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EFFECT OF STORAGE TEMPERATURE AND PACKAGING
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FROZEN CARROTS

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DARIO MARTINO

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Bruce Harte
Major professor

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EFFECT OF STORAGE TEMPERATURE AND PACKAGING SYSTEMS ON THE QUALITY OF PACKAGED FROZEN CARROTS

by

Dario Martino

A THESIS

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ABSTRACT

EFFECT OF STORAGE TEMPERATURE AND PACKAGING SYSTEMS ON THE QUALITY OF PACKAGED, FROZEN CARROTS

By

Dario Martino

Frozen packaged vegetables may be exposed to fluctuating environmental conditions during storage. This may result in an increase in amount of frost in the headspace of a packaged frozen vegetable, and thus consumer avoidance, and problems with weight compliance may occur.

The main objective of this work was to understand the origin of frost ice and test the effect of frozen storage and packaging systems on product quality. A secondary objective was to develop a mathematical relationship to predict frost ice formation.

Baby cut carrots were blanched, frozen and stored at –20 °C in nylon/PE and LDPE bags and vacuum and atmospheric filling processes, as well as perforated and non-perforated bags were used. Samples were drawn at monthly intervals for 6 months and evaluated for product weight loss, product color and product appearance. Half of the carrots were transferred to a retail refrigeration unit one week prior to evaluation.

Frost ice was found to increase with storage time and selection of material. Frost decreased when the permeability of the package material was altered using perforations. The less frost ice, the more positively the carrots were perceived by a panel.

The frost ice data fit well (R^2>0.70) as a quality parameter using a first order kinetic-like expression. Using data from different packaging systems and storage temperatures, model parameters were calculated to predict frost formation.

To my dear wife and daughter.

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INTRODUCTION

Industrial freezing as a means of food preservation has been used in the United States for several decades. The original quality of the food product is not improved by freezing; instead, temperature reduction results in the retardation of the processes that reduce product quality.

Moisture migration from the product is the main phenomenon which occurs in frozen foods, and thus has major effects on the chemical and biochemical properties of frozen foods (Pham and Mawson, 1997). It manifests itself in several ways: moisture loss by sublimation, moisture absorption, and redistribution in foods or food components, frost ice formation, recrystallization, and drip loss during thawing. In all these cases, and especially when frost ice is formed, the appearance of the product is negatively affected. Consumers may avoid buying frozen products when they see frost ice. Further, since in-package ice is discarded in net weight control, serious problems with label compliance can occur.

Packaging is one of the most important factors that can effect the final quality of the frozen product. Retail packaging systems used by the frozen food industry can be classified into three categories depending on the product end-use: a) atmospheric filling into simple bags and skin-packaging for loose uncooked product or cuts; b) modified atmosphere packaging (MAP) and vacuum packaging, for precooked products, and c) ovenable and dual-ovenable packaging for prepared foods. Frozen, minimally processed vegetables, are typically packaged in atmosphere, in bags and are often found to develop frost ice.

It is widely accepted that quality deterioration in foods during frozen storage is temperature dependent. Fluctuations of temperature are believed to negatively affect the product. During post-freezing, storage and handling, two factors: temperature fluctuation and packaging, converge. Jul (1984) stated, "The importance of temperature fluctuations and handling abuses in the retail stores are clearly an area in need of further clarifications". There exists limited data regarding the effect of retail conditions on quality of frozen, packaged vegetable products. Temperature fluctuations during retail are believed to represent an important issue affecting the quality of the product since they are often *large* and rather *frequent*. In turn, packaging systems can influence these quality changes and can help reduce their negative effects.

Semi-empirical kinetic models are often developed to describe the change in quality of frozen foods. Bhattacharya et al. (1988), Lanari and Zaritzky (1991), Chen et al. (1989), and Lanari et al. (1993) used kinetic models to explain color changes. Drip and cooking losses were modeled using kinetic relationships (Bhattacharya et al., 1988), and water holding capacity and lipid autooxidation (Chen et al., 1989). Since the rate of quality loss during the post-freezing phase (i.e.: distribution, storage, retail cabinet display, in-home freezer storage) is temperature dependent, methods are often developed that can predict or determine the temperature distribution within a product. Among them, numerical models are regarded as the most accurate, and yet most difficult to develop. Heat transfer analysis has been approached in several different ways. Sastry and Kilara (1983) modeled the thermal response of stacks of frozen peas exposed to energy-conservation practices involving di-thermal storage cycles. Zuritz and Singh (1985) simulated the effect of storage temperature changes through a simulated frozen-food distribution channel using a finite element model. Mittal and Parkin (1985) studied the response of frozen foods in insulated containers to a step change in the ambient temperature. Moureh and Derens (2000) presented a finite-volume heat transfer model which predicted temperature within a pallet as a function of time, storage conditions, product initial temperature, palletization pattern and thermal characteristics of the products and packaging.

Though numerical models have been widely used, the most fruitful work is often in finding simple, accurate equations for food products that can be used with relatively little effort. In addition, of the models cited, only few take into account the effect of packaging. Some of the models cited include some quality parameters, though none included frost ice formation as a quality parameter.

In this study, frost ice development, product color change and general appearance of frozen baby cut carrots (a widely available product) was investigated from a packaging perspective.

The importance of this work is in exploring the effects of different packaging systems on quality attributes of a frozen product during the post-freezing phase.

Specific objectives include:

a) To describe the physical phenomena that occurs within the headspace of the packaged frozen vegetable during post-freezing conditions.

b) To study the effects of four packaging systems on product quality. Nylon/PE multilayer bags using atmospheric and vacuum packaging and perforated and non-perforated LDPE bags; two post-freezing conditions: frozen storage and frozen storage and retail temperatures; and time, a six month storage period, all were investigated as to the quality of the frozen packaged baby cut carrots in terms of product color, general appearance and frost ice formation.

c) To develop mathematical relationships using curve-fitting experimental data, that can be used to evaluate the potential quality damage of a food product exposed to similar post-freezing conditions.

CHAPTER 1

LITERATURE REVIEW

1. Freezing vegetables

1.1. Pre-freezing processes

Vegetables are prepared for freezing by cleaning and washing to remove field dirt and to reduce microbial contamination. Grading, material handling, peeling and inspecting are followed by blanching. The blanching process consists of heating the vegetable for a sufficient time to inactivate most of the enzymes responsible for off-flavors and undesired product color change during storage. Oftentimes, vegetables are heated at 190 °F (88 °C) for several minutes or a half-minute at 212 °F (100 °C)(Desrosier and Tressler, 1977). Presence of catalase and peroxidase in blanched product has been used as common indicators even though they have not been specifically indicted as causative agents of frozen vegetable deterioration. Blanching times take into account the type and size of the vegetables. The time recommended for vegetables also depends on the final use of the frozen product. For example, "boil-in-the-bag" vegetables are essentially fully cooked before freezing since little or no additional cooking takes place during the heating process prior to use. Vegetables are blanched either in steam or hot water. Hot water at 200 to 205 °F (93 to 96 °C) is mainly used for large vegetables (i.e.: artichokes) while steam is used for smaller ones. Carrots are usually blanched using steam; blanch times vary from 2 to 8 min. depending on size, maturity and texture. For example, vegetables with 0.375 in diameter often require 2 to 3 minutes in hot water (Desrosier and Tressler, 1977).

