6000-7000

*For 1 mil flat (unless composite laminate) at 30°C and 50% RH.

where RO_2 = rate of permeation in cc oxygen per day
k/x = permeability in cc per day-m^2-Atm
A = area of package in m^2
P_{out} = partial pressure of oxygen outside the package in Atm (For air @ 21% oxygen, this is 160 mm Hg or 0.21 Atm)
P_{in} = partial pressure of oxygen inside the package

At the same time that the enclosed fruit or vegetable is using up oxygen by respiration, it is theoretically producing one molecule of CO_2 for each molecule of O_2 used up in aerobic glycolysis. This rate of respiration can be assumed to be fairly linear for oxygen pressures between 0 and 100 mm Hg (0–12% oxygen). A simple linear approximation of respiration gives:

$$R_r = [B]\,[W_s]\,P_{in} \tag{3}$$

where R_r = respiration rate in cc oxygen per day used
B = constant in cc oxygen—atm per gram per day
W_s = grams of food contained
P_{in} = internal package oxygen pressure in atm

At higher oxygen levels, the rate of respiration levels out as was shown in Fig. 1. Computer methods have been devised by Simon *et al.* (1971) for handling this mathematical situation. In combining these two equations the steady state condition can be found since by engineering principles, input minus output equals accumulation or depletion. Thus, after some period of time, in any semipermeable container, the inside gas atmosphere composition will reach a constant oxygen and carbon dioxide level. The same equations could be used for calculating the constant level of CO_2 that would be reached. This can be seen graphically in Fig. 3

The crossover point of the two lines is the steady state condition and is calculated by setting both equations equal to each other, i.e., accumulation is zero. Thus:

$$P_{in} = \frac{P_{out}}{\frac{B\,W_s}{[k/x]\,A} + 1} \tag{4}$$

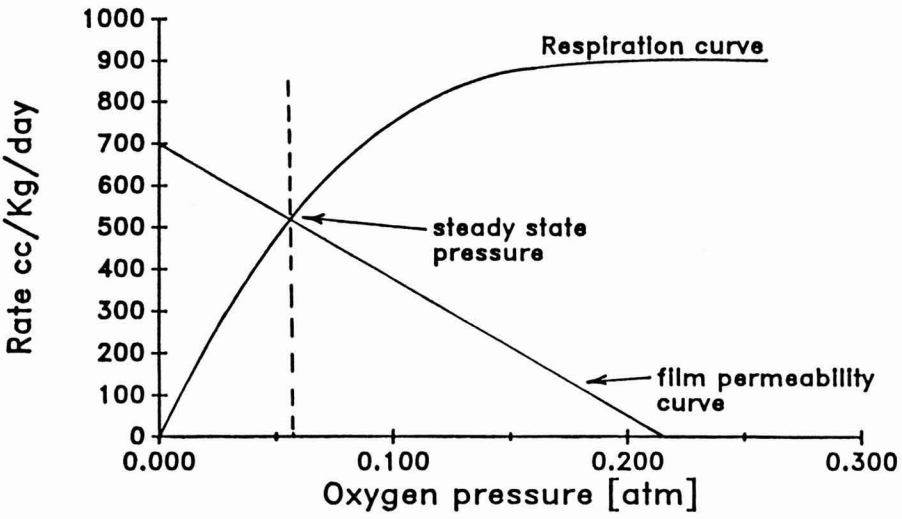

FIG. 3. COMPARISON BETWEEN THE THEORETICAL RESPIRATION RATE AND FILM PERMEATION RATE AS A FUNCTION OF OXYGEN PARTIAL PRESSURE.

Jurin and Karel (1963) confirmed these equations in a study with McIntosh apples. They used gas chromatography to measure the head space concentrations of gases in containers with different permeabilities. The apples in low density polyethylene bags reached steady state in two days. In a similar study for oranges (Labuza and Karel 1967) it was found that the B value was 1280 cc atm per Kg day with the respiration leveling out at 8–10% oxygen. Steady state occurred within 4 days for 2 oranges (1 Kg) in LDPE bags at 4°C. Thus, if one measured the oxygen level in a package after a few days, had data for respiration rate as a function of oxygen pressure and the total amount of oxygen that needs to react to reach end of shelf-life at the given conditions (T, a_w etc.) one could predict the shelf-life. Unfortunately very little of this type of data is available in the literature especially for nutrients with respect to total oxygen reacted at the point of significant nutrient loss.

Geeson *et al.* (1985) described a study in which 14 different films were tested for their effects on the sensory and color shelf-life of nonripe tomatoes at 10°C. The PVC film ($k/x = 7000$) and butadiene-styrene copolymer film ($k/x = 4500$) developed an oxygen/carbon dioxide atmosphere of about 9%/3% and 6%/5%, respectively, within 3–5 days. Polyethylene ($k/x = 1750$) developed a 4%/12% ratio while cellulose acetate ($k/x = 3200$) developed a 1%/18% oygen/carbon dioxide ratio. These results do not fit the expected permeances with respect to the cellulose acetate. Most likely the problem was in the reported permeance values used by the authors. The results on tomato quality did fit the gas ratios, with the slowest ripening for the first two films (PVC and butadiene-styrene) extending shelf-life for an extra 10 days as compared to open perforated packs. The tomatoes in the cellulose acetate did not ripen at all; within 1 week they had a high incidence of rotting and off flavor as expected. All packed tomatoes were inferior in flavor and color to vine ripened tomatoes from the same batch. This indicates that when the oxygen level is decreased another mechanism affects the secondary metabolism in regard to flavor development. The highest degree of rotting was in the film with the lowest water vapor transmission rate (polyethylene), which also developed the highest internal %RH.

The above studies point out one of the problems: a given film results in a specific oxygen/carbon dioxide ratio that is specific to the properties of the film and the type and the quantity of fresh fruit or vegetable enclosed. This means that the final gas composition ratios cannot be controlled independently. If carbon dioxide gets too high or oxygen too low the fresh food will rot more rapidly. Veraju and Karel (1966) showed, however, that one could make packages with windows of different films to specifically control the permeability. Methods were given to calculate the specific areas and permeabilities needed to match the gas ratio that would be optimum for a specific product.

Twenty years have elapsed since the 1960 studies and little has been invested in this technology except for shipment of bananas (United Brands with their

Bananavac Bag), fresh apples (for example, Rhone-Poulenc of Paris, France) and to some degree pears, lemons and cabbage, the latter one more with respect to storage rooms. In fact, the major developments have been on a large scale with respect to storage rooms, bulk freight containers and transportation vehicles. Grumman Allied Ind., in a joint venture with Armour, developed a hypobaric vacuum system (Dormavac) which was used for meats but never applied commercially to fruits or vegetables. This system does not seem to be in use at this time probably because of the cost as related to the price of meat.

The lack of interest over the last twenty years to utilize the in-package CA/MA technology is hard to understand. R. Eidman of DuPont has estimated that India loses 30–35% of its fruits and vegetables due to rot and Brazil loses at least 25% (Chem Week, March 13, 1985). As was noted earlier, the waste in the U.S. may be as much as 15–20%. The upswing in interest in healthful fresh foods and nutrition in the U.S. has perhaps stimulated new awareness. Also, it may take as much as twenty years for basic research in an area to be recognized and developed into a sellable technology. It is intersting that Ben-Yehoshua (1985) described CA/MA packaging as a new technology even though it was first described in the technical literature in England in the 1920s and in the U.S. in the 1940s and MIT pioneered the theoretical development in how to select the proper film in the 1960s. Recently in a meeting on CAP/MAP technology in the U.S. (Schotland Industries, Princeton, NJ, 1986) the Cryovac Div. of W. R. Grace Co. demonstrated a wrapped orange that was kept at 50 F for 6 months and was perfectly edible. The type of film was not described. W. R. Grace supported much of the early packaging work of Karel at MIT in the 1960s. D. Roddick (Personal Communication, 1987) of Fresh Wrap, Inc. (Yuma, Arizona) has said that the whole process is trial and error, at least in their work with lemons. Most likely they did not have enough of a data base to make the proper calculations. They did note that there is some objection from customers who cannot pick up and smell the individually wrapped product to determine if it is fresh. This objection should be easy to overcome if the consumer learns to trust the system. The reduced oxygen level should also slow the browning that develops if the produce gets damaged by bruising (e.g., bananas, lettuce) or when produce is precut. This browning is due to an enzyme reaction, polyphenoloxidase, which requires oxygen. The reduced oxygen level should reduce the rate of action of formation of quinones from polyphenolics that this enzyme causes.

Ben-Yehoshua (1985) reported that individual wrapping of fruit to produce an internal CA/MA atmosphere is practiced in Japan for citrus fruits and persimmons (25 μm LDPE) and in Australia. In Australia, these fruits are being successfully shipped overseas and can withstand higher shipping temperatures. He also reported 3 trials of this "UNIPAK" system in Florida in 1982–83 and in Texas. The Fresh Wrap Co. is reported to do this at a charge of 1.5 cents per fruit. It was also reported (Chem Week March 1985) that the TransFRESH

Co. of Salinas, CA used some form of CA packaging for the 1984 crop of strawberries. It was suggested that they flushed the package with carbon dioxide. This would slow metabolism by mass action to some degree. It was not mentioned how much shelf-life extension was achieved or whether this was continued. A significant quantity of fruits and vegetables packaged in Japan may be in a package which is using some type of CA/MA system since they were being kept at room temperature and seemed to be of good quality from personal observation. Also people in Japan shop more often so the turnover may be higher.

Other Technologies for Shelf-Life Extension of Fresh Fruits and Vegetables. Several other technologies that can be used to improve the shelf-life of fresh produce have been reviewed by Shewfelt (1986). These are presented below.

Chemical Treatment. Chemical treatment includes sprays on the plant before harvest (gibberelins, auxins, cytokinins, etc.) to control ripening as well as for other effects. Chemicals used on crops are allowed in the U.S. only if they are first approved under the food pesticide regulations, whether they are a pesticide or not. Firstly they must be approved under the EPA pesticide regulations and then accepted by FDA even though they are used in the field on the growing crop. A specific tolerance is set for the amount allowed after harvest on the food directly. Use of antmicrobial sprays, washes, fumigants such as sulfur dioxide or EDB and wraps that have been impregnated with antimicrobials to control rotting is another application. Dennis (1983) has reviewed this recently. Only FDA approved substances can be used. Very little has been done in this area and it is rarely used because of the problems of the past based on toxicity (e.g., mercuric wraps for oranges, EDB on oranges). Although a recent patent (U.S. 4,547,381) has shown the effectiveness of using chlorine dioxide gas on closed crates of fruits and vegetables to prevent decay, again there is concern over the toxicity and most likely the method will not be used.

Some work has also been done with an enriched carbon monoxide atmosphere (Kader 1985c; Sommer 1985b). This poisons the metabolic cycle of the respiring fruit or vegetable and can increase shelf-life. Because of the highly toxic nature of the gas, however, the only allowed application with FDA is as a combustion gas at no more than 4.5% carbon monoxide (21CFR 193.65).

Irradiation. Irradiation at low dose (<0.1 MRad = 100 kRad = 1 kGy) can also be used for the extension of shelf-life of fresh foods. In the U.S. the FDA cleared low dose irradiation for fresh foods on April 18, 1986 (51FR 13376 et seq). The new regulation is in 21 CFR 179.25 and 179.26. The summary section gives a very adequate discussion of the safety of the process. The FDA would consider any fresh fruit or vegetables to be fresh, i.e., "unprocessed" food. In the summary, they note the confusion of the term fresh foods (51FR at 13393) but do not adequately clarify it beyond saying fresh food may include "fruits

and vegetables, and mushrooms that are capable of further growth and maturation, but that may be treated with ionizing radiation to inhibit those processes." They do not signify at what level of processing a food such as a fruit or vegetable would be fresh or what further maturation is. The original petition in the Federal Register (49FR 5714) specifically was for fresh fruits and vegetables, but the final version is worded more broadly as it seems to give clearance for use of 100 kRads for all fresh foods. However, they do note (51FR at 13393) that irradiating meat, fish or poultry at such low doses would not be sufficient for microbial control to be self limiting. They also noted that over-irradiation would cause fresh fruits and vegetables to deteriorate faster. Of other interest, the FDA noted that at the maximum dose allowed, few spoilage bacteria will be destroyed, thus outgrowth of *C. botulinum* spores may not be a concern (51FR 13381) because of the competition.

Few facilities for food irradiation are available in the U.S. and a negative consumer opinion with regard to irradiation exists especially since the Three-Mile Island and Chernobyl incidents. In the U.S., recent NRC concerns over the worker safety and record keeping of one major radiation processing firm may be an additional setback to this process. The FDA will also require that any food that is irradiated with gamma rays or electrons be labeled "Treated by irradiation" and that the label include the international symbol for irradiated foods. It is expected that the first major use will be for mangoes or papayas from Hawaii (Zurer 1986). Up to now, about the only means to slow loss of quality of mangoes has been with EDB, and that has been made illegal to use.

Another radiation process that could be used, but has found few practitioners, is ultra-violet (UV) irradiation. The FDA regulation (21CFR 179.39) allows the treatment of all foods with UV to limit surface microbial growth. The wavelength is limited to the range of 2200–3000 Angstroms (nm) with 90% of the energy (maximum 1 Watt per 5–10 ft^2) at 2537 nm. There must be no ozone production and high fat foods (e.g., avocadoes) would have to be treated under vacuum or an inert gas. No references could be found to show that this is being practiced.

Extended Shelf-Life Refrigerated Fresh Salads and Prepared Meals—"Chilled Foods"

Current Market. The growth in the number of health oriented consumers who are looking for reduced calories, a natural supply of vitamins, real or perceived protection against some disease such as cancer or atherosclerosis, and garden fresh taste has resulted in a blossoming of salad bars in restaurants. This has spilled over into the deli sections of supermarkets and convenience stores where consumers can get supposedly "fresh" green salads or freshly prepared healthy meals to take to work for lunch or home for a light dinner. The supermarkets have expanded their deli sections to take advantage of the upscale

consumer who does not want to spend time in meal preparation. This is nothing new and has been practiced in Europe, Japan, and New York City for many decades; the trend, however, is sweeping the U.S. The new consumer wants an easy to reach location to get the food, high quality at an affordable price, and enough extension of shelf-life so that the product can last from several hours to up to 2 weeks after reaching the home without any loss of desirable nutritional factors. Thus, between 1–6 weeks shelf-life are needed depending on the distribution system that will be used. These products lead to less time spent shopping and in meal preparation. In Japan, England, and France, the major supermarkets have long aisles devoted to refrigerated prepared meals (Chilled Foods). The Leatherhead Food Research Association estimated that the market for chilled foods in the UK exceeded $2 billion in 1984 excluding carcass meat and fish. They also noted that the "Chilled Foods" market in the UK was the most sophisticated in the world being pioneered by the Marks & Spencer Company as early as 1979. Buchalski of the Campbell Soup Co. reported that 43% of the food dollar is spent on chilled foods in Europe (Food Chem News, Feb. 2, 1987; p. 37). At the present time, different technologies are being used for each specific food, with refrigeration the most commonly practiced but unable to achieve the total shelf-life needed.

Products such as prepared salads or semi-cooked meals may have less than 4–6 h of high quality life at refrigerated temperature and under two hours at room temperature. Because no preservatives are added and the consumer or the store may abuse the product by holding it at room temperature, such abuse may result in sufficient increases in growth of pathogens to render the product unsafe.

McDonald's Corp. now sells a line of pre-packaged salads with meat, chicken and shrimp, which has become very popular with the health-imaged consumer. They chose to pre-package it rather than have the open salad bar as previously done in the Burger Chef stores. Burger King Co. is also marketing pre-packaged salads. McDonald's Corp. already serves over 20 million meals a day, in 46 different countries accounting for 10% of all meals consumed in the U.S. on an average day. They are looking to expand their market into new areas such as the health conscious consumer. With typical salad bars there has always been concern for contamination by the customer and the previously prepared product gets around this.

Another recent new product line is the supermarket salads which are either preprocessed by a local salad manufacturer or nationally by companies such as Orval Kent and Campbell Soup. The latter company had many different items combining both fresh fruits and vegetables with pasta, potatoes, bacon, turkey, ham, cheese, tuna, egg and shrimp. These salads had a shelf-life of 30–60 days at refrigerated temperature. To prevent quality loss and microbial problems, the company had to take complete control of the distribution system. In addition, for added protection, most of these products have the maximum allowable

amounts of sorbate and benzoate (microbial inhibitors) added to them, and they may also be nitrogen or carbon dioxide flushed for additional shelf-life extension. In mid 1987, Campbell Soup Co. withdrew their products from the market for undisclosed reasons; however, it may have been due to lack of consumer awareness. On the other hand, Orval Kent has had great success. Orval Kent Food Co., Inc. (Wheeling, IL) has a line of extended shelf-life prepackaged consumer size salads (crab, chicken, tuna, potato, cole slaw, ham, etc.) with at least 42 days refrigerated shelf-life. The consumer product is sold under the trade name "Salad Singles" which come in a 3.5 oz plastic cup. The method of shelf-life extension includes acidification and a mild pasteurization. They also sell prepared salads to deli bars in supermarkets. They are the largest supplier of freshly made salads to the supermarket delis (>$100 million sales).

General Foods is also interested in this area and has set up a separate company (Culinova Group, Hawthorne, NY) to pursue this technology. Presently they are marketing a veal and vegetable dish (with gravy in a tomato boat) and a chicken and mushroom dish, among other items. The price is reported to be over $7 per item with 7–9 days refrigerated shelf-life at point of purchase. Different specific O_2/CO_2 levels are used for preservation.

Gerald Haute Cuisine of Fairfield, Vermont makes high quality French foods with 8–45 days shelf-life using high levels of CO_2 in the package. Campbell Soup Co. has also test marketed a line of prepared meals under the trade name "Today's Taste" (Campbell's Distributing Co., 6461 Edsall Road, Alexandria, VA 22342). They specifically designed a catering kiosk for placement into the supermarket. The kiosk presumably had very good temperature control and was tested with an internally generated modified atmosphere. They were using every day delivery so the shelf-life extension of the food itself may be low. The items included a wide variety of entrees and soups. No preservatives were used and the products were labeled with a use by date. The items were geared to be heated directly in either a microwave oven or a regular oven with a maximum cooking time of 20 min, which suggests some precooking. Fleury Mickon (Paris, France) has a line of twice heated ready-to-eat meals with 4 weeks shelf-life. These are partially cooked both before and after packaging to reduce microbial load.

Famiglia Industries, Ltd. (Jersey City, NJ) has introduced a line of CA packaged pasta meals. They claim a 45–60 day shelf-life under refrigeration. The products include meat, cheese and vegetable filled pasta entrees in both consumer (12 oz) and food service (2–3 lb) sizes. In the Famiglia process, after nitrogen flushing and sealing the package, the product is given a pasteurization treatment. This process has been in use in Italy for over 15 years. The pasteurization can be either by infra-red radiation or with microwaves (Omac system imported by T. W. Kutter, Inc., 91 Wales Avenue, Avon, MA 02322). This heating would not be acceptable for green salad items as it would cause undesirable texture and flavor change. It was noted (Anon 1986) that the product may actually have

a six month shelf-life. Other companies such as Central Foods (Benicia, CA), with a tortellini product, are also entering this arena. Usually the type of foods delivered and the technology employed is not known; however, in the latter case, Central Foods is using an oxygen scavenging system for shelf-life extension. It is estimated that the deli sales of a supermarket run about 3% of volume ($5.9 billion in 1985) but with these new products sales could easily reach 6–8%. Con-Agra (Omaha, NE) is intensely looking at meals to go along with their Armour line of shelf stable retorted products.

Mechanisms of Decay and Shelf-Life Data.

Browning of Cut Fruits and Vegetables. The broad range of products in this category makes it difficult to adequately cover all the modes of shelf-life deterioration. In cases where fruits and vegetables are used exclusively, the shelf-life data presented in the previous section will be applicable. However, when the products can be shredded as with lettuce, chopped as with tomatoes, or sliced as with fruits, the shelf-life will be greatly reduced. This is because the mechanical action disrupts the cells and spills the cellular contents together so that reactions can start. Of major concern is the action of the polyphenol oxidase enzyme (PPO) system leading to enzymatic browning. This reaction is very rapid, even at refrigerated temperature, and is initiated by any tissue damage. PPO is sensitive to oxygen level, decreasing in rate with decreased oxygen level. For example, frozen fruit manufacturers vacuum pack cut fruit or enrobe them in a sugar syrup to minimize availability of the oxygen to the tissues. Frozen fruits are generally not heat treated to inactivate enzymes because of the cooked flavors that may develop.

Most salad manufacturers previously used different forms of sulfite to inhibit the enzymatic browning reaction; however, because of recent FDA actions banning its use on fresh fruits and vegetables because of the sulfite sensitivity of asthmatics, this practice has been discontinued. Sulfite had been used at 200 to 4000 ppm under controlled conditions to inhibit oxidation, prevent browning and inhibit bacterial growth. Unfortunately some restaurants did not control the addition of sulfite to salads very well and delivered a fatal dose to some asthma sensitive individuals. As many as 10 deaths have probably been caused by the consumption of sulfited foods (Food Chem. News, April 13, 1987, p. 47). The FDA ban is for the use of sulfites on raw fruits and vegetables that would be eaten directly, as in a salad product (50FR 32838). They are also expected to issue a regulation which would ban sulfite use on all potato products. The USDA has a total ban on sulfites for use on meat and meat products (9CFR 317.7(d)(2)); however, sulfite is allowed to be used in other products which are then combined with meat as long as the presence of sulfite is indicated on the package label. Based on these regulations, it would not seem logical to develop a film

that would release sulfite at a controlled rate into a food, since it could not be used for most foods where shelf-life extension is needed.

Citric acid at 1% in combination with 0.5% ascorbic acid as a dip helps to control enzymatic browning of freshly cut fruits and vegetables but cannot extend shelf-life much beyond one day. Recently, FDA has received a petition for the use of L-cysteine to inhibit browning (51FR 26469, July 18, 1986 Skymart Enterprises, Inc., 6338 North Burton Avenue, San Gabriel, CA 91778). There is little information as to the mechanism of action of cysteine. Arnold (1969) felt that it prevents nonenzymatic browning by reacting with the reducing compounds to form noncolored end products. Whether cysteine will react with quinones to form noncolored products is unknown. Cysteine is presently approved for use as an amino acid nutrient and as a dough conditioner for baked goods (21CFR 184,1271). Another area under research is the use of substituted ascorbic acid compounds (G. Sapers 1987; presented at Annual IFT meeting). Since these are not approved as food additives, their potential use is questionable.

Another method to control browning would be to have a controlled release of specific enzymes that compete for the enzymatic browning substrates and produce noncolored end products or nonreactive products. Finkel and Nelson (1963) showed that the enzyme, O-methyl transferase, would convert ortho-phenolics into a methylated form which would not further react. The optimum rate is at pH 7, while many fruits that brown are at pH 2–4, thus the enzyme might have to be genetically modified. However, this pH would be acceptable for many vegetables, including potatoes. Another potential enzyme is protocatechuate, which converts the phenolics to a di-acid open chair form. This needs further investigation and would require a petition to the FDA for a new additive.

If the food product can withstand some heating without losing flavor, color or texture, then some degree of heat pasteurization can be used. If the produce is to be marketed precooked, as in a prepared pasta salad, most likely the PPO enzyme will be heat inactivated, so an inhibitor would not be needed. Other mechanisms of decay would then predominate.

Meats for Salads and Prepared Meals. The meats used in salads or prepared meals can be either partially or fully cooked. The meals may also contain cured meat products such as ham or bacon. In addition, canned sterilized product might be used. Cured meats, such as ham, because they are treated with nitrite and salt and may be fully cooked, would have a fairly long shelf-life at refrigerated temperature. Bacon is also vacuum packaged and can have a high quality life of up to 2 months at refrigerated storage (Labuza 1982). Fully cured ham may last over 6 months under refrigeration. In fact some of the dried cured Virginia hams take that long to fully develop desired flavors. Little data for shelf-life or nutritional losses in cured or refrigerated meat as a function of temperature can be found in the literature. The major modes of deterioration include surface

growth of molds and slime yeasts as well as oxidative rancidity of the fat leading to off odors and a bleaching of the pigment. The nitrite reduces the probability for growth of the deadly pathogen, *Clostridium botulinum*. Uncured sausage meat kept at room temperature is a major cause of botulism in some countries.

Other meats that would be used in salads could include fresh, partially cooked, cooked, or canned sterilized turkey, chicken and beef. The sterile product, once handled, will become contaminated with microbes. Cooked fresh poultry and meat products will contain a reduced number of microbes but will not be sterile. If the fresh cooked meats are improperly chilled, they can be a major source of food poisoning microorganisms, especially *Clostridium perfringens*. The meat or poultry will also serve as a source to transfer microbes to the other food components. The cleaner the preparation step, the slower the rate of microbial decay, but in any case, unless some preservative system is used, refrigerated shelf-life will be no more than 2 to 7 days.

Uncooked red meat will rapidly lose its dark red color depending on temperature and oxygen availability, but may still be of good eating quality. Atmospheres of 20–25% CO_2 help to inhibit microbial growth. In a vacuum, fresh meat will remain purple, while if kept above 25% O_2 (highly explosive) it will stay bright red. Several of the CA technologies described previously are being employed outside the U.S., especially in Great Britain (Marks and Spenser) and Australia. Garwood, Ltd. of Australia employs a novel package which uses 20% CO_2/80% oxygen for red meat and 70%/30% for poultry. Cryovac in the U.S. has been the leader in CA/MA for poultry. They have a film with a transmission rate of 30 cc oxygen/day m^2 atm which gives a shelf-life of 14 days at 2°C. Dixie Union of Germany also has similar technology. Fresh meats for pet foods are CA/MA packaged in the UK and Germany. No useful data exist for nutrient loss in meats under CAP/MAP storage conditions.

Shrimp and Other Seafood. Another typical product in prepared meals and salads is shrimp. If frozen, it may have to be thawed, cooked, cleaned and chilled. Canned tuna fish and salmon are also other common salad ingredients. Canned shrimp and fish products would be sterile until opened and used. Generally, canned shrimp is not used unless it is the tiny baby shrimp. Fresh shrimp must be cooked, peeled and deveined. The noncanned fish and shellfish products will serve as a significant source of microorganisms as well as pathogens because of the way they are harvested, thus, care must be exercised in order to keep the initial counts low. Refrigeration is necessary. Fresh shrimp will keep about 6 days before they must be cooked, while frozen shrimp has about 3–4 months of high quality shelf-life at -18°C (Labuza 1982). Canned products, before opening, can last for over 12 months. No data are available for nutrient loss during extended shelf-life holding at refrigerated temperatures.

Eggs. Another food that might frequently appear in prepared meals and salads is slices or chunks of hard cooked eggs. Extended shelf-life hard cooked eggs

are prepared by boiling in the shell. They are then cooled, peeled and immersed in a citric acid/ascorbic acid/sorbate solution. These eggs have a shelf-life of at least 60 days under refrigeration. An uncooked egg in the shell will last for 120 days but will lose its desirable flavor and functionality. The shell, unless cracked, prevents bacteria from entering and spoiling it. Eggs immersed in oil will last for 180 days. Cooking, although killing some bacteria, reduces shelf-life because of membrane destruction and mixing of the reactants inside the matrix. The handling in peeling and slicing then reintroduces spoilage organisms to shorten shelf-life. For salads, eggs have to be cooked and sliced. Because eggs are such a significant source of nutrients and come from a somewhat dirty environment, they can be potential sources of pathogens, especially *Salmonellae*. A frozen version of a hard boiled egg slice is available for food service in the form of a log of slices. They have been treated so as to minimize loss of fluid and stickiness after thawing. There are no data existing to show the extent of loss of water or of fat-soluble vitamins during extended shelf-life storage of eggs.

Pasta Ingredients. Another common ingredient used in salads and prepared meals is pasta. The pasta must be precooked (fully or partially) and then washed, cooled and drained before combining with the other ingredients. This processing should not introduce many microbes into the system. Cooked pasta products have a shelf-life of 1 to 6 days at refrigerated temperature with no other technology applied. One main problem would be the toughening that occurs during storage which is something that cannot be solved solely by packaging. One can slow down microbial growth by acidifying the water in which the pasta is boiled or by adding acid to the dough prior to extrusion. One company makes an acidified pasta (<pH 4.6) in an acid spaghetti sauce which needs only a typical acid food hot fill or hot cook in boiling water. This results in a much more tender pasta than that in thermally processed canned spaghetti meals which require a much longer heat treatment at higher temperature because the pasta is a low acid food. It has at least a one year shelf-life. CA/MA pasta products, as mentioned above, have 45–60 days shelf-life. In most cases they are also acidified or an antimicrobial agent is added to the dough before extrusion. Extensive work was published on the loss of nutrients in dry pasta, but nothing exists for precooked pasta during refrigerated storage (Kamman and Labuza 1983).

Sanitation, Microbial Control and Pathogens. The shelf-life of the cooked or prepared versions of all the above CA/MA ingredients alone or in meals at refrigerated temperature will be around 2–10 days if the initial microbial counts are low and if the finished product is kept at <4°C. The food components with the shortest shelf-life will dominate the shelf-life of a mixed food system. At room temperature, the products will begin to spoil in a matter of hours since the temperature sensitivity (Q_{10}) for microbial growth is about 3 to 10 (i.e., a 3 to 10X increase in rate for each 10°C rise above refrigeration temperature). Off colors, off odors and a slimy taste and mouthfeel will develop. The same will

be true for any partially cooked or canned vegetables or fruits. The shelf-life will be very dependent on the sanitation practices of the personnel and the equipment used in meal preparation. Many food service establishments have had poor sanitation records based on speeches from FDA personnel and unless properly trained the supermarket personnel making prepared meals will do no better. An FDA survey in 1985 of airline food service vendors and on board the plane itself, showed that over 50% of them had unsanitary operations. Commercial food processors should be expected to do a better job because of their insistence on QA/QC operations using HACCP principles. The National Food Processors Association (NFPA) has warned against use of CA/MA technology unless good sanitation and temperature control is practiced (Scott 1987). Most likely the food will spoil long before a significant loss in nutritional quality occurs but there is no data at this time to support this contention.

One concern about CA/MA modified food systems would be the lowered oxygen tension inside the pouch setting up anaerobic conditions. Eleven deaths occurred in 1984 in Japan from a vacuum packed CA/MA food item, namely semi-cooked lotus root packed in a mustard sauce and distributed in poorly controlled temperature conditions. This incident mounted a massive investigation of the food processing and food service industry involved in this type of packaging. The Japanese Ministry of Health and Welfare found that many small take-out shops were practicing this technology with no knowledge of the potential microbial pathogen problem (Anon. 1986). Good temperature control (<3.5°C) will prevent the growth of the botulinum organism. This is especially true if cooked fish products (not canned) are used in the meal since many fresh fish products are good sources of the type E botulinum spore which has the potential to outgrow under refrigeration. Lower temperatures may be necessary if fish products are to be used in the meals. An oxygen concentration of less than 4–8% at the food surface will allow growth of anaerobic pathogens to occur. This situation can be produced very easily, solely by allowing aerobic organisms to grow in a sealed package of low oxygen permeability. They quickly lower the oxygen level down to where the anaerobic pathogens can start growing.

Genigeorgis (1985), Palumbo (1986) and Hintlian and Hotchkiss (1986) recently reviewed the food safety problem involved with CA/MA storage of foods. Besides *Clostridium botulinum*, there are other problem pathogens that will grow quickly when the food product temperature is raised. *Salmonellae* will begin to grow at about 5.2°C while *Staphylococcus aureus* requires at least 10°C. An organism of new concern is *Yersinia enterolytica*. It will grow as low as −2°C under the lowered oxygen tension. The public health significance of this is unknown. Other minimum temperatures for food pathogens include 6.5°C for *Clostridium perfringens* and 5°C for *Vibrio parahemolyticus*. If an enriched carbon dioxide atmosphere is used along with reduced oxygen the *Campylobacter* organism is favored to grow.

Another microbe of concern is *Listeria monocytogenes*. Until recently it was unknown as a causative infectious agent transmitted in foods because it was so difficult to isolate and identify. Newer techniques make it easier, but a confirmative identification still takes over 8 days with a 50% false positive error rate. Of concern is the fact that it can grow rapidly at refrigerated temperature and down to a pH of at least 4. It has a slow incubation period in the body and causes flu-like symptoms. The major problem is that the infection can cause death in immuno-compromised people such as AIDS cases, and those on drug therapy for cancer. In addition, it will cause fetuses to be stillborn. A recent outbreak from cheese in the Los Angeles area led to 19 confirmed deaths. If present in an extended shelf-life meal, the organism may be able to out-compete the other microbes and present a hazard. The Center for Disease Control estimates at least 800 serious cases a year that could lead to death. There is concern that introduction of this extended shelf-life technology may increase the numbers of *Listeria* incidents. Jennifer Johnson of the Wisconsin Food Research Institute has reported that *Listeria* will survive and grow for 14 days in ground beef even under low oxygen conditions (reported in Food Chemical News, August 11, 1986, p. 56).

The Center for Disease Control of the U.S. Public Health Service has calculated that a botulism incident will cost a food company over $7 million per person infected; for *Staphyolococcus* and *Salmonellae* food poisoning it costs about $30,000/person. Data for other organisms is too meager to evaluate what the cost will be, but a *Listeria* death should be comparable to one caused by botulism.

One major unanswered question is whether organoleptic spoilage will occur before the pathogen numbers or toxin levels become a risk. Since different metabolic pathways and different organisms are affected differently by temperature increases, this creates a real problem. Several papers have reviewed the difficult problem of modeling microbe activity as a function of temperature. As was noted there is no straight line Arrhenius type function; rather there is a parabolic type curve (Mohr and Krawiec *et al.* 1980; Reichardt and Morita 1982; Ratkowski *et al.* 1982, 1983). There is little agreement amongst microbiologists as to what is the best model to apply. Interestingly, an increased carbon dioxide level does seem to raise the temperature minimum for some pathogens, giving some margin of safety from abuse.

Figure 4 graphically shows the problem when there are several modes of deterioration (Labuza 1971). Each mode has its own temperature sensitivity. The shelf-life at any temperature is determined by the mechanism which gives the shortest time. Most sensory quality factors, have a Q_{10}, or temperature sensitivity of 2–3 in the refrigeration range, microbial spoilage may be 3 to 6, and pathogen growth or production of toxin may be equivalent, higher or lower. The time to reach a given number of spoilage organisms versus the time to reach a critical concentration of toxin or disease organisms will also vary with tem-

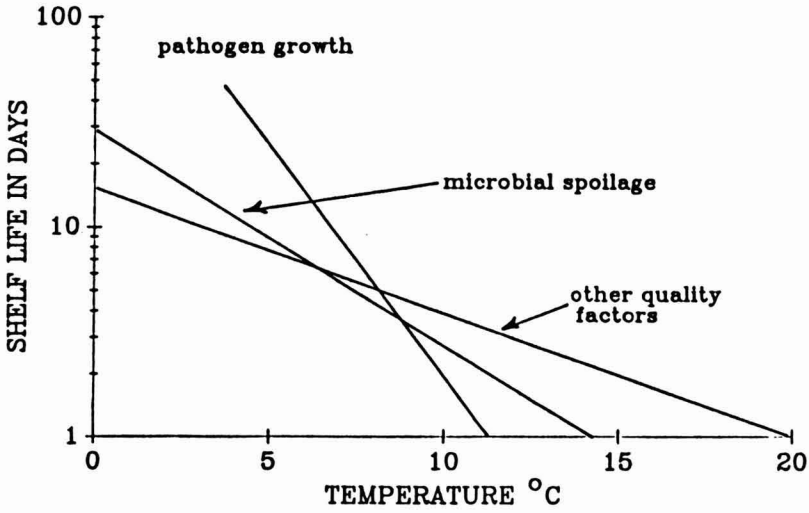

FIG. 4. SHELF LIFE PLOT SHOWING THE INFLUENCE OF TEMPERATURE ON DIFFERENT REACTIONS THAT LIMIT SHELF LIFE.

perature. There are no conclusive data, so the graph is merely a representation of a possible situation. As seen in Fig. 4, a crossover curve is developed. Below some temperature, sensory changes will limit shelf-life while above this temperature, first spoilage microbes will limit shelf-life and then at a higher temperature, pathogens will make the food unsafe, both before sensory properties may limit the quality of the product. There are no data as to what would happen as the temperature during distribution fluctuates throughout this range.