1.2. Freezing systems – Freezing rate and quality

A convenient classification of food freezing systems can be made according to the rate of freezing or the rate of movement of the ice front from the product surface to the thermal center of the food. The freezing rate depends on the thermal properties of the food and the ratio of the freezing medium to the food product surface (medium heat transfer coefficient). Effectively, the freezing rate of a small product (large surface area to volume ratio) is controlled by external freezing conditions, whereas that of a large product (low surface area to volume ratio) is controlled more by the internal characteristics of the product (George, 1997). Table 1 lists heat transfer coefficients of common freezing processes.

The faster the formation of ice (faster freezing rate, higher heat transfer coefficient), the smaller and more numerous are the ice crystals. An operational definition of freezing rate in cellular systems is that fast freezing produces internal freezing in cells and slow freezing produces cellular dehydration and only extracellular ice. When there is a low rate of heat removal with either low or high cell water permeability, the rate of change of the unfrozen matrix is slow, and water can transfer from the interior fast enough to minimize internal supercooling. Under these conditions the cell dehydrates, with the loss water becoming external ice crystals. It should be noted that internal cell freezing is more likely to happen in animal cells than in vegetable cells (Haard, 1997).

Table 1. Typical freezing processes and heat transfer mediums, and their coefficients *

Type of Freezer	Conditions	H (W/m^2 K)
Cold store	Still air	5-10
Air-blast freezer	Air velocity: 2.5 m/s	17-20
	Air velocity: 5 m/s	26-30
Tunnel freezer	Counterflow of air and product	15-60
Contact freezer	Contact to cold plate	50-120
Fluidized-bed freezer	Suspending airstream	80-120
Cryogenic freezer (liquid N2)	Gas zone (prefreezing)	40-60
	Spray zone (freezing)	100-140
Liquid immersion	Circulating brine	60-90
	Specialized refrigerant	500-600
Scraped-surface heat exchanger (i.e. ice cream freezer)	Contact to cold surface and mixing of food product	1500-2000

* adapted from George (1997).

Although the relationship between freezing rates and product quality is not totally clear for many food products, the cumulative effect is very important for vegetables and fruits. Considerably better results (i.e. in texture) were reported when freezing fruits very quickly rather than by slow freezing (Jul, 1984).

It is inevitable that a portion of water in a product, will evaporate during air blast freezing (IIR, 1986). The amount of evaporated water will be smaller at a higher freezing rate, provided all other factors are constant. When the product is enclosed in a water vapor proof package before freezing, the proportion of moisture which escapes from the package will be negligible. However, frost may be deposited on the inside surface of the package by the same amount as moisture evaporating from the product. In particular, this is found when there is an air gap in the order of millimeters between the surface of the product and the internal surface of the package (IIR, 1986). Faster freezing methods are more effective in reducing this frost formation by reducing the surface temperature of the product quickly to a value where the rate of moisture evaporation or sublimation is low.

Since commercial operations strive to reduce the time spent on freezing, these operations tend to use faster methods. Industrially, diced, sliced and baby cut carrots are individually quick frozen (IQF) in fluidized freezing beds (Desrosier and Tressler, 1977).

1.3. Crystal formation

Crystal formation results from a change of state of the water in the food. Temperature is the fundamental descriptor of the state of any system. At high temperatures, molecular motions tend to be more rapid, and collision frequencies for the same molecular densities are greater. As temperature falls, the molecular motions decrease (Desrosier and Tressler, 1977).

For the temperature to decrease, heat may have to be removed from a product. Transformation from liquid water to crystalline ice is a typical first-order phase transition. In foods, the presence of a soluble solute alters the phase relationships between ice and water due to a vapor pressure reduction effect (colligative effect), which lowers the freezing point of the water.

2. Frozen Storage and Retail

The temperature history of the frozen product after freezing is the most important factor determining product quality. Zaritzky et al. (1982), cited two types of temperature changes that frozen product may be exposed to during post-freezing: 1) fluctuations in the temperature of the storage chamber; and 2) sudden increases in temperature during loading and unloading of the product during transportation and distribution. Temperature fluctuations such as those previously cited are unlikely to pose any problem as long as they are sporadic and small, and an "effective average" is maintained under an appropriate temperature. However, temperature fluctuations during the retail sales period represent an important factor affecting the quality of the product since they are often large and rather frequent (Jul, 1984).

Gortner et al. (1948) presented one of the early studies dealing with fluctuation in the storage temperature. They showed that an increase in the rate of desiccation at the surface of the product occurs, especially when exposed to temperatures above zero °F.

Quality changes and moisture loss from the product (or in-package product desiccation) during frozen storage are more serious than what occurs in freezing because of the storage duration (Bevilacqua and Zaritzky, 1982; IIR, 1986). The combined effect of temperature fluctuation (time-temperature tolerance of product), product type and initial quality, process and packaging system determine the final quality of the frozen product, and should be addressed when developing mathematical models to predict quality changes.

The effect of these variables on common product quality parameters and product desiccation (in-package desiccation) is explained in the next section.

2.1. Temperature fluctuations and crystal growth

Change in shape and size of the ice crystal in frozen foods may occur due to periodic variation in temperature during storage. The greater the amplitude of these variations, the greater the change and rate of cellular destruction. Crystals grow by the adherence of water molecules to formed crystals. Small crystals are unstable compared to larger ones and will grow where free water molecules are present (Reid, 1983). Even when small ice crystals are formed by very rapid freezing, crystal growth during storage can take place and damage the cell wall. It is well known that such growth will be greatly accelerated by fluctuating temperatures. Several researchers (Martino and Zaritzky, 1988; Martino and Zaritzky, 1989); (Bevilacqua and Zaritzky, 1982) found crystal growth to occur under fluctuating temperature conditions.

2.1.1. Water migration

In addition to changes in size and number of ice crystals, storage conditions can markedly influence the location of water within a product. This is a consequence of the temperature dependence of the vapor pressure of water. Water vapor will transfer from a region of higher vapor pressure to a region of lower vapor pressure. Since temperature fluctuation cannot be avoided in storage, temperature gradients will exist within products. These gradients will reverse in direction during a cyclical pattern. This does not mean, however, that the moisture transfer also reverses; especially at the surface of the product and within internal cavities. When the void volume is colder than the solid volume, moisture easily transfers within it. It is more difficult for the moisture to transfer back to the initial location when the void volume is warmer than the solid volume, and so there is an overall tendency for moisture to move toward surfaces and leave the denser regions of the product. If there is a void space around the product in the package, moisture will transfer into this space and tend to accumulate on the surface of the product and the internal surface of the package (Jeremiah, 1996).

2.1.2. Irreversibility of water removal – in-pack desiccation

Another phenomenon that may magnify the effect of temperature fluctuations is irreversibility. When a capillary porous food is packaged in a vapor barrier film, a drop in the storage temperature cools the wrap, causing water vapor to frost onto it, and a decrease in the water vapor pressure. Moisture inside the pores sublimes and diffuses to the package wall until the food itself equilibrates to the new temperature. When the environment warms up again, the ice on the package sublimes but does not diffuse back into the pores, since the pores may have partially collapsed or shrunk due to loss of the water that gave them structural strength. In addition, ice may bridge some of the pore openings, preventing further resorption. The loss of unfrozen water with consequent ion concentration and chemical penetration, may also impair the water binding capacity of the food. Thus, after a cooling-warming cycle, there may be a net migration of moisture from the inside of the food toward the surface and the package wall. This frost ice is a common feature in packaged food and may occur even in foods that are wrapped after freezing (Erickson and Hung, 1997). This phenomenon is commonly known as in-pack desiccation, and its mechanism was summarized by the International Institute of Refrigeration (IIR, 1986) as follows:

a) "A layer of air between product and package is subject to temperature variations. If the outside temperature decreases, the temperature of the inside surface of the packaging will drop below the product surface temperature and ice from the product will sublime and condense on the inside the package.
b) When the ambient temperature increases, the process is reversed and the water vapor will condense on the product surface.
c) As the cooling-heating cycle is maintained, the crystals on the product surface tend to follow the package temperature more closely (due to quicker thermal response) than the mass of the product, and this results in further sublimation of ice from the product to the package surface. Frost in packages of frozen foods can amount to 20 % or even more of the product weight. Furthermore, desiccation of the surface layers exposes an increased surface area, and thus greater access to oxygen. Thus, the rate of the quality deterioration at the product surface may increase".

The effect of temperature fluctuation depends on the average storage temperature –effective temperature– (Jul, 1984). The effect of temperature fluctuation on desiccation increases with higher storage temperatures, due to increased ice sublimation.

2.2. Product Effect

The most important factors affecting product water loss during storage are: the surface to volume (or weight) ratio, product surface condition, physiological state of the product, product variety, production area and practices, and chemical potential of the water in the product.

The surface to volume (or weight) ratio gives an indication of the potential for product water loss. Small pieces of food have a high area to volume ratio and are more susceptible to moisture loss. Most produce contains more than 80 % water (Wills et al., 1989), and their volume (or weight) could give a fair estimate of the amount of water that it contains. Product surface area controls rate of water loss, according to Fick's law of gas diffusion, as described by Sastry (1985):

$$J = K_{H2O}\, A\, (P_S - P_{\infty}) \qquad (1)$$

Where:

J: rate of water diffusion through the surface of the product (Kg s^{-1})

A: product surface area (m^2)

P_S: water vapor pressure at product surface (KPa)

P_{∞}: environmental water vapor pressure (KPa)

K_{H2O}: area-based overall mass transfer coefficient of water from the product (Kg m^{-2} s^{-1} KPa $^{-1}$). The resistance coefficient involves resistance of the boundary layer; surface of the product; intercellular air spaces, cell wall, cytoplasm, cell membranes, etc.

The condition of the product surface directly affects the A term of equation (1). The driving force for water diffusion is represented by the water vapor pressure difference ($P_S - P_\infty$), and the resistance by the reciprocal of the overall mass transfer coefficient K_{H2O}. The following factors can be regarded as influencing either the driving force or the resistance term.

The physiological state, and variety of the product can affect water movement. For example, a young, vegetative tissue with many stomata and thin cuticles (e.g. baby spinach) loses more water than storage organs with lots of suberin (e.g. potatoes).

Seasonal, climatic and production differences influence the make-up of the product and also affect the water loss from the product.

The initial amount of water available for movement is best represented by the chemical potential of the water in the product which in turn depends on the make-up of the product (i.e. sugar content).

2.3. Process Effect

The process which the product has been subjected to, prior to freezing has a significant effect on water loss and quality during storage. Blanching substantially increases the keeping quality in frozen storage (Dalhoff and Jul, 1963). Antioxidant treatment prior to freezing has been found to help maintain the original quality of fish (Jul, 1984).

Simple coating treatments prior to freezing (i.e. with dressings) appear to reduce in-package desiccation (Jul, 1984)

2.4. Packaging Effect

2.4.1. Material and Packaging types

Among the most common plastic materials used by the frozen food industry are, polyamides (i.e. nylon), polyesters such as polyethylene terephthalate (PET), or its crystallized form (CPET), polyolefins such as low-density polyethylene (LDPE), and polypropylene (PP), polyvinyl chloride (PVC), polyvinylidine chloride (PVDC) and ethylene vinyl alcohol (EVOH). Average permeation values for the different plastic films are presented in table 2.

The systems used to package frozen food products for retail sale can be classified into three categories depending on the product end-use: a) atmospheric filling into simple bags and skin-packaging for loose uncooked product or cuts; b) modified atmosphere packaging (MAP) and vacuum packaging, for precooked products, and c) ovenable and dual-ovenable packaging for prepared foods. The first two categories are of importance in this study.

Atmospheric filling in bags is the most common choice for packaging uncooked vegetables, because of process simplicity and material low cost. Skin-packaging, however, is a modified form of vacuum packaging, in which the air between two films (one of which is heated), or a film and a backing material is withdrawn and the film is formed around the food (Pham and Mawson, 1997). This process is primarily used for frozen meat products.

Table 2. Properties of selected barrier films used for frozen food systems*

Film	Water Vapor Transmission Rate (g m^{-2} day^{-1} at 38 °C and 90 % RH)	Oxygen permeability (cm^3 m^{-2} day^{-1} atm^{-1} for 25 μm film at 25 C)
Polyester (oriented)	25-30	50-130
PVDC-PVC copolymer (Saran)	1.5-5.0	8-25
LDPE	18	7800
HDPE	7-10	2600
Nylon-6	84-3100	40
Polypropylene (oriented)	6-7	2000
Plasticized PVC	15-40	500-3000
Polystyrene (oriented)	100-125	5000
EVOH	16-18	3-5

* adapted from Balasubramaniam and Chinnan (1997)

MAP systems comprise the enclosure of food product in gas environment that has been changed or modified (Young et al., 1988). Vacuum packaging involves packing the product in a pouch or tray made of a good oxygen barrier film, removal of air from the package with subsequent package sealing. Due to reduction of the oxygen level inside the package, this method has been reported effective in inhibiting microbial growth for a number of food products (Bramsnaes, 1969; Piazza, 1988; Steinbuch, 1979). However, vacuum packing alone has been reported not to be as effective as blanching (i.e.: inferior organoleptic quality) for long term quality preservation of frozen spinach (Bimbaum et al., 1979).

In a packaged frozen product, frost forms whenever there is headspace (IIR, 1986). Thus, vacuum packaging is often proposed as a way to reduce that headspace and minimize frost formation. For this process to be effective, uniformity (regular shape and size) of the product is important. When vacuum-packing loose, relatively large and rigid products, gaps remaining will allow water migration into the depressurized headspace, and thus ice can form.