Given these problems, the FDA has become quite concerned that CA/MA methods may proliferate before we have good pathogen control. Dr. Fred Shank, Director of FDA's Office of Physical Sciences in the Center for Food Safety and Applied Nutrition, has expressed this concern a number of times and suggested that FDA may issue some good manufacturing practice regulations (Food Chemical News, May 25, 1987, p. 20) and the NFPA has submitted a draft to the FDA.

Current Technology. The technology used for extension of the shelf-life of fresh salads and prepared foods may employ the same technology as for fresh uncut fruits and vegetables with some additions. The major techniques currently used in the U.S. are temperature control, oxygen lowering and CO_2 elevation. This gives 7 to 60 days shelf-life for many products, but may be longer for others. Little information on shelf-life or nutrient loss as a function of temperature is available although there is a great demand for this information, especially in hospitals where they would like to cut back on in-house food preparation. Abuse temperatures during holding of these foods will lead to rapid growth of spoilage

organisms decreasing shelf-life and enhancing the growth of microbial pathogens, a serious health consideration. Many supermarkets and quick stop food stores use open refrigerated cabinets, and the food may be piled too high. The same is true in food service lines. This could lead to rapid decay as well as allowing pathogens to grow which are usually inhibited at refrigerated temperature. Closed refrigerated cabinets should be made mandatory for these extended shelf-life foods during distribution. Time temperature integrators to monitor distribution have been used by some companies (Campbell's) to weed out problem areas. Most likely other companies will follow suit. A single food poisoning incident could ruin a business. The FDA is also considering writing GMPs for this area of food processing as was noted previously.

The Japanese have instituted a system in which they chill foods to near the freezing point (-1 to -5°C). The food is distributed at this temperature and then stored refrigerated in the market store. A description of this system was presented by K. Ono of the Snow Brand Milk Products, Ltd., Tokyo, Japan at the April 1986 Japan Packaging Conference, Rutgers University, New Jersey. A question exists as to the control of temperature, since if the food is actually frozen, freezing would lead to a concentration of reactants with resultant rapid development of off flavors and colors. In addition, freezing would irreversibly damage the tissues of some foods, especially fruits and vegetables. This would result in loss of crispiness and a mushy texture. It is well known that slow freezing/slow thawing and storage at -3 to -5°C are very damaging to food quality (Fennema 1986). Of course at these temperatures, the growth of microbes is greatly reduced as compared to 4–5°C, perhaps by as much as 5 to 10 times which should relate to an increased shelf-life. Good temperature control would be needed to insure that the food is actually not frozen, if this is damaging. Most present refrigeration systems could be modified to run at the lower temperatures but the controls and energy to maintain the temperature exactly will be costly.

Oxygen Control. Since tissue foods are utilizing oxygen to some degree (by respiration, oxidation, or microbially) one would expect that CA/MA storage or packaging would have some major effect on shelf-life extension of fresh salads and prepared meals. In fact, the rate of the reactions leading to decay will be faster for salads and prepared meals than for the fresh product, since when they are cut and handled the tissues are damaged, releasing degradative enzymes and increasing exposed surfaces. Cooking, of course, would denature most of these enzymes. Enzymatic browning by PPO would take place rapidly, especially with apples, bananas, lettuce, cauliflower, etc. Thus, reduction of oxygen by vacuum packaging or by nitrogen flushing is currently being employed. With some products, vacuum packaging is impossible to employ because of the fragility of the product itself (e.g., lettuce); thus, gas flushing with nitrogen is employed. Little data exist regarding the shelf-life of the prepared mixed products under normal vs CA/MA storage and especially the effect on nutrient loss. The Tiromat Co. (Germany) has data to show that with their gas flush packaging system, fresh

meat will have 12 days shelf-life at 70% oxygen/20% CO_2. In Europe, Tiromat Co. has 75 machines installed for meat and 6 for salad products. The latter is packaged at 2.25% O_2 and 10.5% CO_2.

There is little use of an oxygen scavenging system in the package for these foods in the U.S. while it is very prevalent in Japan. The only known applications of an oxygen scavenger have been for roasted coffee in cans and for the tortellini product mentioned earlier. This scavenging would be useful since there would be no need to flush with nitrogen, making the packaging line faster.

Data as to the relative oxygen versus water vapor permeabilities of the film would also be needed, since if the lowered oxygen increases shelf-life by slowing respiration and other oxidations, there now exists a longer time for moisture loss by diffusion. This leads to wilting and other tissue damage, thus, the water content must be retained. Although no data exist, any vitamin that would be lost by oxidation (e.g., vitamin C) should be preserved in this process so the concern with respect to nutrition may be unwarranted. There is much debate as to the value of CA/MA for fish, especially because of the potential for pathogen growth. In the U.S., government agencies frown on its use and the Department of Commerce will not allow fish to be graded if CA/MA packaging is used although it is being used for surimi and cooked shrimp. There are five fisheries in France using 80% CO_2/15% O_2 for fresh fish. The oxygen is used to prevent anaerobic growth.

Carbon Dioxide Gas Atmospheric Control. Coupled with lowering of oxygen in the package is the possibility of raising the carbon dioxide to a high level. This functions to increase shelf-life probably by creating carbonic acid on the surface of the food, thereby inhibiting the growth of some spoilage organisms. Daniels *et al.* (1985) prepared an excellent review of this technology and has discussed the mechanism of action. It has been researched for over 100 years and has been applied to fruits, vegetables, pork, red meat, poultry and seafood. If the spoilage of the food is dominated by gram-negative, aerobic psychrotrophs, high carbon dioxide levels work best. Thus, increased CO_2 best applies to pork, poultry and fish while with fruits and vegetables, very high levels may decrease shelf-life due to initiation of anaerobic glycolysis. In mixed foods it would probably be useful. Several early studies include Clark and Lentz (1972) Coyne (1932) and Gee and Brown (1978).

The pigment in red meat may become grey brown if the CO_2 level is raised above 25%. Work as early as 1882 showed that elevated carbon dioxide levels would increase the shelf-life of meats by 3 to 5 weeks. By 1938, 26% of all New Zealand beef and 60% of Australian beef were being shipped out of the country in this way. Both Europe and Japan employ carbon dioxide to a much greater extent than the U.S. Recent interest in the prepared meal line has again spurred interest in this technology. Some examples of its use in Europe, presented at several CAP/MAP meetings, include a 20% CO_2 atmosphere for a 21 day

shelf-life pizza, and egg roll and a bread stuffed with ham and cheese using 50% CO_2 giving 21 vs the normal 5 days shelf-life and pasta at 80% CO_2 with 14 days shelf-life. Liquid Air Products is involved in producing specific gas mixtures for these products. In Germany, high CO_2 atmospheres are used to supplant propionate use in bread products to extend shelf-life. Finally, nitrogen/carbon dioxide mixtures are being used extensively for shrink wrapped poultry. A mixture with 20% CO_2 gives 7 days shelf-life, 60% gives 2 weeks and 70% gives 3 weeks at refrigerated temperature. Poultry tissue whitens slightly under these conditions. In the case of fish, a 40% CO_2/30% O_2 atmosphere with the balance as nitrogen is recommended for lean fish and 60% CO_2/40% N_2 for fatty fish, the latter to prevent the oxidation of the unsaturated fatty acids.

In general, an increase of the carbon dioxide level to 25% results in a two-fold increase in microbial generation time (time for population to double) at 10°C, a 2.5X increase at 4.4°C and a 3.5X increase at 0°C. These increases could be translated directly in shelf-life increases if there were no other modes of quality loss except microbial decay. There is considerable controversy as to whether CO_2 levels above 25% give any more shelf-life extension. As noted above, higher levels cause a discoloration of the surface of uncooked fresh red meat and are detrimental to some fruits and vegetables.

There are many ways to introduce the carbon dioxide into the package. The easiest way is to use directly injected compressed gas. This process requires an excess to flush out the interior or it involves a vacuum pulling step which is slow and may damage the product unless the package is rigid. Several chemical generating systems also have potential and will be discussed later in this paper.

Ethylene Control. Ethylene control is not practiced for salads or prepared meals, it would also have no effect on meats, fish, etc.

Preservatives. As noted earlier, one method to extend the shelf-life of prepared salads and possibly meal items is to add a microbial inhibitor system. In the U.S., addition of microbial inhibitors requires that a food additive regulation be granted for the specific application, unless one exists already. In essence, inhibitors such as sorbate, benzoate, and propionate can be used since they are approved as GRAS (Generally Recognized as Safe) substances. The first two of these are less effective at high pH, so for some foods acid (e.g., vinegar or citric) must be added. A sorbate/citric acid dip on fish can extend the shelf-life to 24 days from a microbiological standpoint. Cut cheese may be dipped in pimaracin (Natamycin®) for preservation. Food additive order 21CFR 172.155 allows its use at 200–300 ppm for cheese only. Some of the salads currently sold in the U.S. contain some combination of these inhibitors along with CO_2 to extend shelf-life. A review of the labels does not indicate the use of any antioxidant such as BHA or BHT in these foods. Of course this would not be needed in an oxygen free atmosphere but would be almost mandatory for high oxygen levels especially with meat, poultry or fish.

Pasteurization. As noted in some of the examples of prepared meals, a short cooking treatment or some other type of in-package pasteurization can be employed to extend shelf-life. This can be applied through normal heating, or with microwave or infra-red radiation. There are no known examples of the use of UV; however, it could legally be employed under 21CFR 179.39. Use of microwaves for heating is allowed under 21CFR 179.30. There are no regulations covering normal heating, unless the products are made sterile (21CFR 113 and 114).

Recently, Maxwell Labs (San Diego, California) patented a process for magnetically pasteurizing foods in nonmetallic containers (U.S. #4,524,079, June 18, 1985). The process uses a Magneformer, which is designed to magnetically weld metals without generation of heat. Maxwell makes an 8 Kjoule ($38,000) and a 12 Kjoule ($48,000) machine. For pasteurization, the equipment operates at 2–100 Tesla (Earth's magnetic field is below 0.0001 Tesla) and the field is pulsed at 5–500 kHz. Use would seem to be allowed under 21CFR 179.30 which covers radio-frequency radiation, including microwaves, for heating foods. The effective magnetic frequency is more than three orders of magnitude below the 915 and 2450 MHz allowed for home and industry microwave cookers. Whether FDA would classify this as radiofrequency processing is not known. The process claims at least 2 log cycles of kill of vegetative cells and mold spores with a single pulse of radiation, and with little to no heating. However if indeed any kill occurs it is probably due to a heating effect. There have been no publications to verify in fact that this is a useful method of pasteurization.

Irradiation, with gamma rays or electrons, would seem to be limited to fresh fruits, vegetables and mushrooms according to the regulations listed earlier; however, it might be allowed for a meal that would contain other ingredients such as meat or fish. Certainly it would be allowed for a prepared fruit or vegetable salad, such as those distributed by McDonald's Corp. The meals would have to be labeled as irradiated, which might cause some marketing concern. The use of any of these pasteurizing methods should reduce the initial number of microbes, and in combination with the other technologies, might provide a synergistic effect that would result in the desired extended shelf-life and minimum nutrient loss.

ACTIVE PACKAGING TECHNOLOGIES

Physico-Chemical Means for Oxygen Scavenging

The prior section discussed the need for a means of controlling the oxygen level in a package other than by just having a low permeability barrier and pulling a vacuum. One possibility is the use of some chemical reaction that scavenges the oxygen from the inside of a sealed package and continues to do so as it

diffuses into the package. Recently, some of these scavenger systems have been applied to the extension of shelf-life of refrigerated foods, salads and meals. A list of U.S. Patents that have involved oxygen scavengers includes: #2,825,651 (sulfite for milk); #3,016,336 (oxygen remover); #3,169,068 (scavenger); #3,415,702 (tape application); #4,094,121 (automotive piston); #4,166,807; #4,299,719; #4,317,742; #4,421,835 (various uses).

The primary oxygen scavenger now employed by the food industry worldwide is the Mitsubishi product "Ageless." It has been in use for about two years. The product is basically iron which oxides to the ferric state. The water activity of the food has to be high enough so that the iron will oxidize. A level of 0.01% oxygen is achievable (European Packaging Newsletter 19: No. 5 1986). The iron is separated from the food by keeping it in a small (1.5 x 1.5 cm) highly oxygen permeable sachet or pouch. The pouch is labeled "Do not eat." The reason for this is the potential toxicity if the sachet were accidentally consumed. The LD_{50} (lethal dose that kills 50% of a population) for iron is 16 g/Kg body weight. The largest sachet commercially available contains 7 grams of iron so this would amount to only 0.1 g/Kg for a 70 Kg person, or 160 times less than the lethal dose. Of course the dose would be higher for a small child. The product has been approved by the Japanese Ministry of Health (Notification 20, 1982). In 1983, the FDA noted to the company that they had no objection to the product as long as there was a warning label on the package ("Do not eat") and that all the films and dyes used conformed to the requirements of the Food Drug & Cosmetic Act. The U.S. Department of Agriculture also approved its use in direct contact with beef jerky, dehydrated meat and similar poultry products (July 8, 1986 letter to Mitsubishi).

The idea of an oxygen scavenger is not new, there have been at least 50 patents granted around the world using different technologies including the above one as well as photosensitive dye oxidation, ascorbic acid oxidation, use of ferrous carbonate, and use of sulfur. The Mitsubishi U.S. patent covering the commercial application is U.S. 4,421,235 issued 12/86. Carnation Co. has a patent (US 2,825,651) which uses a sulfite salt and copper sulfate. In the mid 1970s American Can Co. developed an oxygen scavenger film that required packaging in 8% hydrogen. The hydrogen reacted with oxygen at internal sites in the film where paladium was deposited. It was used by the Army but never became a commercial success. Toppan Printing Co. in Japan also holds several U.S. and Japanese patents and commercially markets a sachet similar to the Mitsubishi product.

"Ageless" sachets can be found in the U.S., Japanese and European supermarkets in packages of many foods including bakery items like bread, cakes, cookies, pizza crust and pastry, as well as in packages of precooked pasta, cured or smoked meats and fish, dry tea, dried fish, cheese, the Japanese Nabisco-branded soft cookies, beans, potato chips, dried eggs, spices, nuts, coffee, and

chocolates. The Gerber baby food cereal package in Japan is designed to contain the "Ageless" sachet, in which the sachet is in a separate compartment so as to prevent its accidental consumption. The compartments are connected by five air channels.

Nakamura and Hoshino (1983) of Mitsubishi have calculated the stoichiometric basis for the reaction of iron with oxygen at atmospheric pressure and different relative humidities. The reaction is very complex but in general, 1 gram of iron can react with 0.0136 moles of oxygen which is equivalent to:

$$V = n\,R\,T = 0.0136 \times 0.0825 \times 298 = 0.336\ L \tag{5}$$

The nominal chemical reaction is:

$$4\ Fe + 3\ O_2 \rightarrow 2\ Fe_2O_3 \tag{6}$$

Thus under ideal stoichiometric conditions one gram consumes 3.36×10^5 L of oxygen if the iron is in solution and totally available. In the solid form less iron would be available; however, the powder disintegrates rapidly and thus almost all the iron becomes available. Given the oxygen transmission rate of a 3 mil polyester film as 4 cc per m^2 day (k/x = 20 cc/m^2 day atm), a sachet containing one gram of iron should be able to handle the oxygen coming in for 84 days for a package with one meter square of area. This assumes that the oxidation rate to the ferric state is faster than the diffusion rate of oxygen into the pouch atmosphere. Note that this is for one square meter of surface area for the food package, which would be at least three times that necessary for a typical salad or meal; thus, the iron level could be reduced. Instead of a sachet, this amount of iron could easily also be spread out over the whole area of a film if it were entrapped so as to not get into the food. No such product is available at this time. One interesting patent (U.S. #4,501,162; April 9, 1985) combines iron with active dry yeast on a piece of cotton cloth or cotton ball which has been moistened. As expected, the material reacts with oxygen faster than without yeast because of the active enzyme system. Iron in the range of 50–280 mesh was used but, as noted, a smaller particle size would be more effective. U.S. Patent #4,421,235 (December 20, 1983) which covers different aspects of iron scavenger systems is held by Mitsubishi.

The amount of iron that needs to be used depends on the initial oxygen level in the headspace, the amount of dissolved oxygen that is in the food and the film oxygen permeation rate. Although it is not easy to calculate all the above factors, a rule of thumb is that one gram of iron will react with 300 cc of oxygen. One "Ageless" configuration is designed for water activities of less than 0.85. It takes 1–4 days to reach 100 ppm residual oxygen. The scavenger sachets are available in sizes that can react with 20 to 2000 cc of oxygen based on using a

film with a permeability no greater than 20 cc per m^2 day mm Hg. Films with higher permeabilities will drop to 100 ppm oxygen in a few days but then return to 21% in a matter of weeks. However, if the desired shelf-life is short, a high permeability film could be used.

Two other "Ageless" types work best at the higher water activities and have a faster reaction rate (0–2 days). They have the same oxygen scavenging capacity. One of these, Type FX, does not absorb oxygen until it is exposed to an a_w greater than 0.85. It thus can be easily handled if kept dry. The other types require that they be handled in a low or zero oxygen atmosphere as they begin to react immediately. A fourth type (E) also contains calcium hydroxide which scavenges carbon dioxide as well. It is used for ground roasted coffee packages; the carbon dioxide removal reduces the chance that the package will burst. It has a very high reaction rate. This product is being used for canned ground coffee in the United States under the trade name "Fresh Lock" by Maxwell House Coffee (General Foods).