In gas packaging, the product is stored in an atmosphere containing an appropriate composition of nitrogen and carbon dioxide. This technique is often used for frozen storage of precooked, ready to eat products (Pham and Mawson, 1997). Since this process does not reduce the headspace, water migration and thus frost can still occur.

2.4.2. Influence of package parameters on quality

The following package material parameters can have an effect on the quality of the food product: gas and water vapor permeabilities and material thickness, packaging process, package surface area, transparency and product storage environment (ambient gas composition and storage temperature) (Lee et al., 1991).

Package material permeability is an important factor affecting headspace composition (Pham and Mawson, 1997). Several studies have shown that materials and processes that excluded oxygen, delayed lipid oxidation and/or prevented loss of color especially in meat products (Brewer and Harbers, 1991a); (Ahn et al., 1998; Bhattacharya et al., 1988; Formanek et al., 2001; Houben et al., 2000; Jo et al., 1999; Lanari and Zaritzky, 1991; Nam and Ahn, 2003; Wang et al., 1995). It has been shown that packaging materials with low oxygen transmission rates (OTR) had less microbial spoilage (Kotzekidou and Bloukas, 1996). The use of oxygen barrier films has been reported to help retain carotenoid and ascorbic acid in oxygen sensitive foods (Thakur and Arya, 1988).

Films with high water vapor permeability can lead to dehydration of the product, protein denaturation and lipid oxidation (Jul, 1984). For vegetables, it is desired that water vapor permeability be low enough to minimize dehydration and related quality changes. However, a package with low water permeability could trap excessive moisture, which may lead to undesirable microbial growth (Pham and Mawson, 1997). This water becomes frost at freezing temperatures. Several studies have related the presence of frost to the package permeability and concluded that less frost formation occurs using permeable materials (i.e.: cartons) compared to less permeable plastic bags (Méndez Bustabad, 1999; van den Berg, 1966).

Temperature also affects the permeability of a film. A film that creates a near-ideal headspace at ambient conditions may not necessarily provide the same headspace in frozen storage.

Transparency of the package material can greatly affect the quality of food products that are susceptible to light, infrared radiation and fluctuating temperatures (Pham and Mawson, 1997). Light-impermeable materials would likely improve surface color retention of foods containing carotenoids (i.e.: carrots), since they would reduce the degradative effects of short wavelength radiation (Ahvenainen and Malkki, 1985). Transparent packaging materials did not protect refrigerated food in the critical wavelength range of 400-500 nm. Odors and color changes were notable after several hours of exposure to fluorescent light (Mortensen et al., 2002).

The package environment significantly affects the quality of the frozen food. Within a display cabinet, the shelf position of the food product will determine the amplitude of temperature changes it experiences (Jul, 1984). In home freezers, these temperature fluctuations may be higher than those in commercial storage due to less precise thermostats (Pham and Mawson, 1997).

2.4.3. Quality changes associated with packaging

Color, nutritional loss, biochemical and sensory changes, frost formation, moisture loss, drip loss, and overall appearance are among the quality changes associated with packaged frozen foods. In this section, the quality changes discussed will be color, weight loss and frost formation.

Frost formation is related to the permeability of the package material, and fluctuating temperatures. Klose et al. (Klose et al., 1955) measured the effect of storage temperature in the range of – 10 °F to +10 °F on frozen turkeys wrapped with materials of different permeabilities and found that while the eating quality was not impaired, the appearance of the product was negatively affected by appreciable product moisture loss deposited as frost inside the package. Frost not only increased with temperature, but its formation in the – 10 °F to +10 °F range was about twice that for the approximate mean temperature (0 °F). This indicates "a marked tendency for the cycling temperature to 'pump' water out of the food".

The amount of frost ice formed in commercial products was also studied. van den Berg (1966) surveyed packaged frozen vegetables and found that about 80% contained frost greater than 2%. In addition, it was found that frozen vegetables had a tendency to clump – product flowed less freely – in plastic bags; freezer burn (light-colored patches) was more widespread as the amount of frost increased. The author reported that in extreme dehydration, peas were found to shrivel and to have turned brown.

Chen et al. (1989) explained that the decrease in drip loss and color change in frozen hamburger meat was related to the "migratory recrystallization" process (simultaneous sublimation-diffusion-condensation of ice), which was facilitated by a large air space volume, approximately 0.55 dm^3, between the food and the package wall.

2.5. Combined effects and mathematical models

2.5.1. Kinetic models

Semi-empirical kinetic models are often used to describe the change in quality of frozen foods. These models facilitate package design resulting in a product with desired quality attributes (Reid, 1997). A food constituent can be characterized by a quality attribute, p. The change in p as a consequence of deteriorative reactions can be described as:

$$dp/dt = -k\, p^n \qquad (2)$$

Where p is the food quality attribute, t is time, k is the rate constant, and n is the order of reaction. Quality degradation during frozen storage is often modeled using linear relationships (zero order reaction) or as a first order reaction. Mathematical derivations of reaction kinetics can be found in the literature (Arabshahi and Lund, 1985; Labuza and Riboh, 1982). The rate constant, k, is temperature dependent, and usually can be modeled using an Arrhenius relationship. However, the Arrhenius equation does not account for the effects of pressure and concentration of reactants. It was originally developed for monoatomic reactions though many authors have reported success when modeling quality loss. Packaged food quality has been studied using different quality attributes such as change in color (Bhattacharya et al., 1988); (Lanari and Zaritzky, 1991); (Chen et al., 1989); (Lanari et al., 1993), drip and cooking losses (Bhattacharya et al., 1988), water holding capacity and lipid autooxidation (Chen et al., 1989). Lanari et al. (1993), used a first order kinetics to explain the decay in skin and vacuum packaged frozen and frozen, and thawed beef. Lanary and Zaritzky (1991), used a first order model to explain the effect of vacuum packing on myoglobin oxygenation during storage of frozen and partially frozen beef. Chen et al. (1989) calculated apparent activation energies for lipid meat auto-oxidation, discoloration and changes in water holding capacity using the Arrhenius equation.

Kinetic parameters are often complex summations of all individual elementary reactions. In these models, it is assumed that the temperature history of the product is known.

2.5.2. Temperature distribution and fluctuating temperature

The rate of quality loss during the post-freezing phase (i.e.: distribution, storage, retail cabinet display, in-home freezer storage) is temperature dependent (Pham and Mawson, 1997). Methods which can predict or identify the temperature distribution within a product are useful in assessing the loss of quality due to fluctuating temperatures during post-freezing.

When developing temperature prediction models, data from freezing processes were initially used to develop the models. Later, these models were adapted to post-freezing studies. According to Scott (1987), these models can be categorized into two groups: 1) those producing freezing time estimations, and 2) those producing temperature distribution profiles within the food. For post-freezing studies, models which predict temperature distribution within the food are of most related.

Most of these models are based on either heat transfer analysis or coupled heat and mass transfer analysis (Delgado and Sun, 2001). The heat transfer analysis is usually taken as a one-dimensional problem (Scott, 1987), and has been approached in several different ways. These approaches range from analytical to numerical methods. Analytical techniques often assume pure components, constant heat transfer coefficients and change of phase at a specific, single temperature (Scott, 1987). However, food products, which are a solution or mixture of components, do not have a specific, single freezing point. The change of phase takes place over a wide range of temperatures because as the mixture freezes, the liquid portion becomes more concentrated with solute, and the freezing point is depressed further. Thermal properties, which are composition-dependent, become significantly temperature dependent as well. Thus, it has been argued that analytical methods are inadequate for predicting temperature changes within a product during freezing, or during periods of fluctuating temperatures close to the phase change (Zuritz and Singh, 1985). Numerical methods have the advantage that they can analyze the effect of the phase change over a range of temperatures, and can be considered to be the most accurate if they are implemented correctly (Delgado and Sun, 2001).

Numerical models (i.e. using finite difference or finite element methods) and studies have not taken into account packaging since it has been assumed that it would have a beneficial effect in terms of damping temperature fluctuations (due to the stagnant air in the headspace). The fluctuation period, temperature range and package size have been regarded as the more important factors (Zuritz and Singh, 1985).

Sastry and Kilara (1983) modeled the thermal response of stacks of frozen peas exposed to energy-conservation practices involving di-thermal storage cycles. The authors reduced the model to ordinary conduction heat transfer with temperature dependent thermophysical properties. Zuritz and Singh (1985) simulated the effect of storage temperature changes through simulated frozen-food distribution channel using a finite element model. Mittal and Parkin (1985) studied the response of frozen foods in insulated containers to a step change in the ambient temperature.

More recently, Zuritz and Sastry (1986) and Scott and Heldman (1990) demonstrated that the contribution of packaging materials to the total resistance is important when the convective resistance of the surrounding air is negligible. The resistance due to the packaging interface is greater than zero but less than infinity. Thus, the assumption for thin packaging materials that there is no resistance to heat flow, should be corrected when modeling the temperature response of a food product especially when using insulatory material.

Moureh and Derens (2000) presented a three-dimensional finite-volume heat transfer model which predicted temperature within a pallet as a function of time of exposure, storage conditions, product initial temperature, palletization pattern and thermal characteristics of the products and packaging. They reported good agreement with actual temperatures recorded at different locations in the pallets of packaged frozen fish when placed in closed or open dock areas.

Though there is great promise in numerical models, it is difficult to develop precise prediction methods since accurate experimental data are not easy to obtain. Furthermore, heat transfer coefficients are hard to estimate with errors of 10 to 20 % reported (Delgado and Sun, 2001). The most fruitful work is still in finding simple, accurate equations for foods with regular shapes that can be used with relatively little effort.

CHAPTER 2

MATERIALS AND METHODS

1. Materials

1.1. Carrots

Baby cut carrots were used in all experiments. They were selected to have uniform size and shape. Fresh carrots were purchased from a local supplier (Steve's Produce, Lansing, MI) and were blanched prior to packing. The blanching process was performed using a steam blancher (Dixie, Inc.). The product was heated in steam at 90 psig for 3.5 minutes in 20 lb-batches and then cooled for about 10 minutes at room temperature. The carrots were then packed into the test packages and sealed.

1.2. Packaging Materials

Two different packaging materials (nylon/polyethylene multilayer and polyethylene) were used (Table 3). For the nylon/polyethylene multilayer film, vacuum and atmospheric packaging processes were employed. Vacuum packaging was performed using a MULTIVAC A 300/16 machine (MULTIVAC INC., Kansas City, MO) set at -800 mbar. For the PE structure, punctured and non-punctured bags were used. Punctured PE bags were fabricated by poking six evenly distributed perforations (about 0.5 mm in diameter) in both sides of the bag material.

All bags, with exception of the vacuum processed ones, were sealed using a SENCORP SC-12 impulse heat sealer (Sencorp Systems Inc., Hyannis, MA) at the settings listed in table 4. The bags used for the vacuum process were sealed using the MULTIVAC A 300/16 machine.

Table 3. Bag Materials Specifications

	LDPE	Nylon/PE multilayer
Supplier	VWR International (Batavia, IL)	Koch Supplies Inc. (Kansas City, MO)
Thickness, mils	3	3
Composition	LDPE	(0.75 mil nylon, 2.25 mil polyethylene)
Dimensions from seams, cm	18 x 13.5	18.5 x 13

Table 4. Parameters for impulse sealing

Parameter	LDPE	Nylon/PE multilayer
Impulse time, s	1.1	1.5
Dwell time, s	1	1
Jaw pressure, psi	34	34

2. Processes

2.1. Freezing and Frozen storage of the samples

The packaged samples (≈1 lb per bag) were frozen using an air freezer set at -20 ºC (-4 °F) with an airflow estimated to be about 200 feet per minute (ALNOR Series 6000-P velometer (Niles, IL). Once frozen, the samples were kept in the freezer until they were evaluated or moved to the retail cabinet. One week prior to evaluation, half of the bags designated for each packaging material/process combination were moved to a retail cabinet (Zero-Zone Inc., Waukesha, WI) set at -26 °C (-15 °F) at a local store. Figure 1 presents a layout of the experimental design.

3. Methods

3.1. Temperature monitoring

Temperatures in the air freezer, and commercial retail cabinet were monitored and recorded throughout the experiment using a set of OMEGA OM CP IFC 101 temperature data loggers (+/- 1 ºC). In all cases, the devices were set to record the temperature every 5 minutes. Retail cabinet: A temperature data logger was attached to the lower frame of the retail cabinet at the same tray level as the samples were placed. Only the lower level tray was used for sample placement throughout this study (Figure 2). Air freezer: 3 temperature dataloggers were used for approximately two months each to record the temperatures inside the freezer. The device was placed in the middle tray throughout the entire experiment (Figure 2).

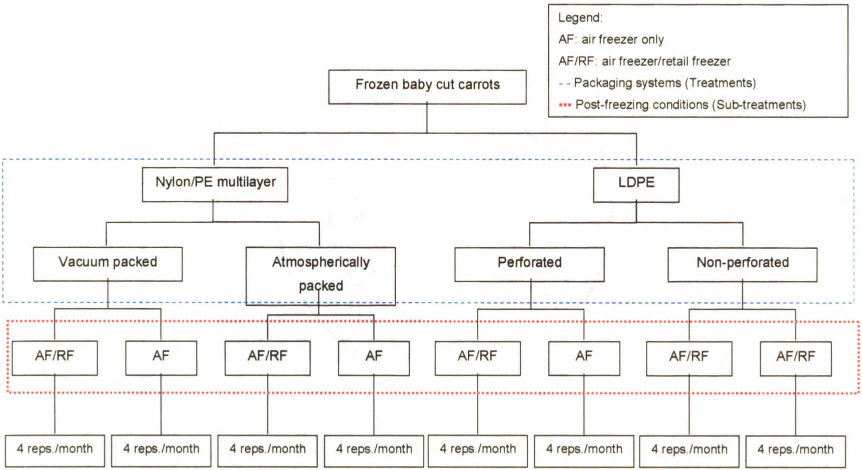

Figure 1. Experimental Layout: treatments (packaging systems), and sub-treatments (air freezer or air freezer/retail)