Data have been collected to show significant shelf-life improvement with the oxygen scavenging sachet (Nakamura and Hoshino 1983). For example, white bread in a polypropylene film will show mold growth at room temperature in 4–5 days while with the sachet in the package the mold-free shelf-life is over 45 days. Pizza crust which molds in 2–3 days at 30°C will be mold-free for over 10 days. Removal of oxygen also eliminates flour beetles in stored flour packages which may be a significant development for humid environments.

The sachet also eliminates the oxidation of fats that occurs in potato chips, dry fish, beef jerky, and semi-moist cookies. Data in Japan Packaging (Vol. #1, p. 15, January 1980) indicate that the "Ageless" packet can keep packages of snack foods at less than 0.1% oxygen over a period of three months, while similar pouches nitrogen flushed to 2% oxygen gained oxygen over that period of time. Only laminated foil kept the pouch at 2% oxygen continuously. A KOP/PE pouch without the sachet rose to 7% oxygen in the three months. This indicates that in the present configuration, the sachet can handle the influx of oxygen. In one study, fried rice cakes in a package with the scavenger never rose above a peroxide value of 10 meq/Kg fat while the cakes stored in air went to a PV of 100 in 60 days and the gas flushed package (5–7% oxygen) reached a PV of 100 in 150 days at the end of the study. The Japan Ministry of Health precludes selling foods having a PV above 30. As noted earlier, the sachet is being used by Central Foods (Benicia, CA) to give at least 60–90 days shelf-life for cheese-filled pasta products.

It must be pointed out that an oxygen-free atmosphere at a water activity greater than 0.92 can be conducive to the growth of many microbial pathogens including *Clostridium botulinum*. Thus, use of the sachet under certain conditions could be dangerous if the temperature is not kept close to 0°C. A study by the Japan Tokai Regional Fisheries Research Lab in 1978 (Nakamura and Hoshino

1983) using similar sachets showed rapid development of botulinum toxin in fish. There also may be a consumer resistance to the use of sachets in a food package. Another problem is that the iron containing-sachet will set off on line metal detectors. This means the process stream may have to be reorganized. Interestingly, Mitsubishi also has under development a sachet set for home use and a "fur preservation bag" for summer storage of fur coats.

U.S. Patent #4,299,719 (Mitsubishi Chem Co. and Teikoku Co., Osaka, Japan) discloses a different method in which ferrous carbonate is used as the oxidizable substrate. It is prepared to a particle size of at least 20 m^2/g and mixed with either iron powder, a metal halide or an alkaline earth metal. One mole of carbon dioxide is produced for each mole of oxygen reacted, thereby building up the CO_2 level, possibly to a high enough level to have some antibacterial effect on the anaerobes. An aqueous reaction medium is required and 0.01 to 5 parts of iron per part of ferrous carbonate are required for catalysis along with an oxidizable substrate. In addition, the patent requires 0.001 to 1 part of a metal halide, preferably NaCl, as a catalyst. In the presence of fresh foods of high a_w, no water is needed as the system absorbs it from the internal environment. A metal hydroxide is also incorporated to raise the pH so that the carbon dioxide will be evolved into the gas space to replace the volume of oxygen reacted. The patent mentions that these materials are incorporated into small polyethylene bags which are then placed into the container with the food.

Teijin, Ltd. of Osaka, Japan has another U.S. Patent (#4,230,595) in which iron powder along with an oxidizer selected from sodium silicate, sodium alum or sodium borohydrate is incorporated into a pouch with a $k/x = 72000$ cc/day m^2 atm to insure rapid permeation of oxygen into the pouch. The object is to prevent the formation of hydrogen gas, which can occur with some of the other oxygen scavenging systems. They also note that there should be 0.2 to 100 cm^2 of surface area of the film per gram of oxygen scavenger system. In one example they mixed 10 g iron powder with 8 g sodium metasilicate nonahydrate, 4 g sodium chloride, 16 g calcium sulfate dihydrate and 1 gram activated charcoal under nitrogen in a V blender for 20 min (particle size, <150 μ). Three grams of the mixture were added to a 5×5 cm perforated polyethylene-paper laminated sachet (permeability stated as 0.2 cc oxygen/cm^2 min atm). The sachet was then put into pouches (18×27 cm) containing either 10 g bread, 40 g unboiled Chinese noodles, 50 g rice cake, 40 g sponge cake or 20 g kamaboko fish gel with a headspace of 500 mL air. The oxygen did not rise to detectable levels during the 5 weeks of the test. The products were acceptable in flavor and color after 5 weeks at 25°C. A nylon/EVOH/polyethylene bag was used for the food itself (Toyo Seikan Kaisha, Ltd.). No mold appeared on the test food or the control. Other examples presented were for dry foods.

A Mitsubishi patent (US 4,166,807) utilizes iron with 0.05 to 5% of sulfur on a weight basis and a halide catalyst for the scavenger system. The sulfur in the iron prevents the evolution of hydrogen gas, thereby making the system safe.

Data are presented for various configurations and the resulting gas compositions evolved. In one test, 100 g of iron containing 0.3% of sulfur was mixed with 50 mL of a 1% aqueous NaCl solution and dried. Two grams of this powder were placed in a container with bread at 25°C. In 30 h the oxygen went to 0%. No mold was observed after 30 days, while the control became moldy in 8 days. The flavor was still acceptable at 12 days, while the control became unacceptable in 4 days. A similar example with strawberries stored at 5°C showed about a four day increase in shelf-life over the control, while a test with a sponge cake showed a 3 times longer shelf-life at room temperature.

Australian workers have published extensively on chemical systems for oxygen scavenging (Rooney 1981; Rooney *et al.* 1981; Shorter 1982) in which they have reviewed the field and made studies on some of the systems. The tested systems used photosensitive dyes among other compounds. Rooney has suggested that for practical purposes, the reaction of iron with ground state oxygen is too slow for shelf-life extension, especially at room or refrigerated temperature. However, if the oxygen can be excited to the singlet state, the reaction is much faster and the scavenging products are better oxidizing compounds.

In the Rooney process (1981), a photosensitive dye is impregnated onto a piece of ethyl cellulose film. Upon exposure to UV light, the dye activates oxygen to the singlet state. This oxygen then can react with any acceptor to form an oxide. They first described this system in Chem. Ind. (p. 900, 1979). The 1981 paper describes a number of systems made with a 4 cm × 12 cm strip wrapped into a coil and placed into a pouch with the food. The dye used was erythrosine. The singlet oxygen acceptors tested were difuryllidene erythritol (DFE), tetraphenyl porphine (TPP), dioctyl thallate (DOT), and dimethyl anthracine (DMA) however, these are not approved for contact with foods. Ascorbic acid was also tested as the oxidizable substance in combination with iron. It does not work as well as iron alone and requires high water activities. One advantage of the latter system (ascorbic acid-iron) is that it would not trigger any metal detector on line. The FDA status of the dyes noted is as unregulated additives; however, it is possible that they may be allowed in some packaging material, if a functional barrier exists to prevent their migration into food. The Australian work showed that the rate of oxygen scavenging was dependent on the extent of exposure to UV light. This means that the process would be ineffective in some flint glass and in opaque packages or containers. However, for locally produced and distributed salads or meals, a clear package would be used which would be displayed under lights most of the time, until the product went to the home refrigerator. The second limitation was oxygen flux into the film. In all cases, the oxygen was scavenged from 30 mL of headspace in 30–80 min, with the rate slowing down after the level reached 2% oxygen. The rate followed first order kinetics. There was no attempt to design a system for scavenging the oxygen over the whole period of shelf-life; rather, the work was directed towards initial removal of the oxygen. The tests with pouches of potato

chips showed similar drops in oxygen within 30 min. This use could be valuable, since you cannot pull a vacuum on a bag of chips and they are made and generally distributed within a few hundred miles. To make the film, the dyes and acceptors were dissolved in methanol with a plasticizer (dioctyl phthalate) at concentrations to give about 10^{-2} to 10^{-3} M on a film volume basis. This was then cast onto ethyl cellulose which would be a poor film for the outer package because of its high permeability to moisture. The coils of the cast dried film were put into the pouches which were then irradiated with UV from fluorescent lights at several wattages.

American Can Co. developed a scavenger film (Miraflex 7 Scavenger Web), that used a platinum or palladium catalyst for reacting oxygen with hydrogen (Zimmerman *et al.* 1974). The water vapor formed is trapped in the multilayer film since the water permeability of the film is much less than that of oxygen. The food is put in the pouch which must be flushed with a 92% nitrogen–8% hydrogen mixture (Warmbier and Wolf 1976). The U.S. Army Natick Laboratories did extensive work with this film for extending shelf-life of dry foods for use in the military food caches located around the world. Waletzko and Labuza (1976) showed this to be very effective in extending the shelf-life of intermediate moisture foods for the space program. Oxygen levels as low as 0.001% were maintained over a 6 month period of time. There were few commercial uses of this system because the film cost was 30 times greater than that of foil alone and the government restricted use of the precious metals. In a study using this film in Ireland, it prevented brown discoloration of fresh beef for over one week of storage (O'Keefee and Hood 1981). Other systems including vacuum packaging and a carbon dioxide flush were not acceptable.

The Carnation Co. has a patent (US 2,825,651) which uses a sulfite salt and copper sulfate as the catalyst for scavenging oxygen. Sodium sulfite and the copper must be intimately mixed and ground and then formed into pellets under high pressure. The reaction is SO^{-3} to SO^{-4}. As noted earlier, use of sulfite in foods is under scrutiny; however, if this preparation were incorporated into a film the sulfite might not migrate into the food. The Carnation patent involves incorporating the compounds into a separate sachet. In their application, pellets eqivalent to 10 meq of lithium sulfite with 4 meq of copper sulfate pentahydrate removed 8.5 cc of oxygen in 5 h. To be made equivalent to a 3 mil PET film with a $k/x = 4$ cc/day m^2 atm, one would need the following weights of sulfite salts spread out on a 1 meter square area of film along with an equivalent weight of the copper catalyst:

lithium sulfite-1 H_2O, 42 mg
sodium sulfite, 47 mg
potassium sulfite-$2H_2O$, 73 mg
ferric sulfite-$3H_2O$, 70 mg
calcium sulfite-$2H_2O$, 58 mg

The advantage of this is that the pelletized particles can react without the presence of water because of their intimate contact. In addition, since they can be ground to a fairly fine particle size, they should be easily incorporated into a film. Yoshikawa *et al.* (1977) showed that a similar sulfite based scavenger system could remove 13 cc of oxygen in 10 h. This application was granted a U.S. patent (Teijin, Ltd., Osaka, Japan; #4,317,742) in combination with a heat generator for nonfood uses. Japanese patents covering this application include 72JP #19,729 and 76JP #12,741. The promoters can be other than copper including tin, lead, chromium, selenium, nickel, cobalt, iridium, palladium and platinum. Many of these would be precluded from food use. The Teijin patent claims uses for prevention of oxidation of fats and oils, dried foods, raw and fresh foods of all categories and pharmaceuticals. The claims are for composition of the scavenger, not for the method of employment. The U.S. Department of Agriculture has a patent assigned to it that uses bisulfite salts (US #3,169,068 Feb. 1965). A molecule of bisulfite will react with an atom of oxygen (1/2 O_2) to form a molecule of bisulfate. The invention encompasses supporting the bisulfite on some type of carrier surface to increase the reaction rate. In addition, a heavy metal is added as a catalyst. If a 2 mil thick polypropylene film were to be used, fifty times more of the sulfite salts would be needed, which is about 2–3 grams per square meter. This would probably be possible to achieve, although it may give a rusty cast to the film. It might also be possible to vapor or sputter coat any of these metals onto a film.

Toyama *et al.* (1980) tested three of the commercially available oxygen scavengers in Japan on intermediate moisture confectionaries. Mold growth was suppressed for at least 5 weeks; however, where a scavenger pack allowed carbon dioxide to build up, yeasts grew with subsequent alcoholic odors being formed. In a study of ground beef (Izumimoto *et al.* 1982), an oxygen scavenger pack significantly prevented brown color formation for up to 10 days with no off odors developed. Similarly, Ma and Kim (1980) studied the use of an iron based scavenger for improvement of the storage life of deep fried instant noodles compared to air or vacuum packaging. The scavenger improved shelf-life by about 20–30 times over that of air and two times over that of a foil laminate-vacuum packed product based on peroxide values and TBA numbers. As a final note of caution, Sasajima *et al.* (1978) noted that low oxygen levels, formed either by chemical scavenging systems or the growth of aerobic organisms which decrease the oxygen content, can induce botulinum growth in Japanese fish gel (kamaboko). In addition, no reported study evaluated the effect on loss or change in nutritional value.

Glucose Oxidase Enzyme Oxygen Scavenger System

Another method to control the oxygen level in a food package in an active way rather than a passive way (i.e., permeation only) would be by the use of

an enzyme reactor surface which would react with some substrate to scavenge incoming oxygen. This would be especially applicable if the cost of the enzyme were not too high. One problem, because of cost, is that until enough data are collected on the oxygen utilization rate and oxygen partial pressure tolerance of the food, it will be difficult to estimate the amount of enzyme needed and the level of oxygen developed to give an economic estimate. However, one can develop the product on the basis that an internal oxygen level of 0%–1% is adequate and that growth of anaerobic pathogens will not be sufficient at this condition to cause food poisoning. To be equivalent to the amount of oxygen just coming through a good foil laminate film with a k/x of no more than 0.1 then, an enzyme surface will have to react with oxygen at a rate of at least:

$$\text{Rate} = \text{permeability} \times \text{area} \times \text{oxygen pressure difference between the outside and inside} \tag{7}$$

$$\text{Rate} = 0.1 \times 1 \times [0.21 - 0.01] = 0.02 \text{ cc per day per m}^2 = 20 \ \mu\text{L/day} \tag{8}$$

Improper seals and creases which crack the film could effectively raise this rate by 2 to 50 times. This calculation above assumes air outside and $< 1\%$ oxygen inside. For the worse case and with a good foil that is creased, there would be the need to scavenge 1000 μL/day (1 cc). This is equivalent to the Japanese Ministry of Agriculture standard for dry foods. Any film could be made equivalent to a good foil or EVOH (ethyl vinyl alcohol) laminate by binding the oxygen scavenging enzyme to the inside surface of the film to react with the excess oxygen, letting only the amount equivalent to that coming through foil to contact the food. Polypropylene, for which there is some technology for binding enzymes, has a permeance of about 2000 cc/day m^2 atm. Taking this value and subtracting the maximum amount coming through foil (1 cc/day m^2) gives:

$$\text{Rate} = (2000 \times 1 \times [0.21 - 0.01]) - 1 = 417 \text{ cc/day} \tag{9}$$

This value of abut 400 cc/day obviously is significantly greater than foil alone which is less than 1 cc/day m^2.

Glucose oxidase (E.C. 1.1.3.4), one of the most promising enzymes that could be used as a scavenger, is a classical oxidoreductase. It transfers two hydrogens from the -CHOH group of glucose to oxygen with the formation of gluconodelta-lactone and hydrogen peroxide. The lactone then spontaneously reacts with water to form gluconic acid. One mole of glucose will use up one mole of oxygen; thus, in an impermeable pouch with 500 cc headspace, to reach zero oxygen, only 0.0043 mole of glucose (0.78 grams) is needed as a substrate. The major factors will be the speed at which the enzyme works (activity per mg), the amount of glucose available, and the rate at which oxygen permeates into the package. In the presence of catalase, a normal contaminant of preparations of glucose oxidase, the hydrogen peroxide is broken down to water and oxygen,

thus in the presence of catalase one glucose will only react with a half mole of oxygen decreasing the overall effectiveness of the system. Pure glucose oxidase without catalase is very expensive.

There have been many proposed uses for the oxygen scavenging properties of glucose oxidase but few have been commercialized. Reed (1966) has summarized some of them. One use is the elimination of oxygen from bottled beer or wine. Since the presence of oxygen in the finished product leads to undesirable flavor changes, adding both glucose oxidase and catalase or passing the fluid through an immobilized enzyme bioreactor, can improve shelf-life. Since the manufacturers do not have to list ingredients on alcoholic beverages, the extent to which this is done is unknown. This same function was proposed for mayonnaise. Reed (1966) stated that, unfortunately, since the enzyme was not listed as an ingredient in the Standard of Identity, it could not be used. In 1975, the FDA revised all standards, allowing for the use of any safe and suitable additive or ingredient as long as it was listed on the ingredient label. A perusal of present labels for mayonnaise and salad dressing does not indicate that the industry has decided to use glucose oxidase for this purpose. Most likely deaeration equipment can be used more cheaply. Reed (1966) also stated that the enzyme was used in canned club soda to prevent oxidation of the inner metal surface. Since the change over to aluminum, PET, and PVC containers, this is no longer done.

One major use for glucose oxidase is in the preparation of dried or frozen whole eggs. Eggs naturally contain about 0.5% glucose which upon spray-drying or freezing interacts with the egg protein. This results in production of a brown color, off flavors, and a decrease of functionality (more rubbery). Scott (1958) was the first to recognize that the Chinese fermented their dry eggs first, to rid them of glucose. He patented a process (1956; US #2,758,934) for direct addition of glucose oxidase/catalase to the egg magma to degrade the glucose, a process still used today. This latter process, and the enzyme kits for detecting blood and urine sugar, are the present major uses for glucose oxidase.