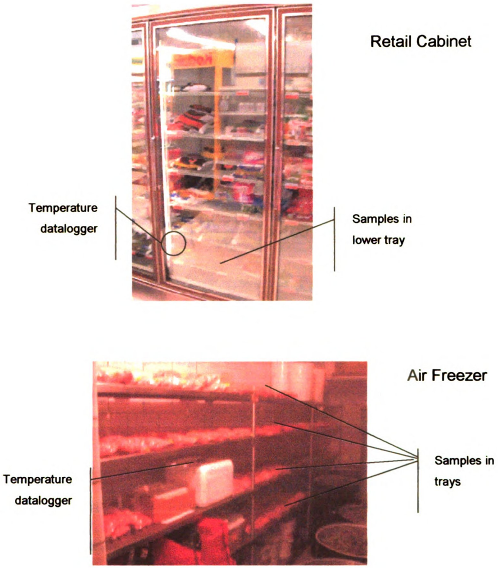

Figure 2.Temperature datalogger location inside the freezer and retail freezer cabinet

3.2. Frost and glassy ice content

Evaluations included: a) package weight loss; and product weight change; and b) amount of frost ice formed inside the bag.

a. Package gross weight was initially (prior to freezing) determined to 0.1 g, using an electronic Ohaus balance (Florham Park, N.J.), and again at the end of storage. The difference in weight is expressed as a percentage of the initial weight according to the following relationship:

$$P_{wl} = \left(\frac{W_o - W_f}{W_o}\right) \times 100 \qquad (3)$$

Where,

P_{wl}= package weight loss, %

W_o= initial package gross content weight, g

W_f= package gross content weight at moment of evaluation, g

b. Frost ice crystals were separated by shaking the contents of each package into a standard sieve (0.263 in opening). This was done in a chamber at 38 °F. Frost which adhered to the inside of the bag was removed using a dry cloth. To prevent temperature differences and water condensation from interfering with the performance of the electronic Ohaus scale, the content of each bag without frost, was then weighed, as quickly as possible at 23 °C. The frost content is assumed to be the difference between the final gross weight and the weight of the contents, without frost, and the empty bag. This is expressed as a percentage of the initial net weight according to the following relationship:

$$\text{Frost content percent} = \left[\frac{W_f - (W_b + W_c)}{W_o - W_b} \right] \times 100 \qquad (4)$$

Where,

W_o= initial (prior to freezing) package gross content weight, g

W_f= package gross content weight at moment of evaluation, g

W_b = empty bag weight (without frost), g

W_c = contents weight (without frost), g

c. Glassy ice (from frozen vacuum packed carrots): The glassy ice was allowed to melt in a room at 38 °F for 30 min. Then the sample was placed on a standard sieve (0.263 in opening). This was done in a chamber at 38 °F. Ice which adhered to the inside of the bag was removed using a dry cloth. To prevent temperature differences and water condensation from interfering with the performance of the electronic Ohaus scale, the content of each bag without the glassy ice, was then weighed, as quickly as possible at 23 °C. The frost content is assumed to be the difference between the final gross weight and the weight of the contents, without glassy ice, and the empty bag. This was expressed as a percentage of the initial net weight according to equation 4:

3.3. Moisture content determination

The method used is an adaptation of the AOAC Official Method 984.25 (AOAC, 2000) for moisture determination in frozen french-fried potatoes.

A sample of product was cut in pieces, homogenized and weighed in aluminum dishes in duplicate (ca 10 g), using a Mettler balance accurate to 0.1 mg. Dishes containing the test samples were subsequently dried in a vacuum oven at 55-60 °C +/- 3 °C for 24 h. When cool, they were weighed as quickly as possible.

The moisture content (M.C.) was then calculated as a percentage, according to:

$$M.C.\,\% = \left(\frac{M_1 - M_2}{M_1 - M_0}\right) X\, 100 \qquad (5)$$

Where

M_0= mass in g of tared dish;

M_1= mass in g of tared dish, and undried test sample

M_2= mass in g of tared dish and dried test sample

3.4. Color Assessment

Samples of product thawed for one day were assessed using the colorimeter. A D25-PC2Δ Hunterlab Colorimeter (Reston, Va) was used for color evaluation on L (lightness), a (redness), and b (yellowness) values. Reported results are averages of two readings of every replicate (after first reading, the sample was rotated for a second reading, to avoid interference due to sample orientation).

The severity of surface white coloration was estimated by Whiteness Index (WI, in the range of 0 to 100), which is expressed as (Bolin and Huxsoll, 1991):

$$WI = 100 - ((100 - L)^2 + a^2 + b^2)^{0.5}$$

Where a, b and L were the Hunter parameters. The numerical scale of WI is from 0 to 100, where higher WI values represent more severe white surface discoloration (Bolin and Huxsoll, 1991).

3.5. Product appearance – Sensory Evaluation

The objective of this study was to identify whether time or treatment had an effect on the appearance of the product. Thus, it comprised two evaluations: a) Carrots at package opening (degree of frost covering carrots), and b) product overall appearance (color, size, shape and texture combined) after frost removed. Following there is a summary of the major features of this evaluation.

Rating

9.0 to 7.0 | 6.9 to 5.0 | 4.9 to 3.0 | 2.9 to 1.0

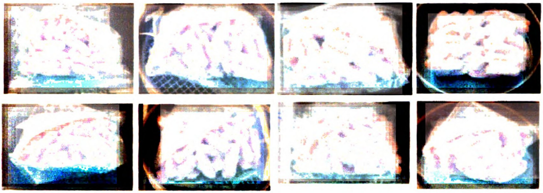

Figure 3. Reference standards for carrots upon package opening

Rating

9.0 to 7.0 | 6.9 to 4.0 | 3.9 to 1.0

Figure 4. Reference standard for overall appearance of carrots after frost removal

Digital pictures of the samples were evaluated using a panel of 15 subjects. To test the effect of time, pictures were taken of two replicates at month one and month six of a specific treatment (nylon/PE multilayer bags, atmospherically filled and exposed to retail). In order to test the effect of packaging systems, digital pictures were taken of two replicates of every treatment at month 6.

For carrots upon package opening (degree of frost on the carrots), the panelists rated each picture using a scale from 1.0 (worst condition) to 9.0 (best condition); reference standards were available and are presented in Figure 3. Likewise, for product overall appearance, the panelists judged each picture on a scale from 1.0 (worst condition) to 9.0 (best condition); reference standards were available and are presented in Figure 4.