Scott (1958) and Scott and Hammer (1961) also suggested using insert sachets for the scavenging of oxygen, especially for dry foods where the sachet could contain the moisture necessary for the reaction. A patent was issued to Scott for this purpose (1956; US #2,758,932). Scott and Hammer also have a patent for dispersing the glucose oxidase throughout the food in a fine particle matrix (US 3,016,336; 1962). The main goal of this latter patent is that the water and oxygen penetrate into the matrix where the reaction takes place and where the reactants are trapped. There has been no commercialization of this application to date, perhaps because of easier methods to remove oxygen during packaging, but certainly this would be applicable for prepared salads and meals. In 1956, Sarett and Scott also patented a glucose oxidase treated sheet product (cellophane film) (US #2,765,233) to be placed on foods to extend shelf-life. No examples were given, but this would be applicable to fish and cheese.

Enzymes are regulated as Secondary Direct Food Additives under the FD&C Act (21 CFR 173). Glucose oxidase (with catalase), was in use prior to the Food Additives Amendment of 1958 and was granted GRAS status. It is not listed specifically in 21 CFR 182 or 184; thus it comes under 21 CFR 182.1 (a) which states that it is impractical to list all substances that are GRAS.

The molecular weight of glucose oxidase varies depending on the source, but it is around 150,000 daltons. The isoelectric point is 4.2–4.3 and the pH optimum is between 5.5 and 5.8 depending on the source. The rate is fairly constant over the range of pH 5–7. The enzyme has more than 2 h stability in water at 40°C and a pH of 4–6. One molecule of enzyme also contains two FAD molecules, removal of which inactivates the enzyme. The acid produced could shift the pH down below the optimum and if the hydrogen peroxide is not reacted with surface materials it might also inactivate the enyzme. As noted, most commercial sources are catalase/glucose oxidase mixtures. The catalase degrades the peroxide as it is produced. If there is no surface for the peroxide to diffuse into, the glucose oxidase will be inactivated, precluding this application. Since many foods may have minimal contact with the package surface, except on the sides and bottom, this may not be the best approach for oxygen scavenging.

Reed (1966) reviewed some data on the kinetics of glucose oxidase. The rate falls as oxygen partial pressure falls, but does not level out as oxygen increases above 21%. The rate at 5% oxygen was 1/4th that in air, and at 50% oxygen it was double that in air. At 100% oxygen, it rose to 2.33 times that in air, showing a slight leveling off. Unfortunately, the data were given in total amount reacted, not as a function of time. This is common with many enzyme assays. However, one can graphically estimate from these data that the rate at 1% oxygen would be at least 50 times less than that in air. Keilin and Hartree (1948) reported that pure glucose oxidase, at 30–40°C, had a rate of oxygen consumption of about 150,000 μL/h/mg. Based on this, and spreading 1 mg per m^2 on a film, this would be equivalent to reacting with all the oxygen coming through a film with an oxygen permeability of about 18000 cc/day m^2 atm.

The calculation comes from assuming an enzyme reaction rate of:

$$150{,}000\ \mu L/h \times 24\ h \times 10^{-3}\ cc/\mu L = 3600\ cc\ oxygen/day \qquad (10)$$

At a partial pressure difference of 0.20 atm (i.e., 1% internal oxygen), and assuming no decrease in enzyme rate with oxygen pressure, this means the glucose oxidase can handle a film with a permeance of:

$$(k/x) = \text{Rate/pressure difference} = 3600/0.2 = 18000\ cc/day\ atm\ m^2. \qquad (11)$$

This k/x value is greater than any film in Table 5 suggesting that the use of the enzyme would be a viable approach. Thus at room temperature, a 1 meter square surface with 1 mg of enzyme spread out on it should be able to handle

all the oxygen coming through any film listed in Table 5. One advantage is that both polypropylene and polyethylene are good substrates for immobilizing enzymes; thus they could easily be made equivalent to or better than a good foil or EVOH laminate at a cheaper cost. Work done at Ocean Spray indicates a permeability of 35–40 cc/day m^2 atm for the Brik Pak aseptic container (Borque 1984), which is a seven-ply laminate. Even this film has a high enough permeability to limit shelf-life and would benefit from an enzyme surface. One key factor that will have to be determined is the heat and acid stability of the enzyme when bound to the film since the uses proposed may involve a lowering of pH or some type of pasteurization step (Weetall 1985).

For storage of extended shelf-life refrigerated foods, the enzyme reaction rate, with a typical Q_{10} of 2, would be decreased by a factor of at least 6 times at refrigerated temperature. In addition, the lower oxygen pressure (1%) on the inside surface of the package should cause at least another 50-fold reduction in the rate of oxygen utilization, giving, most likely, an overall 300 fold reduction in the rate of oxygen consumption. This would be equivalent to consuming only 3600/300 = 12 cc/day of oxygen coming through the film. This is equivalent to a film permeability of 12/0.20 = 60 cc/m^2 day atm. Thus with a 300-fold drop in activity, the 1 mg amount of enzyme could only handle the oxygen from PVDC, acrylonitrile, or the unfolded Brik Pak films. It would be borderline for polyester (PET), but would not be enough for the more permeable films. For example, with polypropylene, which has a penetration of 456 cc/day m^2 (2280 $\times$ 0.2), the amount of enzyme would have to be increased to 38 mg per meter square (456/12). These examples point out the synergism permeance determined by thickness also between the permeance of the film and the amount of enzyme scavenger needed.

It should be noted that the permeability data in Table 5 are for 30°C. Based on diffusion kinetics, the actual permeability at refrigerated temperature could be 30% lower. Thus there is a built in safety factor in the calculations. The actual bonding of the enzyme to the film could at worst cause it to lose 20–80% of its activity, so the amount would have to be further increased, perhaps offsetting the lower temperature diffusion advantage. Once the enzyme is bound it should have fairly good stability over the 30–60 days needed when it is activated in the presence of water (Wehnert *et al.* 1985).

Several companies, including Worthington Chemical and Finnish Sugar Biochemical Co., presently produce glucose oxidase on a large scale. Scott, holds many early patents for the industrial use of the enzyme as a scavenger and pioneered its use in eggs to remove glucose. The source is from *A. niger*. Most commercial sources have a ratio of glucose oxidase to catalase of 200–300:1, so it is not totally pure, thus there is not a one-to-one use of oxygen for each glucose. This, however, might help to slightly stabilize the enzyme. A typical enzyme unit is about 190,500 moles of oxygen consumed per minute per gram

at 37°C and in air. The activity and enzyme costs suggest that a film with bound enzyme that would effectively scavenge oxygen would be in an acceptable price range. It should be noted that all of the enzyme data are for high water activities. There are no data on glucose oxidase activity as a function of a_w but it is known that enzymatic activity will decrease with a decrease in a_w. Despite this, Kristein and Kuehn (1981) suggested that impregnation of the surface of packaging materials with glucose oxidase is one of the four main key food industry applications for this enzyme in the future.

A major unknown factor is how stable the enzyme will be on the film over time. Wehnert *et al.* (1985) showed that glucose oxidase bound to a plastic surface (Eupergit C) underwent a 50% drop in activity in 2–3 weeks followed by little loss over the next 4 weeks. Hartmeier (1979) and Hartmeier and Tegge (1979) reported on a fairly stable preparation in a gelatin gel matrix hardened with glutaraldehyde and formaldehyde. These latter are unapproved food additives, but may be allowed for use in preparation of packaging films.

The Japanese have done a lot of work on binding of enzymes to chitosan, which is an insoluble polymeric carbohydrate from shellfish shells. Kasumi *et al.* (1977) reported a 70% loss in activity for bound glucose oxidase. Atallah and Hultin (1977) reported that crosslinking glucose oxidase to itself with glutaraldehyde produces a water soluble preparation with increased stability. Wasserman and Hultin (1980) reported that glucose oxidase immobilized on polyethylenimine coated glass beads retained 78–87% of the activity and was more stable to heat inactivation. This suggests that some type of heat pasteurization for further shelf-life extension could be used without inactivating the enzyme. Greenfield and Lawrence (1975) studied immobilization of glucose oxidase on clay supports using glutaraldehyde. Moderate activities (20–50%) were found. Herring *et al.* (1972) showed less loss of activity on an alumina surface. All of these reports suggest that the immobilization process will decrease the enzyme activity by 20 to 70%, but probably not by more than 90%.

Since the enzyme is a protein and can serve as a nutrient for microbes along with the glucose substrate, a microbial inhibitor may be needed in the film. Ukrainian workers have developed a package surface preparation called "PROLON" to prolong shelf-life of foods. It contains sorbate to prevent microbial attack of the enzyme (Levenia *et al.* 1973).

It is unknown whether the hydrogen peroxide produced at the required level of activity will have any benefit to shelf-life with respect to food surface microbial inhibition and whether the concentration buildup is within regulatory limits. One must assume that there is good surface contact between the film and the foods such that liquid diffusion of the peroxide into the food will be occurring. As an estimate, the enzyme bound to a good film with 40 units of activity will produce 40 mole of peroxide per day, under ideal conditions. At a molecular weight of 34, this is eqivalent to about 0.0014 grams of peroxide spread out over 1 square

meter of surface. Assuming a rapid penetration to a 1 mm depth in the food, the peroxide would dissolve in 100 g of food for 1 square meter of surface area. This concentration would be equivalent to 14 ppm at the surface if none of it reacted in 24 h. If the actual depth of penetration were 1 cm, this would amount to an overall concentration to 1.4 ppm. With a limit of 0.5 ppm in the U.S. for the residual level of peroxide in food in aseptic packages, this would be unacceptable. If it were to be calculated on an hourly basis the concentration would be $1.4/24 = 0.06$ ppm. In this case one could reason that since the peroxide would be produced slowly over the day and would be reacting or further diffusing into the food, the overall level in the food would be less the FDA maximum allowed for peroxide.

Under actual refrigerated use conditions, the 40 active units would be producing less than 1/300 of the above concentrations of peroxide. It would be expected then, that there would be little microbial activity at the surface since the concentration would be less than 0.05 ppm even if there were no diffusion. Field (1981) did report that 1 unit of glucose oxidase in excess 4% glucose solution was bacteriostatic to *Bacillus subtilis*.

One theoretical way to determine what the potential surface concentration and microbial effectiveness would be, is to utilize various diffusion models. For the condition of a single excess amount of material deposited on the surface with a large surface area, one of the Crank (1956) equations for diffusion can be used where:

$$F = [D\ t]^{-1/2} \exp [(-4\ D\ t)^{-1}\ x^2\ ] \qquad (12)$$

and F is the fractional concentration at any point in time and x is the distance from the surface for the values of time (t) with a diffusion coefficient of (D). This equation was solved for diffusion coefficients from 0.000001 to 0.001 cm^2/h. Typically, noncharged solutes will diffuse at 10^6 cm^2/s in moist gel-like structures while a dense structure will decrease this by a factor of 1,000 (Guilbert *et al.* 1985). For sorbate, which is a microbial inhibitor, the diffusion coefficient is 7.2×10^{-3} cm^2/h (Guilbert *et al.* 1985). Calculations were made in our lab using Eq. (12) at 1 mm increments and for a period of 54 days. For the smallest diffusion coefficient, 0.000001, in 21 days, the diffusing material was still at the surface since the concentration at 1 mm was only 17% of that at the surface. At all other depths, it was zero. It reached just under 0.1% in 54 days at 2 mm depth. Thus the material would accumulate and build up quickly on the surface. This diffusion coefficient would be that typical for a dense food like raisins.

At a diffusion coefficient equal to 0.001, the diffusion rate will be so rapid, that in 1 day, the maximum amount will be reached at a depth of 3 mm. After two weeks, the surface concentration will begin to be depleted, but by that time, the material will have been almost evenly distributed down to a depth of 6 mm at an average concentration of about 70% of what was on the surface. For sorbate,

with the highest diffusion coefficient, in moist foods, any surface deposit would thus quickly dissipate throughout the food. This suggests then that for hydrogen peroxide, which would most likely have a diffusivity value similar or greater than sorbate, one can logically assume that the concentration as eaten should be based on the whole food. Thus the effective surface concentration would be based solely on the rate of production, which would be the limiting factor. The high diffusion rate also suggests that microbial effects would be limiting unless the food had a dense surface skin with a low diffusivity as, for example, an apple or unskinned fish.

Any application of the enzyme also requires the correct amount of glucose released per day for the enzyme to react on. In order not to have the rate of scavenging fall, one needs to have a large substrate to enzyme ratio. For the above example and with a desired 60 days shelf-life, about 10–15 grams/m^2 are needed. This can be either incorporated into the film directly, incorporated as microcapsules that would slowly release the glucose or the food can be dipped into the sugar. The latter would be the least likely way to do it. However, Nutri-Sea Foods, Inc. of Narragansett, Rhode Island were using the enzyme by incorporating it into the packing ice and dipping the fish as they were caught into a glucose solution for extending their shelf-life. They found that the shelf-life of ocean flounder so treated was extended to 17 days as compared to a normal 10 days (Anon 1986b) although Rand (1972) found that the effect on shelf-life was minimal.

Oxygen Scavenging with Alcohol Oxidase

Besides glucose oxidase mentioned previously, other enzymes have potential. One such enzyme is ethanol oxidase which oxidizes ethanol to acetaldehyde. This enzyme has been extensively studied for its ability to detect ethanol in gas streams, essentially because it can react with ethanol in the vapor state. It has been used primarily as a breath alcohol analyzer and many patents are pending. The reaction is extremely rapid. At present, it has no known application for food preservation, but since it can react in a wide a_w range, it has been of interest. The Provesta Co. (Bartlesville, Oklahoma), which is part of Phillips Petroleum Co., is a key center for this work since they produce the enzyme from yeast. The idea would be similar to that for glucose oxidase, i.e., the enzyme would be bound on a film or put into a sachet and some source, a sachet, microcapsules, or the film itself, would be used to control release the alcohol. No kinetic data are available for this enzyme. On the basis of a 0.4 m^2 package with a k/x of 1,000 and 1% oxygen inside, the enzyme would need to handle 80 cc/day under refrigeration conditions. This amounts to 0.0036 moles of ethanol required per day. For 100 days shelf-life, about 16 g of ethanol would be required, which is

substantial, especially since it might impart an off odor in the package. In addition, considerable acetaldehyde would be formed which would give the food a yogurt-like odor.

Carbon Dioxide Scavenging/Emitting:

As noted in the section covering oxygen scavenging, there are several commercial systems that can be used to either emit or scavenge carbon dioxide. One of the "Ageless" products contains calcium hydroxide, which at a high enough humidity reacts with carbon dioxide gas and produces calcium carbonate; its main use has been for fresh roasted coffee. Coffee, when roasted, can contain up to 15 atm of dissolved CO_2 internally due to the Strecker degradation reaction between sugars and amines. If the coffee is packed in a can or foil pouch, as CO_2 is released the package expands and can burst. Thus, the trade typically vacuum packs the coffee in a can (which also reduces oxidation) or uses a very poor barrier film which prevents bursting but does not prevent flavor oxidation and loss of shelf-life.

The Mitsubishi "Fresh Lock" sachet contains both an oxygen and a CO_2 scavenger. It is being used worldwide for canned and foil pouched coffees with great success, but has not been applied to refrigerated foods since high not low levels of CO_2 are desired.

Mitsubishi has another system that consumes oxygen and produces CO_2, which could be used for high CO_2 applications. Ferrous carbonate and a metal halide catalyst are mixed, with one mole of CO_2 produced per mole of oxygen used. Their US patent (#4,299,719) describes an aqueous system inside a pouch that would be placed in a food package but no applications have been found in the marketplace.

One novel application is that of a CO_2 emitting system for microbial studies. For example, Becton Dickinson, through their BBL Microbiology Systems (Box 243, Cockeysville, MD 21030) has developed a pouch into which streaked petri plates can be placed for the determination of the presence of *Campylobacter* organisms in foods. This system replaces the need to set up a chamber with an enriched carbon dioxide atmosphere. This pathogen grows better in an enriched carbon dioxide atmosphere which points out a potential microbial problem for CA/MA storage of foods. The pouch consists of a sachet containing 5g total of a mixture of iron powder, calcium carbonate and citric acid with a binder to hold the compounds together. The pouch has a volume of about 500 cc which is quite large. When the activating liquid (buffered water) is mixed into the reagent containing sachet, carbon dioxide is produced from the carbonate and oxygen is scavenged by the iron. Within one hour this system reaches a composition of 5–12% oxygen and 7–12% carbon dioxide in the atmosphere. Based

on these values, and with one mole of carbon dioxide theoretically generated per mole of carbonate, only about 0.25 g (0.00244 moles) of carbonate are needed.

In 500 cc of package headspace, there is less than 0.0041 mole of oxygen, thus only 0.3 g of iron is needed to use up all the oxygen. This could easily be deposited along with the citrate and carbonate onto a film or in a sachet. Since most applications would have less than 500 cc of headspace, these numbers would represent a maximum needed if no oxygen diffused into the package. Given a 25 by 10 cm surface area, this means a total impregnation of about 1 g of these chemicals per 0.05 m^2 of film, which seems reasonable to create an oxygen scavenging/carbon dioxide producing film. However, with the higher permeability of films to carbon dioxide, even films with a low carbon dioxide transmission rate, such as PVDC, would require 0.2 g of carbonate and 0.4 g of citrate per day per square meter to just handle the carbon doxide loss through the film. For 21 days of shelf-life, this would amount to 12.6 g of deposited chemicals which may not be technically possible. Based on the calculations, it would seem that perhaps the best way to achieve high CO_2 levels for a refrigerated food would be through gas flushing and then use of a film that has been surface treated to reduce the transmission rate of CO_2 while not changing the oxygen transmission rate.

Chemical Preservative Films

Another "active packaging" concept is the release into the package atmosphere, of a preservative which then deposits on the food surface and inhibits microbial action. A second method would be direct deposition on the food. As with oxygen scavengers many patents exist and they cover a wide range of potential food applications. A similar approach has been used by the cereal industry in which the antioxidants BHA or BHT are incorporated into a wax liner. The antioxidant diffuses into the cereal flakes where it exerts its protective actions. Recently, Hoojjatt *et al.* (1987) reviewed the kinetics of diffusion of BHT from polyethylene films and the influence on stability. They showed that about 80% diffuses out of the package, but the remaining 20% goes into the cereal and gives as good protection as when the antioxidant is incorporated directly. Miltz *et al.* (1987) has also evaluated these kinetics. Few companies are using this approach, however. The key is that the only action is against lipid oxidation, and thus it may not achieve the shelf-life desired, especially with moist foods.