Pictures: Due to the length and nature of this study, it was decided that pictures of the samples could be used. Potential advantages were the convenience of avoiding the handling of the refrigerated product and short panel evaluation times. It was assumed that potential drawbacks could be related to poor picture resolution or inconsistent characteristics (contrast, color, brightness, size, zooming) of the pictures and thus impaired evaluation. To assure a fair picture quality, all pictures were taken with a high-end digital camera -NIKON Coolpix 995 of 3.1 megapixels (Tokyo, Japan)-, in the same room, with the same lighting. The samples where placed on a table over a black background at the same distance of the digital camera placed in a tripod. The digital camera controls (brightness, zooming, color, contrast, etc.) were set to the same manufacturer default values throughout the study. The digital pictures of the samples were screened and found to be representative of each treatment type. Pictures were then electronically uploaded to a computer and presented in a questionnaire using SIMS 2000® sensory evaluation software (Sensory Computer Systems, Morristown, NJ).

Panel: 15 panel members were selected on the basis of past performance in an initial screening of carrot pictures. Panelists attended one 15-min training session and two 45-min evaluation sessions each on separate days. All 15 panelists rated each picture. Panel members were informed that the samples were digital pictures taken of the actual carrots. The identity of the individual samples was not disclosed.

Location: The panel worked in a room specifically used for sensory evaluation studies at the Food Science Department at Michigan State University. The room was lit with 40-watt fluorescent bulbs. Members worked individually in 7 booths and no discussion took place during evaluation. Each booth was equipped with a seat, desk, computer terminal and monitor. The questionnaire was displayed separately in each monitor and members could enter their responses by clicking the computer mouse. The standards (Figures 3 and 4) were displayed in every questionnaire and could always be seen by scrolling up the screen. For carrots upon package opening (frost on the carrots), the samples were presented in sets in a balanced, random order. Likewise, for the overall appearance determination, the samples were presented in sets in a balanced, random order. For this determination, the panel was informed in the electronic questionnaire that overall appearance of the carrots was a combination of product texture, firmness, color and shape.

Statistical evaluation: The experiment was treated as a qualitative descriptive analysis for attributes including a BIB (balanced incomplete block design) rating test, and the results were evaluated using an analysis of variance (ANOVA) test according to Meilgaard et al (2000).

CHAPTER 3

RESULTS AND DISCUSSION

The following results refer to the treatments, sub-treatments, and time variable for the different samples. There were four treatments: 1) Frozen carrots atmospherically packed in nylon/PE multilayer bags (A-NPE), 2) Frozen carrots vacuum packed in nylon/PE multilayer bags (V-NPE), 3) Frozen carrots atmospherically packed in LDPE bags (LDPE), 4) Frozen carrots, atmospherically packed in perforated LDPE bags (P-LDPE). The sub-treatments were two: 1) Samples exclusively kept in the air freezer (air freezer sub-treatment), 2) Samples kept in the air freezer and then moved to a retail freezer cabinet one week before analysis (air freezer/retail freezer sub-treatment). The duration of the experiment was 6 months. Samples were analyzed at monthly intervals.

1. Frost content and origin

Throughout the six months of storage, an increase in frost ice amount was noted in all treatments and sub-treatments. The ice amount was the highest for vacuum packaged samples, though the ice formed had a hard, glassy-like character, not the typical frosty appearance. For the rest of the samples, the ice formed had a frosty appearance regardless of the packaging material or sub-treatment (Figure 5), and frost determination was carried out as described in the methods section. The difference between the two methods may make a consistent comparison of the data difficult. Thus, the statistical analyses that follow only consider the carrots atmospherically packed in perforated and non-perforated LDPE bags and in nylon/PE bags. Analysis of the data from vacuum packed carrots is considered separately (pg. 46).

Figure 5. Appearance of frost ice on atmospherically packed samples

Sample data (except vacuum packaged) was processed using a nonparametric model (Appendix B), and tested to determine whether the treatments, sub-treatments, and time had any effect on frost formation. It was found that time had a significant effect on increase in frost ($p<0.05$) (Figures 6 and 7). A Kruskal-Wallis test (Appendix B) was used to perform a multiple comparison analysis of the data. It showed a consistent tendency of frost to increase over time, regardless of treatments or sub-treatments.

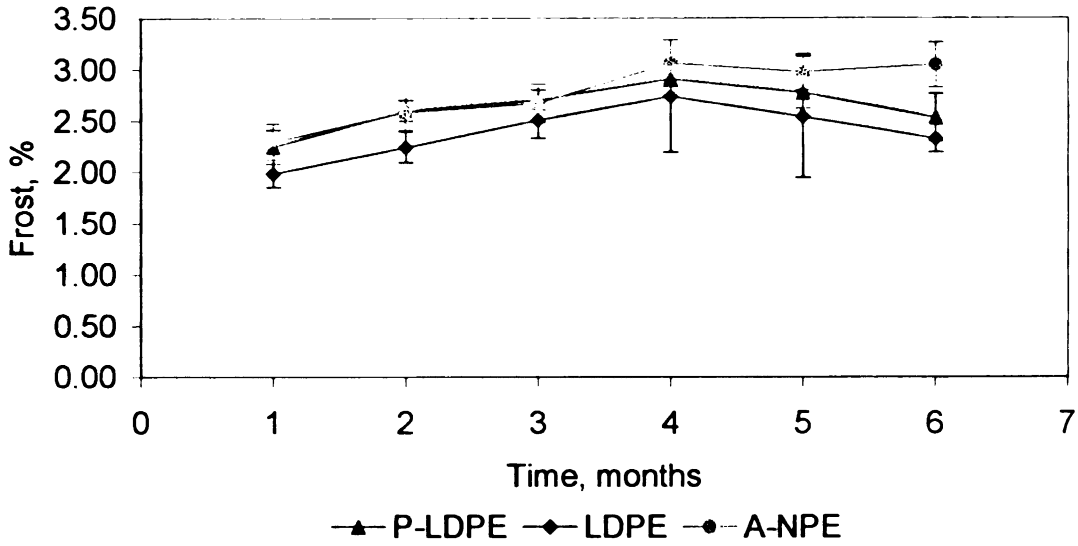

Figure 6. Comparison of frost ice during time for "air freezer" bags (V-NPE bag data not included)