There are a number of interesting publications that describe applications of a surface preservation system. Ghosh (1977) reported on a greaseproof paper coated with a layer of CMC containing sorbic acid. This was used to extend the shelf-life of Indian bread. Union Carbide has marketed a sausage casing for large bologna. The casing contains sorbate and glycol which then form a preservative-

bearing surface. Ben-Yehoshua of the Volcani Agricultural Research Center in Israel has advocated an inhibitor wrap using Imazalil (Israel patent #52177) for citrus fruit. Decay of inoculated oranges with this wrap was reduced from 100% to only 4%. In fact, parchment wraps employing mercurial compounds were in use in the U.S. during the 1940s–60s employing mercurial compounds. They were eventually eliminated from use because of toxicity. Torres *et al.* (1985) evaluated a sorbate loaded edible barrier for mold inhibition on food surfaces. The antibiotic "Pimaracin" has been approved for use as a surface application to extend the shelf-life of cheese. Field *et al.* (1986) advocated using glucose oxidase/glucose as a dip for shelf-life extension of fish. The action is three-fold, oxygen is depleted at the surface, acid is produced and hydrogen peroxide is produced. In fact, there are several old patents held by Fermco, one of which is for applying these compounds in a sheet wrap for prevention of mold growth of cheese (US 2,765,233, Oct. 2, 1965). There is also a similar Japanese patent covering many different food applications (80-JP23071), but no one has brought the invention to practice. There also is a series of medical products which can be placed over wounds that achieve a controlled release of anti-microbials, so as to speed wound healing (Chem. Week, 1/2/85, pp. 12–13).

The level of the preservative needed to achieve an antimicrobial effect is quite low, and combinations of them can be synergistic (Acott and Labuza 1976). The previous calculations presented show that the agent would most likely stay at the surface for acceptable times. Torres *et al.* (1985) used an edible film in which the ionic potentials were adjusted to force the acid and sorbate to stay at the food surface because of Donnan equilibrium. Their work suggests another potential technology, i.e., use of an edible film rather than a disposable film, as long as it is safe toxicologically. This then could be combined with a scavenging system if CO_2 and O_2 control were needed. Kester and Fennema (1986) recently reviewed the edible film area.

Another interesting system being introduced is that of the "antibiotic film" of Dai Nippon Printing Co. The exact nature of its action has not been disclosed, but it has a metal bonded zeolite on the inside surface. Supposedly ozone or active oxygen is produced as it comes through the film, which in turn then kills any surface microbes. The material comes in three forms: (1) an antibiotic absorbent sheet; (2) a nonwoven drip sheet; and (3) conventional sealable films. It is being directly sold in supermarkets to consumers who then use it in the home on cheese, fish, meat, and bread. Supposedly, white bread will keep over two weeks at room temperature without molding.

Ethanol Emitting Active Packaging

Another approach to lengthen shelf-life has been to spray ethanol or another alcohol on the surface of a food. The earliest work published was a Japanese patent (72JP-073439) issued to Showa Tansen Co. in which both ethanol and

propylene glycol were sprayed onto the surface of bakery goods. Nippon Polycello Co. of Japan built machinery to do this using at least 2% ethanol in the gas space (78JP-016118). Another Japanese scientist in fact patented a process for sterilization of foods at reduced temperature by using ethanol, hydrogen peroxide or propylene glycol in the sterilizing steam. Two U.S. companies researched this extensively in the 1970s (Keebler and Creative Crust) for application to shelf stable intermediate moisture pizza crusts with a_ws of 0.85–0.90. Since this constituted a new food additive application, they had to petition FDA. A food additive order (21 CFR 184.1293) was eventually granted for this application. The pizza crusts were at a water activity of about 0.84 so were subject to mold deterioration. The alcohol spray amounts to a maximum of about 2% by weight of the total pizza crust. Immediately after spraying, since penetration into the crust was slow, the top 1 mm layer had over a 10% ethanol concentration. This exerts both a biocidal effect on any microbes or spores that land on the surface after baking and an inhibitory effect on outgrowth for any microbes that do not get killed. Shapero *et al.* (1978) showed that the effect was more than just a depression of water activity and in fact increased as the water activity was depressed. A key in the granting of this food additive order was the fact that the ethanol would be evaporated from the pizza crust during the eventual baking by the consumer. The only other places where ethanol is allowed for food in the U.S. by the FDA is (1) as a carrier for flavor in confectionaries not to exceed 0.5%, and (2) in wine coolers which contain less than 7% ethanol. Both of these sanctions have brought FDA under attack, first, because they have sought to ban manufacture and importation of liquor-filled candies and second, because the Bureau of Alcohol Tobacco and Firearms feels that wine coolers should be under their jurisdiction.

Many applications of ethanol emitting films or sachets have been patented. Morinanga Co. (82JP-071746) patented an adhesive-backed film that can be taped on the inside of a package. The film contains ethanol encapsulated in some material on the surface which then evaporates into the package airspace to give a preservative effect. A Dutch patent (81DE-133943) involves adding an ethanol containing gel into the package headspace. Mitsubishi has a sachet patent (80JP-153468) which contains encapsulated ethanol as well as glucose, ascorbic acid, a phenolic compound and an iron salt. Thus it scavenges oxygen as well as emitting ethanol. Asahi Denka Kogyo of Japan also patented (78JP-161441) a sachet which emits ethanol. It is encapsulated with cyclodextrins.

The interesting commercial application of the use of ethanol as a surface preservative has come from the Japanese company, Freund Ltd (14-2 Takandanobaba 2-chome, Shinjuku-ku Tokyo 60 Japan). They have both Japanese (80JP-043567, 81JP-108712) and a U.S. patent (#4,550,026 Oct 29, 1985). The patents describe the system as a sachet containing either a gel or silica with 55% by weight of ethanol bound into the solids. The sachet material allows the

slow, controlled release of the ethanol into the package atmosphere where it then deposits onto the surface of the foods. The Freund Co. now markets the product for the bakery industry in Japan and Europe. Because of the odor of alcohol, for some products the sachet also contains a masking compound such as vanillin or citrus flavors. The sachets are also labeled "Do not eat contents" including a pictograph, similar to the "Ageless" product.

Freund has done extensive research on the use of the ethanol emitter sachet for bakery products under the tradenames of "ETHICAP" and "ANTI-MOLD 102". It is published in their own technical bulletin as well as by Takahashi *et al.* (1984). The standard product is 55% by weight of ethyl alcohol (food grade), 35% silicon dioxide, and 10% moisture. The film used for the commercial sachet as well as the printing inks supposedly meets the requirements of the FDA in the U.S. Sachet sizes range from 0.6 to 6 g or about 0.5 to 3 g of ethanol that can be evaporated. They have developed an interesting graph of the sachet size needed versus the water activity of the product based on the work done by Shapero *et al.* (1978). The lower the water activity the less ethanol is needed. Thus 100 g of food at an a_w of 0.92 needs a 2.5 g sachet for long shelf-life while one at 0.7 a_w needs only a 0.5 g sachet. Based on a net content of 100 g of food, this would amount to between 0.5% and 2.5% ethanol needed per weight of food contained. The lower level is certainly within the FDA regulation for pizza crusts. However, in this case the product would not be baked but directly eaten. The higher level is outside the maximum of 2% in the U.S. food ethanol regulation. Freund has determined the actual ethanol content in finished foods by gas chromatography. In most of the bakery products tested (bread, croissant, steamed bun, sponge cake, casteilla) the levels were less than 1% after 20 days.

As noted in their work, some of the ethanol will be lost through the food packaging material. This is beneficial from the regulatory aspect, but decreases the efficacy from the microbial inhibition standpoint. They indicate that typical packaging films such as low density polyethylene will have an ethanol permeability of 20–30 g/m^2 day at 30 C. Thus much better films would be required. Typical PVC-polypropylene-polyethylene laminates, according to Freund, have a permeance of about 1–2 g ethanol/m^2 day which is acceptable.

Freund has tested and compared their results of the inhibitory effects of ethanol vapor to literature data on inhibition by ethanol as a liquid in the medium with at least 10 species of molds including *Penicillium* and *Aspergillus* species, 15 species of bacteria including *Staphylococcus, Salmonellae* and *E. coli* species, 9 species of spoilage yeast and three species of *Actinomyces*. They found better inhibition when applied as a vapor rather than as a liquid in the medium. Actual data on semi-moist cakes show a 5 to 20 times extension of the mold-free shelf-life depending on the size of the ethanol sachet used. They also noted that the products with the sachets did not get as hard as the controls and the effect was

much better than using an oxygen scavenger to inhibit mold growth. Perhaps ethanol reduces the staling rate of starch. Their literature also notes that the ethanol sachet is being successfully used for a wide variety of semi-moist foods in the water activity range of 0.7 to 0.9 including squid, bean jam, and rice cakes. It is especially effective where sorbate cannot be used. The company is in the process of discussing the status of its use in the United States.

Finally, there are several patents that combine ethanol with other volatile materials in a sachet for preservation (81JP-214521; US #4,550,026). Both patents combine the ethanol with volatile short chain fatty acids (C_2 to C_6) the latter at 0.01%–20% with the rest ethanol. The patents show significant increase in shelf-life of raw tuna, bread, and rice cakes. A synergistic effect was demonstrated.

Ethylene Emitting Active Packaging

No attempt was made to review the literature for patents or research on ethylene scavengers. As described earlier, ethylene is a hormone which, if it accumulates in the package, speeds up the respiration rates of raw fruits and vegetables thereby decreasing shelf-life (Ben-Yehoshua 1983). Most applications to date have involved choosing a film with a high permeability and minimizing internal gas volume.

Several recent commercial applications use a scavenging system. The Rengo Co. (Osaka, Japan) produces a sachet which contains potassium permanganate imbedded in silica (Green Pack). The silica gel absorbs the ethylene and the permanganate oxidizes it to acetate and ethanol. This system is being extensively used in the Orient, especially for specialty fruits like kiwis. Their industrial literature shows about 8 weeks shelf-life for kiwis at room temperature, thus eliminating the chill damage that occurs in the refrigerator. However, according to Kader (1985b), kiwifruit is not chill sensitive. Arpaia *et al.* (1986) have shown the significant impact of ethylene control on kiwi shelf-life. The Natural Pak Co. (Alpine, New Jersey) uses a similar scavenger for room temperature stored tomatoes which are sold at a high price to restaurants in the New York City area. Tomatoes degrade and lose flavor if kept below 9°C. Another Japanese Company makes a powder, "BC powder" which is being used in the UK (Derck Rowlands Technology Transfer, Westgate, Kent, UK). This can be incorporated into films during lamination or coextrusion to about 5% by weight. It contains silicon dioxide which acts both as a drier and an ethylene absorber with some catalyst system. The film permeability is also reduced because it is kept drier by the silica. In the U.S. it would have to be approved in this form because of the direct contact. If senescense is slowed down, the loss of nutrients should also be slowed down.

Drier Film for Active Packaging

One novel approach to extend the shelf-life of refrigerated foods is to decrease the water activity at the surface. The Showa Denko Co. (Tokyo, Japan) has developed and is marketing such a film (Pitchit Film) directly to the consumer. They are the world's largest manufacturer of propylene glycol which produces the "active packaging" action. The film is a sandwich composed of two sheets of polyvinyl alcohol (PVA) sealed along the edge between which is a layer of propylene glycol. The PVA film is very permeable to water but is a barrier to the glycol.

The product is sold directly to the consumer in a box containing the PVA blanket and 10 sheets of cellophane. The consumer is instructed to put a sheet of cellophane around the food to be preserved (whole fish, fish fillets, other seafood, meat, poultry) and then wrap the blanket around that. It is then kept in the refrigerator for 4–6 h during which time the surface of the food is dehydrated. The action is due to a water activity difference between the food (0.99) and the glycol (0.0); thus water is rapidly drawn out of the food surface. This surface dehydration not only inhibits some microbes but also may injure others without causing change in fish quality. Most likely some glycol also transfers to the food surface also slowing growth. The package reportedly provides an extra 3–4 days prolongation of the shelf-life of refrigerated fish. After the removal of the blanket, it can be washed in water, dried out and reused up to ten times. Propylene glycol is GRAS in the U.S. (21 CFR 184.1666). Since this is only a surface action, the nutrients should not be lost from the food.

Temperature Control Packaging

Because of the concern for rapid microbial growth of refrigerated foods as the temperature increases (Q_{10}s of 3 to 6), extreme care needs to be taken during refrigerated distribution and on the trip from the store to the home. One approach to solve this problem would be to insulate the food using special insulating packaging material. One such material with potential is "Thinsulate®" from 3M Co. (St. Paul, MN) which is a special nonwoven plastic with much air pore space. Another approach is to increase the thermal mass of the package so as to absorb temperature abuses. The Adenko Co. (Tokyo, Japan) makes such a product called the "Cool Bowl". It is a double walled PET container in which a gel is deposited in between the walls. The container is prechilled with the food and thus acts as a portable cooler when the product is moved to a warmer temperature. No good data exist for either of these "active" packaging technologies with respect to efficacy in preventing outgrowth of pathogens during temperature spikes or their ability to preserve nutrient and flavor quality.

Time-Temperature Integrators

The quality of a refrigerated extended shelf-life food product and its useful shelf-life is very much dependent on its temperature history, from production, through distribution and storage, to consumption. The dependence of a product's shelf-life on temperature, a factor that is usually hard to control, but necessary because of potential pathogen growth as noted earlier, makes shelf-life determination and labeling of the product with a use by date a difficult task. Usually shelf-life determinations are based on the assumptions, either of a most probable average temperature for the food or a worst case temperature distribution. The first approach may result in the product becoming unacceptable or harmful before the stated end of shelf-life because of temperature abuse above the average assumed temperature. The conservative second approach can lead to the waste of a perfectly good product, since the package may, on the average, never be exposed to adverse conditions. Open dating of foods can also lead to suboptimum product circulation in stores, due to the different temperature history of each individual product, i.e., a date on the product is no guarantee of the actual quality of the product.

The above-mentioned problems could be solved if a way could be devised to monitor the product temperature history in order to estimate the remaining shelf-life. Time-Temperature Indicators (TTI) are such devices. Blixt and Tiru (1976) first suggested the use of these devices for refrigerated foods. Lindsay (1985) felt that they are absolutely essential for CA stored ocean fish because of the potential for pathogens. TTIs are devices that show any time-temperature dependence, which is easily measurable. The change should also be an irreversible such that it can be correlated to quality changes of the food product that undergoes the same temperature distribution. Such correlations of TTI performance for a variety of perishable and frozen foods, and for specific types of TTIs, exist (Wells *et al.* 1985; Tinker *et al.* 1985). Nevertheless, no general approach that would allow the correlation of the response of a certain TTI to the quality changes of a food product of known deterioration modes, especially nutrient loss, without actual testing, has been published. This makes the food manufacturer's decision on whether to use and how to use a TTI difficult. In addition, it is difficult to decide what is the most appropriate type of TTI for a specific product. This is probably one of the reasons for limited commercial application of TTIs as active packaging devices.

Loss of shelf-life in any food product is usually assessed by the measurement of one or more characteristic quality parameters. These parameters can be physical, chemical, microbiological or sensory indices. Change of a quality factor, A, can be usually expressed as (Labuza 1984)

$$\frac{-d[A]}{dt} = k[A]^n = k_A \exp(-E_A/RT)\ [A]^n \qquad (13)$$

where n is the reaction order and k the reaction rate constant. The rate constant is an exponential function of inverse absolute temperature, T, given by the Arrhenius expression, where k_A is a constant and E_A is the activation energy of the reaction (in Kcal/mol) that controls quality loss. The rate equation can be solved to a simple linear expression of time:

$$f(A) = kt \tag{14}$$

where f(A) is the quality function of the food. The form of the quality function can be zero, first or nth order. Typical activation energies for the most important reactions in foods range from 10–20 K calories/mole to 30–50 kcal/mole for microbial growth.

One can calculate the change of the quality function during a known variable temperature exposure from the integral equation:

$$f(A)_t = \int_0^t k\,dt = k_A \int_0^t \exp \frac{-E_A}{RT(t)}\,dt \tag{15}$$

T_{eff} can be defined as the effective constant temperature. Holding the product at this constant temperature for the same period of time, t, as in variable temperature distribution T(t) would result in the same quality change as exposure to the variable temperature. Thus, $f(A)_t$ can be expressed as:

$$f(A)_t = k_A \exp\,[-E_A/R\,T_{eff}]\,t \tag{16}$$

The same kinetic approach can be used to model the measurable change $F(\chi)w$, of the TTI. If a function $F(\chi)$ can be defined such that $f(\chi) = kt$, with k an Arrhenius function of T, then the effective temperature concept as described above can also be used for the TTI. The solution will take the form:

$$f(\chi)_t = \int_0^t k\,dt = k_A \int_0^t \exp\,[E_A/RT(t)]dt \tag{17}$$

or assuming again some constant T_{eff}, then:

$$f(\chi)_t = k_{A_I} \exp\,(-E_{A_I}/R\,T_{eff})\,t \tag{18}$$

where k_{A_I}, and E_{A_I} are the Arrhenius parameters of the indicator.

Based on the above kinetic equations, an application scheme can be developed that will allow for the calculation of the quality factor value, A, at any time t, from the measured change of the indicator, χ, at that time.

Once the parameters of the TTI and of the foods are known, one can calculate the amount of food quality or nutritional quality left (A_t) at any time using the proposed application scheme. However, there is a major assumption in this scheme which is that the effective temperature of the food is equal to the effective temperature of the TTI during any distribution. This is true only in the trivial case where the temperature T is constant throughout the cycle or in the case where the activation energies of the food and the TTI are equal, and they respond equally to temperature. It would be desirable to be able to calculate the T_{eff} of the food as a function of the T_{eff} of the TTI and the parameters of the TTI and the food, i.e.,

$$T_{eff_{food}} = (T_{eff_{TTI}}, E_{A_{food}}, E_{A_{TTI}}) \tag{19}$$

A mathematical relation can be derived only when the actual T distribution is known, which in most cases, is not true. An alternative approach is to find an empirical relation between the two T_{eff} using a computer simulation, for a large number of temperature distributions. Results in our lab show that if the absolute difference between the activation energies, $[E_{A_{food}} - E_{A_{TTI}}]$, is less than 10 Kcal/mol, then the two T_{eff} differ by less than 1°C. The error is smaller if the E_A of the TTI is larger than the E_A of food. An error of 1°C results in an error in the estimation of the f(A) value of less than 15% which, in some cases, may be acceptable. If one has to use a TTI with an E_A more than 10 kcal/mol different from the E_A of the food, a correlation of the two T_{eff} would be necessary.

Based on the above discussion, the proposed application scheme will take a different form. From the measured value of the TTI at time t, the value of $f(\chi)$ is calculated from which the T_{eff} of the indicator is derived. The T_{eff} of the indicator is then correlated to the T_{eff} of the food with some algorithm. With the T_{eff} of the food and the quality loss kinetic parameters known, f(A) is calculated and from it the value of the quality or nutritional factor A at time t can be found, thus allowing one to determine how much shelf-life is left or how many nutrients were lost. In all cases, one approach would be to use the loss of a certain sensitive vitamin like Vitamin C as the index for shelf-life loss; however, little data exist for nutritional loss levels that can be correlated to sensory perception. In addition, very little is known as to whether these devices could be used to predict shelf-life loss by microbial degradation. If a mathematical relation exists that can relate the T_{eff} of both the food and integrators, then from the TTI measured value, χ, at time t the value of $f(\chi)$ is calculated and T_{eff} of the indicator is derived. With the T_{eff} and the quality loss parameters of the food known, f(A) is calculated from the food quality equation, and from it the value

of the quality factor left, A_t, is thus found. Knowledge of this quality factor would give the extent of the quality deterioration or potential for microbial growth in or on the food. It also allows the calculation of the remaining shelf-life at any assumed average temperature for the rest of the distribution.

To apply the developed scheme, knowledge of the physical chemical characteristics of TTIs is required. Recent work by Taoukis and Labuza (1987) has characterized the three major types of TTIs available for the refrigerated, extended shelf-life food range. Early work by Kramer and Farquhar (1976) and Schoen and Myrne (1972) had shown that for two of these indicators (Allied Chemical Co. has just entered the market), their performance was poor. Problems were also recently found for their use in evaluation of milk quality (Mistry and Kosikowski 1983) but these authors did not understand the kinetics behind their use.

The 3M Monitor Mark is one TTI commercially available (3M, St. Paul, MN). It is based on a time-temperature dependent diffusion of a fatty acid ester containing a dye through a porous wick. χ is the distance of the advancing diffusing front from the origin.

The form of the $f(\chi)$ function can be theoretically predicted using diffusion mathematics. If the equation for diffusion in a semi-infinite medium is used (Crank 1956):

$$\frac{C^*}{C_o} = \text{erf}\left[\frac{\chi}{2\,[Dt]^{\frac{1}{2}}}\right] \tag{20}$$

where C_o is the concentration of dyed ester at the origin and C^* is the concentration at the visible border. this equation can be rearranged to give:

$$\chi = 2\,[D]^{\frac{1}{2}}\ \text{erf}^{-1}\left[\frac{C^*}{C_o}\right] t^{\frac{1}{2}} \tag{21}$$

$$\text{or } \chi^2 = kt \tag{22}$$

$$\text{thus } f(X) = \chi^2 \tag{23}$$

Figure 5 shows data for several temperatures (12 tags at each temperature) and plotted as χ^2 vs time, indicating the straight line. The 3M tags for the refrigerated range have a melting point (activation temperature) of -9°C and a suggested shelf-life of 30 to 40 days at 4°C, corresponding to a list code of 4P. The results of the studies are shown in Table 6. Other studies of Taoukis and Labuza (1987) have shown that there is no history effect for the 3M tags. A

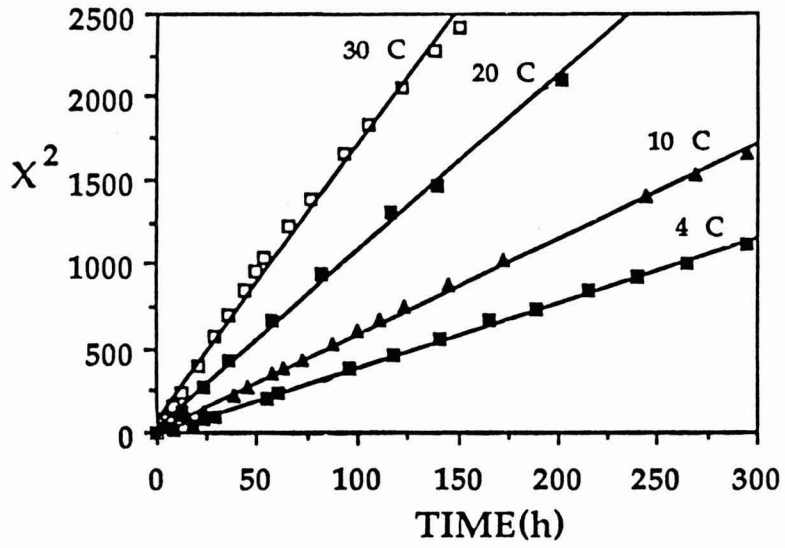

FIG. 5. EVALUATION OF RESPONSE OF THE 3M MONITOR MARK TTI AT 4 TEMPERATURES

history effect is when storage at a higher temperature changes the indicator such that when it is stored at the lower temperature, its rate of change is different than that predicted by the Arrhenius relationship. If one occurs, it makes use of the application scheme difficult, especially if the food also shows a history effect (Kamman and Labuza 1983).

The I-Point Time-Temperature Indicator (I-Point Biotechnology, Reston, VA) is based on a color change caused by a pH change due to a controlled enzymatic hydrolysis of a lipid substrate. Enzyme and substrate are stored in separate mini-pouches within the indicator. Upon activation the barrier between the two pouches is broken and two liquids are mixed. For activation a manual or a mechanical device is provided. Colors 1, 2, 3 on the indicator can be visually recognized and used as measures of change. Because of the very limited ability for developing kinetics from three points, an objective measurement of color with a suitable color reflectance instrument should be used. The a value of the L-a-b format shows "redness" to "greenness" and is the most appropriate because that is the color change the tag undergoes during aging. A normalized value of a color change can be used where χ = a/40 and varies from 0 to 1. Plotting χ vs time gives a Gaussian type line represented by the following equation:

$$\chi = 1\text{-}\exp\left[-(kt)^2\right] \tag{24}$$

TABLE 6.
INTRINSIC KINETIC PROPERTIES OF TIME TEMPERATURE INTEGRATIONS

Temperature °C	3M mm^2/hr	I-point hr^{-1}	Allied
4	3.66	0.0043	0.0029
10	5.61	0.0176	-
20	10.95	0.1243	0.0204
30	17.51	0.5900	0.0560
k_o	3.7×10^8	1.7×10^{24}	3.5×10^{12} hr^{-1}
E_A (Kcal/mole)	10.2	33.7	19.1

This can be rearranged to the firm $f(\chi) = kt$ where:

$$f(\chi) = \left[\ell n \left[\frac{1}{1-\chi} \right] \right]^{1/2} = kt \qquad (25)$$

The results for the I-point device are also shown in Table 6.

The Lifelines Inventory Freshness Monitor System (Allied Chemical Co., Morris Plains, New Jersey) is based on solid state polymerization of a thinly coated colorless acetylenic monomer to a highly colored polymer. The reflectance χ is electronically measured with an optical wand and stored in a handheld scanner. The manufacturers provide supporting hardware and software that allow the transfer of the data with stored information for the food products. The parameters of this type TTI have been explored before and are being used in the supporting software by Allied. If χ/χ_o is plotted versus time on a semilog graph, a linear relation results. thus $f(\chi) = \ell n\ (\chi/\chi_o) = kt$. Results from Lifeline Monitor, code 68, with a shelf-life of about 20 days are summarized in Table 6 along with the activation energies. From this data and given different potential distributions, one should be able to come up with an $f(\chi)$ value which would indicate the end of useful shelf-life for these foods and times at which significant nutritional value would be lost.

CONCLUSIONS

This review was designed to show the commercial potential for and the present status of extended shelf-life food technology especially for refrigerated foods.

Many new packaging technologies can be and are beginning to be applied to this area. They all fall into something that can be called "Active Packaging". If proper care is taken and the needed research done, the consumer will benefit from very high quality and safe foods. One key factor that this review points out, however, is the potential pathogen danger and, secondly, the lack of any information on nutritional losses. Much more data should be collected before these materials can play a major role in the consumer's diet by helping to create higher quality products.

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CHEMICAL AND SENSORY PROPERTIES OF WHOLEWHEAT PASTA PRODUCTS SUPPLEMENTED WITH WHEAT-DERIVED DRIED DISTILLERS GRAIN (DDG)

JOSEPH A. MAGA and KAREN E. VAN EVEREN

Department of Food Science and Human Nutrition
Colorado State University
Fort Collins, CO 80523 U.S.A.

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ABSTRACT

This study was conducted to evaluate the inclusion of wheat dried distillers grain (DDG) in pasta. Pastas were formulated incorporating 0, 25 and 50% DDG from wheat with wholewheat durum flour. Dried samples were analyzed for moisture, fat, protein, ash and fiber. Moisture content was found to significantly decrease as DDG level increased while fat, protein, fiber and ash values significantly increased with increasing DDG levels. Increasing DDG levels produced a darker product. Cooked weight yields decreased significantly with increasing levels of DDG. A trained sensory panel found the appearance, flavor and texture of cooked products containing 25% wheat DDG statistically comparable to the controls but sensory qualities with 50% DDG were significantly inferior to both the controls and 25% substitutions. This study demonstrated that levels of up to 25% wheat-derived DDG can be successfully incorporated into wholewheat pastas.

INTRODUCTION

DDG is a major byproduct resulting from the fermentation of cereals in the production and distillation of alcohol. The starch from cereals serves as the yeast energy source during the fermentation process. Due to the loss of starch, other components, such as protein and fiber, are concentrated thus making the dried residue a potential food for humans.

In most parts of the world the usual grain utilized for DDG is corn but other grains, including wheat, can be used (Wu *et al.* 1984). Previous studies have shown that wheat DDG differs in composition and properties from corn DDG (Satterlee 1976; Walker 1980; Wu *et al.* 1984).

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The incorporation of DDG has been evaluated in various cereal-based products, such as cookies (Tsen *et al.* 1982, 1983), breads (Morad *et al.* 1984; Walker 1980), and extruded foods (Wampler and Gould 1984). Also, dried brewers spent grain, which is the residue from beer brewing, has been incorporated into numerous foods such as cookies (Kissell and Prentice 1979; Prentice *et al.* 1978), muffins (Prentice 1978), and breads (Finley and Hanamoto 1980; Dreese and Hoseney 1982).

During the past few years the American public has become more aware of nutrient composition and especially the significance of fiber in the diet. Thus, the consumption of whole wheat-based foods has increased. Among the products enjoying new popularity are wholewheat pasta products.

The utilization of DDG in pasta products apparently has not been reported in the literature. Therefore, the major objective of this study was to determine if wheat-based DDG could be successfully incorporated into pasta products.

MATERIALS AND METHODS

Wheat DDG

A commercial sample of food grade wheat DDG was obtained from Fibertein Corp., Wheat Ridge, CO 80033. Data supplied with the sample indicated that it was derived from whole, hard, red, spring wheat that had been fermented to produce ethanol. The byproduct had a reported composition of 7.8% moisture, 3.4% fat, 35.3% protein, 17.3% crude fiber, 7.3% ash, and 28.9% carbohydrate.

Pasta Preparation

Wholewheat round and flat pastas were made from the standard formulation shown in Table 1 utilizing a Pasta Matic Model 700 pasta machine (Simac Corp., New York, NY 10022). No salt was added so that the total sensory influence of DDG addition could be evaluated. In addition to the wholewheat control, 25 and 50% of the commercial wholewheat durum flour was substituted (wt/wt) with wheat DDG. These levels of substitution were arbitrarily selected, and it was realized that these high levels could result in products having unique functional and sensory properties. Where wholewheat flour/DDG blends were used, the two ingredients were dry blended in the pasta machine for 10 min before the required amount of tap water was slowly added until a dough formed. It can be seen in Table 1 that DDG influenced water absorption because as the DDG level increased, more water was required to produce a machineable dough. After completion of the water addition, all products were mixed seven min before being extruded through the unit equipped with the appropriate die required to produce either strands of round or flat pasta. After extrusion samples were permitted to air dry on cotton towels at room temperature for 24 h before

TABLE 1.
PASTA FORMULATIONS UTILIZED

	WEIGHT IN GRAMS		
Ingredient	Control	25% DDG	50% DDG
Wholewheat Durum Semolina	454	341	227
Wheat DDG	---	114	227
Water	163	177	214

evaluation. Batches of the three different formulations were prepared on three consecutive days and each variable/product analyzed separately.

Compositional Analyses

The following analyses were performed on the dried products: Moisture by AACC method 44-19 (1982); fat by AOCS method Aa 4-38 (1971) with petroleum ether as the extraction solvent; protein by the Kjeldhal method (AACC method 46-12, 1982); fiber by AOAC method 7.050-7.054 (1975); and ash by AACC method 08-01 (1982). Except for moisture all values have been adjusted to a 14% moisture base.

Color Measurements

Color of the dried pastas was measured utilizing a Model D25D2 Hunter Lab Color Difference Meter (Hunter Assoc. Lab., Reston, VA 22090). L (total lightness/darkness), a (green/red component), and b (blue/yellow portion) values were obtained for all samples after standardizing the unit with a white tile having L, a and b values of 94.65, -0.6 and 0.1, respectively.

Cooked Weights

Preliminary subjective analysis indicated that a cooking time of 4 min was required for the flat pasta while 5 min was needed to properly cook the round pasta. No differences in cooking time were required for the formulation variables. Thirty grams of each dried product were added to 500 mL of boiling tap water and the mixture cooked with high heat for the appropriate times. After the allotted cooking time, each product was placed in a strainer and permitted to drain for 5 min. The resulting product was weighed to obtain cooked weight values. Based on dry and cooked weights, the percent increase in weight was calculated. Analyses were performed on each product/variable made on three successive days.

Sensory Evaluation

A trained 24-member panel consisting of 16 female and 8 male college-age students was separately presented freshly cooked 50g samples of either pasta with no added salt, butter or sauce. The samples were coded with three digit numbers and were randomly presented. A total of six samples representing the three flat and three round formulations were separately evaluated for cooked appearance, flavor and texture using a standard seven-point hedonic scale ranging from like very much to dislike very much.

Statistical Evaluation

Analysis of variance was used to test for significant differences ($P = 0.05$) between the controls and the treatment means of the variables measured.

RESULTS AND DISCUSSION

Compositional Differences

As can be seen in Table 2, increasing the DDG in the formulation resulted in dry products that had decreased moisture contents with the moisture level in pasta containing 50% DDG being significantly lower than that for the 100% wholewheat control ($p = .05$). This is quite interesting in light of the fact that as the DDG portion was increased, more moisture was required to process the pasta. However, immediately after extrusion and during the drying process this excess moisture apparently was lost to the atmosphere.

Since DDG has approximately three times the lipid content of wholewheat flour, it is quite apparent from Table 2 that adding 25 or 50% DDG to the formulation resulted in pasta that had significantly higher fat levels than the

TABLE 2.
COMPOSITIONAL DIFFERENCES AMONG UNCOOKED PASTAS CONTAINING WHEAT DDG

	PASTA		
%	Control	25% DDG	50% DDG
Moisture	5.95	5.54	5.03
Lipid	1.24	5.40	9.47
Protein (N x 5.75)	14.3	18.1	23.0
Crude Fiber	0.9	3.5	6.2
Ash	1.9	4.9	5.1

control ($p = .05$). Fat amounts increased from 1.2 to 5.4 and 9.4%, respectively, in the control, 25, and 50% DDG pastas. These increased fat levels would add to the nutrient density of these supplemented products.

Protein content (Table 2) of the wholewheat pasta control was 14.3%, and as expected, the addition of DDG significantly increased pasta protein content ($p = .05$). The protein content with 25% DDG substitution increased to 18.1% while 50% DDG pasta had 23.0% protein. These protein levels would place these pastas into the same protein range as meats and, thus, would have important applications in vegetarian diets.

As shown in Table 2, there was a linear and significant difference ($p = .05$) in fiber content as DDG substitution was increased. The 100% wholewheat pasta control had 0.9% crude fiber whereas with 25% DDG, the level increased to 3.5%, and with 50% DDG the level went to 6.2% fiber. Thus DDG-containing pasta would be a good source of crude fiber.

Both the 25 and 50% DDG substituted pastas had significantly higher levels ($p = .05$) of ash when compared to the wholewheat control (Table 2). Ash went from approximately 2% in the control to 5% range in the substituted products. From a nutritional standpoint this would also be desirable.

Color Properties

Product appearance is the first and thus foremost factor governing food acceptability. In the case of DDG substituted pasta it is apparent from the L values (Table 3) that substitution of wholewheat durum flour with DDG resulted in darker colored products. The increasing positive a and b values are indicative of the higher levels of pigmentation associated with DDG.

Cooked Weights

Preliminary subjective evaluation of the cooked pastas demonstrated that the addition of DDG did not adversely influence the visual properties of the cooked products because all products had a smooth appearance after cooking. Also, the

TABLE 3.
HUNTER LAB COLOR DIFFERENCE VALUES (L, a, b) AS INFLUENCED BY DDG ADDITIONS IN PASTA

Pasta	L	a	b
100% Wholewheat Durum Semolina	71.5	2.9	10.0
25% DDG	64.1	3.3	10.5
50% DDG	55.4	4.9	11.3

cooking water was clear after cooking indicating that little, if any, product disintegration occurred.

The addition of DDG did significantly influence the final product cooked weights and thus yield (Table 4). In the case of the flat pasta, which had a larger surface area than the round pasta, the addition of 50% DDG resulted in a significant decrease in cooked weight percent gain (220% for the control versus 147% for 50% DDG). However, there was no significant difference between the control and the 25% DDG addition. Thus the addition of high levels of DDG apparently hindered water absorption into the product during cooking. This has both negative and positive practical consequences. One could argue that the yield for flat pasta containing 50% DDG is significantly lower than the control, however, one could point out that the 50% DDG substituted flat pasta had a higher nutrient density because it contained less water.

In the case of round pasta, which had a small surface area, water uptake during cooking in the control was not as high as the flat pasta control but with both 25 and 50% DDG substitution there was a significant decrease ($p = .05$) in weight percent yield.

Sensory Properties

The hedonic means for cooked appearance, flavor and texture for both types of pasta are summarized in Table 5. It can be seen that in all instances the flat pasta scored slightly but not significantly higher than round pasta, probably due to the greater water uptake associated with the flat pasta.

With 25% DDG addition all sensory properties were statistically similar to the controls, in the "like a little" to "like a lot" range, except for round pasta texture which was in the "neither like nor dislike" to "like a little" range. However, when 50% DDG products were evaluated, their sensory properties were significantly inferior to those of the controls, although only round pasta flavor was below the "neither like nor dislike" category. It should be noted that although the objective color data summarized in Table 3 clearly demonstrated

TABLE 4.
PERCENT WEIGHT INCREASE IN COOKED PASTA CONTAINING VARIOUS LEVELS OF DDG

	PERCENT WEIGHT INCREASE	
Product	Noodles	Spaghetti
Wholewheat Durum Semolina	220	180
25% DDG	217	127
50% DDG	147	133

TABLE 5.
SENSORY MEAN HEDONIC SCORES FOR COOKED PASTAS

	Appearance		Flavor		Texture	
Formulation	Noodles	Spaghetti	Noodles	Spaghetti	Noodles	Spaghetti
Control	5.8	5.6	5.5	5.1	5.3	5.0
25% DDG	5.5	5.1	5.3	5.0	5.0	4.7
50% DDG	4.2	4.0	4.0	3.7	4.3	4.2

7: Like very much; 6: Like a lot; 5: Like a little; 4: Neither like nor dislike; 3: Dislike a little; 2: Dislike a lot; 1: Dislike very much

significant color differences among products, the panel did not consider pasta containing 25% DDG to be significantly different than controls.

CONCLUSIONS

It is readily apparent from this study that high levels of wheat-derived DDG can be successfully incorporated into wholewheat pasta products. The resulting products, although obviously different in color, had superior fat, protein, fiber and ash levels as compared to wholewheat controls. However, high levels of DDG significantly reduced cooked yields because of lower levels of water absorption during cooking. Wholewheat pasta products can be made with 25% DDG without significantly changing the sensory properties of appearance, flavor and texture.

In the case of products like bread, the practical addition of DDG has been found to be limited to a maximum of 10–15% before properties such as volume make the product unacceptable (Morad *et al.* 1984; Tsen *et al.* 1983). However, in the case of wholewheat pasta products, major differences in most functional properties were not apparent even at the 25% substitution level. Therefore, it would appear that wholewheat pasta products would be a prime cereal-based food that can effectively undergo DDG substitution to produce products of higher nutrient content.

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EFFECT OF COMBINATION METHODS ON INSECT DISINFESTATION AND QUALITY OF DRY FRUITS

MOHAMMAD WAHID, ABDUS SATTAR, MOHAMMAD JAN and ISMAIL KHAN

Nuclear Institute for Food and Agriculture,
Tarnab, Peshawar
Pakistan

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ABSTRACT

Dried apricots, dates, figs and raisins were irradiated with 0.25 kGy after packaging in clear and colored polyethylene (0.04 mm) and subsequently stored for one year at 10°, 15°, 20°C, and room temperatures (10–36°C). Influence of this treatment on insect infestation, and changes in the color and ascorbic acid was studied. The results revealed that dates and raisins were infested by Tribolium castaneum *while apricots and figs by* Corcyra cephalonica *and* Cadra cautella. *Low dose radiation treatment (0.25 kGy) alone was not effective in controlling insect infestation. However, radiation treatment in combination with low temperatures (10–20°C) checked infestation for one year and resulted in a better product than any other treatment tested. Storage of dry fruits in colored polyethylene protected their color and ascorbic acid more than clear polyethylene during one year storage.*

INTRODUCTION

Dry fruits played a prominent role in the feeding of man and animals in many civilizations and in different parts of the world. They are a major source of income and foreign exchange in several countries and are utilized throughout the year (ITC, 1973). In Pakistan more than 6,800,000 tons of fresh fruits, are produced over an area of 190,000 hectares per year but being a perishable commodity considerable quantity of the total produce is wasted during peak production season and subsequent storage. A major portion of these fresh fruits in the northern areas of the country is sun-dried, which is the only method available there for fruit preservation (Rehman 1979).

Spoilage of dry fruits as a result of insect infestation, microbial growth, color deterioration and chemical changes, is a serious problem especially under hot-humid climate like prevailing in Pakistan (NAS 1978). Gamma irradiation has

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been tried by some workers for insect disinfestation of dry fruits (Brower and Tilton 1970; Guerrieri 1975; Auda 1980). However, the influence of combination methods on insect control as well as biochemical and sensory quality of the dry fruit has been studied less. The present studies were undertaken to investigate the effect of irradiation, temperature and packaging materials on insect disinfestation and quality of dry fruits.

MATERIAL AND METHODS

Dry apricots, dates, figs and raisins were purchased from the dry fruits market of Peshawar. The moisture content of the dry fruits ranged from 14.4 to 18.5% (wet basis). They were sorted for uniform shape, size and appearance. For insect disinfestation studies, the samples were irradiated, after packaging in clear polyethylene bags (0.04 mm) at a dose of 0.25 kGy (1 kGy = 100 krad) in a Cobalt-60 gamma irradiator having a capacity of 8720.2 curies, dose rate of 8.95 kGy h^{-1}, and a maximum/minimum ratio of 2.5. The treated and untreated samples were stored for one year at 10°, 15°, 20°C and room temperature (10–36°C). The influence of different packaging materials such as amber glass bottles, and clear, silver and black colored polyethylene on selected quality characteristics of irradiated and unirradiated dry fruits was investigated.

The fruits were examined for the extent and nature of insect infestation according to Blank (1978), while the insect damage was calculated following the method of Cogburn (1977). Chemical analyses for ascorbic acid and total color, were carried out after 3, 6, 9, and 12 months of storage according to AOAC (1984) and Papodopoulou (1963) procedures, respectively. For total color extraction, 5 g of dried fruits were mixed with an equal volume of ethanol and 10% trichloroacetic acid solution, heated at a constant temperature of 45°C, filtered and the percent transmittance measured at 420 nm using Shimadzu Spectrophotometer Model UV-160.

RESULTS AND DISCUSSION

The effect of irradiation and subsequent storage at different temperatures on insect infestation of dry fruits, is shown in Fig. 1. It was found that the infestation rate was higher in apricots and figs than dates and raisins. Initially all the samples were apparently free of any insect infestation; however, insect attack increased consistently especially during room temperature storage. The fruits used in these experiments were solar dried by private individuals rather than dried at controlled temperature and humidity. The damage was primarily caused by insects developed from eggs present in the dry fruits. There was no insect infestation in the samples kept at 10°C and 15°C throughout the storage period of 12 months. A slight infestation was observed at 20°C whereas almost 100% infestation occurred

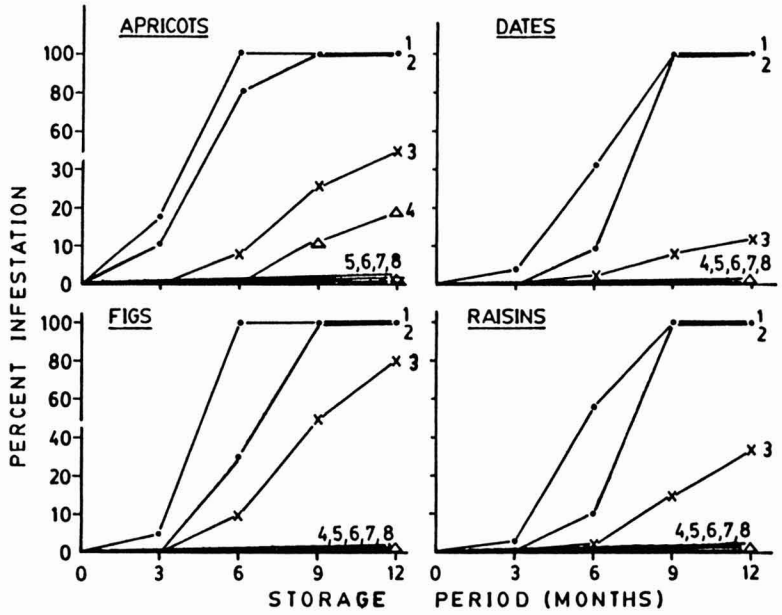

FIG. 1. EFFECT OF IRRADIATION AND STORAGE TEMPERATURES ON INSECT DISINFESTATION OF DRIED FRUITS

1. Unirrad. room temp. 2. Irrad. room temp.,
3. Unirrad. 20°C, 4. Irrad. 20° C.,
5. Unirrad. 15°C, 6. Irrad. 15°C.,
7. Unirrad. 10°C, 8. Irrad. 10°C.

in all the dry fruits on 9 months storage at room temperatures. It was observed that *Tribolium castaneum* (red flour beetle) was the dominant insect affecting both the dates and raisins. The apricots were infested by *Corcyra cephalenica* and figs by *Cadra cautella*. Radiation treatment of 0.25 kGy alone was not effective in controlling insect infestation in dry fruits. However, irradiation (0.25 kGy) and subsequent storage at lower temperatures (10–20°C) completely checked the development of all types of insects during the entire storage. Because of economic consideration, irradiation at low dose of 0.25 kGy and storage at 20°C is suggested for avoiding insect infestation of these dry fruits. Conflicting results have been reported in the literature for the control of dry fruit insects. Papodopoulou (1963) recommended a dose of 1–2 kGy for complete destruction of *Plodia, Cadra* and *Oryzaephilus* species during their various stages of development in dried figs. Beczner and Farkas (1974) suggested that a radiation dose of 0.70 kGy was necessary for the control of Indian meal-moth. However, Brower and Tilton (1970 and 1971) recommended a dose of 0.40 kGy for insect control in dry fruits and nuts.

The effect of different packaging materials on the color intensity of the dry fruits was investigated at every 3 months interval for a period of 12 months and the results are shown in Table 1. The samples had an attractive appearance at the start of the experiment but the color changed from light to dark shades during storage. The data of the extracted color also revealed that discoloration in the samples increased during storage. The sample-extracts exhibited higher transmittance in the beginning which decreased progressively during storage. It was observed that packaging of dry fruits in amber bottles, black/silver polyethylene was better in protecting the color of the dry fruits. Irradiation of samples did not show any significant effect on discoloration of samples during the entire storage period of 12 months. Saravacos and Macris (1963) reported that gamma irradiation of fruits with doses up to 5.0 kGy caused no significant changes in color or in total sugars. Papodopoulou (1963) observed that irradiation with 1–2kGy doses of dry figs had no deleterious effect on the nutritive value including color of the friuts. Schegoleva (1963) found that a dose of 3 kGy had no appreciable deleterious effects on the chemical composition of many dry fruits. Overall acceptability based on the scores for color, texture and taste, was also determined which decreased with storage and the decrease was higher at room temperature than low temperature storage. The samples kept at 10–20°C were found acceptable even after one year storage whereas those stored at room temperature were almost unacceptable after 3–4 months. Radiation treatment had no adverse effect on the appearance or taste of any sample. Farkas *et al.* (1974) also did not find any significant effect of even irradiation dose of 5.4 kGy on the flavor of dates.

Initially the ascorbic acid values were 12.6, 8.4, 13.4 and 2.9 mg/100 g in apricots, dates, figs and raisins, respectively. During storage of one year, a significant loss of this vitamin occurred in all the samples (Table 2). Irradiation dose of 1.0 kGy contributed to the significant loss of ascorbic acid in dry fruits. Irradiation treatments are reported to bring about some losses in ascorbic acid and other vitamins depending upon the type of fruit, condition of irradiation e.g., temperature, moisture level and presence or absence of oxygen level (Josephson *et al.* 1975). The results of the present work indicated that packaging of dry fruits in colored packages was better in protecting the quality of dry fruits. As a result of these experiments it was concluded that irradiation treatment at 0.25 kGy and subsequent storage at 20°C kept the dry fruits in acceptable form for 12 months. Storage of these dry fruits in colored polyethylenes was better than in clear polyethylene.

TABLE 1. EFFECT OF PACKAGING MATERIALS ON THE COLOR (% TRANSMITTANCE) OF DRY FRUITS

Packaging materials	Apricots months				Dates months				Figs months				Raisins months				
	3	6	9	12	3	6	9	12	3	6	9	12	3	6	9	12	C.V.
Unpackaged & unirradiated	6.3	3.3	2.4	1.7	11.0	2.3	1.8	1.0	6.0	2.0	1.7	1.0	21.7	5.7	4.1	3.2	111.32
In package(1.0 kGy)	5.8	3.2	2.5	1.6	12.2	2.5	1.7	1.0	6.0	2.0	1.8	1.1	24.4	5.5	4.0	3.4	119.95
Polyethylene	18.2	6.0	4.1	3.0	17.5	4.8	2.4	1.7	10.5	2.4	1.9	1.3	26.8	5.9	4.4	3.7	103.31
Paper bags	6.5	3.8	2.0	1.8	10.2	2.9	2.0	1.1	6.7	2.1	1.8	1.2	27.0	5.6	4.7	3.3	122.51
Silver color polyethylene	21.5	14.8	12.0	10.2	20.0	15.0	11.5	9.9	12.0	3.0	2.7	2.4	35.	16.5	13.3	10.1	61.37
Black color polyethylene	28.8	15.3	12.7	10.7	19.0	15.9	12.7	10.2	13.5	4.8	4.0	3.0	38.4	17.3	14.2	10.4	61.98
Amber color bottles	26.2	15.0	12.0	11.1	20.15	15.7	12.4	10.3	14.6	4.5	4.0	3.0	30.0	21.4	14.8	12.2	53.54
C.V.	53.8	60.9	69.1	73.0	27.6171.4		78.1	85.3	33.6	39.2	40.2	46.7	48.2	59.1	57.7	58.4	29.23

Initial transmittance values: apricot 34%, dates 22%, figs 16% and raisins 40%.
Storage = room temperature, 10–36°C.
C.V. = Coefficient of variability (Sample standard deviation expressed as a percentage of sample mean).

TABLE 2. EFFECT OF PACKAGING MATERIALS ON ASCORBIC ACID (mg/100 g) OF DRY FRUITS

Packaging material	Apricots months				Dates months				Figs months				Raisins months				C.V.
	3	6	9	12	3	6	9	12	3	6	9	12	3	6	9	12	
Control	9.0	7.2	5.0	3.5	6.6	3.0	2.6	1.2	12.3	10.3	8.7	6.1	1.2	1.0	0.8	0.3	76.696
Irradiated (1.0 kGy)	7.0	3.7	3.6	3.5	3.2	3.7	3.5	1.3	10.2	6.5	6.0	5.3	0.6	0.2	0.2	0.2	77.43
Polyethylene	10.2	7.5	5.6	4.1	6.7	3.5	3.0	1.3	11.2	10.5	8.9	5.7	1.2	1.2	0.9	0.4	72.47
Paper bags	10.2	7.0	5.6	4.3	5.9	3.1	3.1	1.4	10.8	10.3	8.8	5.8	1.3	1.2	0.9	0.3	72.19
Silver color polyethylene	11.3	7.9	5.8	4.5	5.8	3.4	3.0	1.2	11.6	10.7	8.9	5.9	2.1	1.2	1.0	0.3	72.42
Black color polyethylene	11.9	8.4	5.7	4.8	5.3	4.5	3.4	2.1	12.8	11.2	8.9	6.2	2.6	2.0	1.6	0.6	66.81
Amber color bottles	9.2	8.1	5.7	4.8	6.3	4.0	3.3	2.0	12.8	11.2	9.2	6.4	2.6	2.0	1.7	0.5	64.74
C.V.	16.3	22.5	14.9	4.3	8.7	15.7	9.8	26.3	7.0	3.7	9.3	4.6	3.2	2.6	4.3	4.8	75.3

Initial ascorbic acid values: apricot 12.6, dates 8.4, figs 13.4 and raisins 2.9 mg/100g.
Storage = room temperature, 10–36°C.
C.V. = Coefficient of variability (Sample standard deviation expressed as a percentage of sample mean).

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Page one should contain: the title which should be concise and informative; the complete name(s) of the author(s); affiliation of the author(s); a running title of 40 characters or less; and the name and mail address to whom the correspondence should be sent.

Page two should contain an abstract of not more than 150 words. This abstract should be intelligible by itself.

The main text should begin on page three and will ordinarily have the following arrangement:

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Materials and Methods: Enough information should be provided to allow other investigators to repeat the work. Avoid repeating the details of procedures which have already been published elsewhere.

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In some cases it might be desirable to combine results and discussion sections.

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HASSON, E.P. and LATIES, G.G. 1976. Separation and characterization of potato lipid acylhydrolases. Plant Physiol. 57, 142–147.

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Short notes will be published where the information is deemed sufficiently important to warrant rapid publication. The format for short papers may be similar to that for regular papers but more concisely written. Short notes may be of a less general nature and written principally for specialists in the particular area with which the manuscript is dealing. Manuscripts which do not meet the requirement of importance and necessity for rapid publication will, after notification of the author(s), be treated as regular papers. Regular papers may be very short.

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