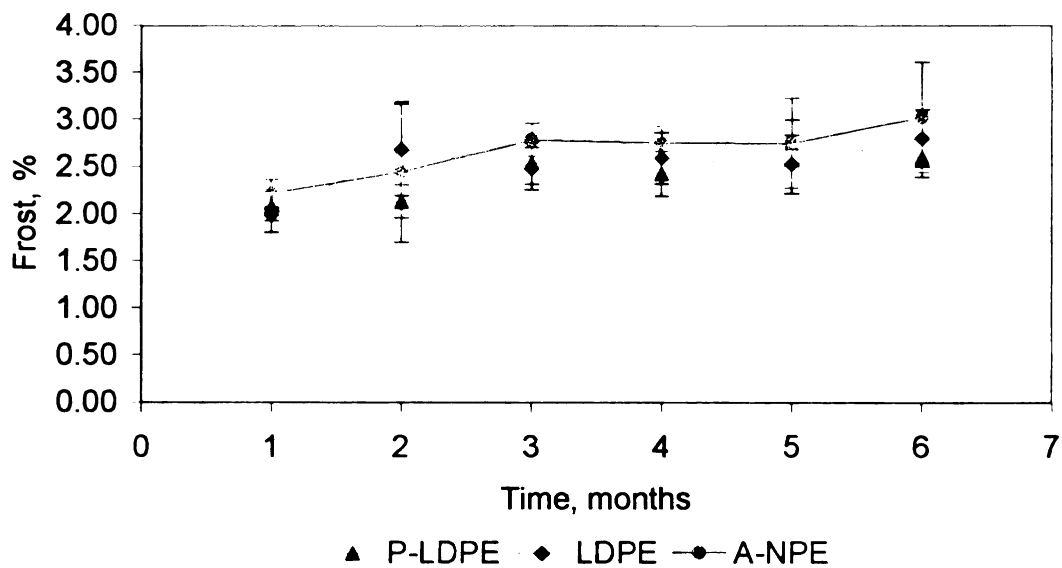

Figure 7. Comparison of frost ice during time for "air freezer/retail freezer" bags (V-NPE bag data not included)

It was also found that there was no significant difference in frost formation between storage conditions and retail conditions, unless the bag had perforations ($p<0.05$). Samples in perforated LDPE bags in the air freezer/retail freezer sub-treatment had less frost compared to perforated LDPE bags in the air freezer sub-treatment. No significant difference in frost ice amount was found between either frozen carrots in LDPE bags (with no perforations) under both sub-treatments, or those packed in Nylon/PE multilayer bags under both sub-treatments (air freezer and air freezer/retail freezer).

Within the air freezer/retail freezer sub-treatment, the data does not show a significant difference between the treatments (material/process combinations). However, within the air freezer sub-treatment, the data shows a significant difference in frost formation ($p<0.05$). Within this sub-treatment, frozen carrots atmospherically packed in Nylon/PE bags had the highest frost formation, followed by perforated LDPE bags and non-perforated LDPE bags.

Several additional studies were performed to determine the origin of the frost. They are listed as follows:

Study 1: The amount of headspace moisture in the air trapped inside the package at the moment of packaging was estimated. By utilizing the relationships of water content of the air at 23 °C (assumed temperature at the moment of packing), the air density at that temperature, and the headspace volume inside the package, it was possible to estimate the amount of water in the headspace air inside the package. This relationship can be expressed using the following equation:

$$W_H = C^{air}_{H_2O} \times \rho_{air} \times P_H \qquad (6)$$

Where

W_H= Moisture inside package headspace, g

$C^{air}{}_{H2O}$= water content in air at 23 °C, 0.0175 g of water / g of air

ρ_{air}= density of air at 23 °C, 1.18×10^{-3} g/cm^3

P_H= Package headspace volume, cm^3

The moisture inside the package headspace at the moment of packaging was estimated to be 0.00165 g., assuming the maximum headspace volume could be 80 cm^3. This amount is very small compared to measured frost amounts (8 g - 20 g) (Appendix A). Thus, headspace moisture can be assumed negligible in accounting for frost origin.

Study 2: The water vapor permeability of the packaging materials was determined using a PERMATRAN W 3/31 instrument (Mocon Inc., Minneapolis MN) (Appendix C). Samples of the plastic materials were tested at 20 °C, 15 °C and 10 °C (2 replicates each). During the actual test, one side of the film was exposed to 100% RH while the other side was kept at 0% RH. Activation energies for water vapor permeation were determined and permeability coefficients for a storage temperature of 0 °C were calculated using an Arrhenius equation (Appendix C). Table 5 shows the predicted amounts of moisture transport through the package for up to 6 months, assuming a maximum storage temperature of 0 °C during the entire 6-month period, and extreme relative humidity conditions (100% RH inside-0% RH outside) on each side of the packaging material.

Table 5. Maximum predicted amount of moisture transported through package at 100% RH and 0 °C after X months

	Month					
	1	2	3	4	5	6
q (non-perforated LDPE), g	0.2863	0.5727	0.8590	1.1454	1.4317	1.7181
q (Nylon/PE multilayer), g	1.1455	2.2910	3.4364	4.5819	5.7274	6.8729

Under these extreme conditions, the amount of moisture transported through the nylon/PE material is higher than that through non-perforated LDPE for any month. This is may be due to the higher water sensitivity of nylon. Comparing these amounts to actual frost amounts (Tables 6 and 7), it is shown that the amount of water vapor transported through the film ranged from 0.3 to 13.7% of the measured frost amounts in the LDPE bags, and 11.4 to 40% of the measured frost or glassy ice amounts in the nylon/PE multiplayer bags. Thus, the amount of moisture coming into or out of the package by permeation is generally not significant for LDPE bags, but may be important for Nylon/PE multilayer bags during long storage periods.

Table 6. Average amount of frost (grams) after X months for air freezer/retail freezer sub-treatment

	Month					
Packaging System	1	2	3	4	5	6
A-NPE	9.93	11.18	12.85	12.50	12.80	17.10
V-NPE	16.18	15.87	24.53	27.20	27.00	21.10
LDPE	8.82	12.05	10.98	11.68	11.33	12.43
P-LDPE	8.95	9.30	11.53	10.95	12.53	10.95

Table 7. Average amount of frost (grams) after X months for air freezer sub-treatment

	Month					
Packaging System	1	2	3	4	5	6
A-NPE	10.35	11.95	12.18	14.05	13.83	14.03
V-NPE	14.75	19.38	25.28	22.97	20.28	17.00
LDPE	8.90	10.08	11.18	12.25	11.38	10.73
P-LDPE	10.10	12.03	12.20	12.65	12.53	10.78

Study 3: To determine how much of the measured frost came from freezing the surface water that was on the carrots before packaging, fresh carrots were blanched, packaged in nylon bags and subsequently frozen. The following day, the bags were opened and the amount of frost ice was evaluated using the same procedure as previously described. The amount of frost was approximately 10 g (2.6%), which is significant when compared to the level of frost ice after the first month (Tables 6 and 7). Possible explanations for this could be related to

water made available by: a) the blanching-cooling-packing procedure used; and b) the freezing process. Following blanching, the hot carrots were left at room temperature to cool down. During cooling, the temperature at their surface decreased in part as a result of water evaporation. Eventually, the water that migrated to the product surface (to compensate for the difference in water vapor pressure) remained there as a fine film since it would not have enough energy to become steam. After cooling, the product was packed into their respective bags. Thus, the surface film of water could have been one of the sources that contributed to the frost formed.

During freezing, a low rate of heat removal can lead to moisture movement within the carrots through an osmotic mechanism, with the lost water going to external ice crystals (Reid, 1997). The length of this process would be mainly dependent upon the medium heat transfer coefficient. The medium heat transfer coefficient for the freezing method (neglecting packaging material) used in this study is rather small (Table 1) meaning that this process would take long. This is reinforced by the fact that in all evaluations, clumping of carrots was noticed. Higher coefficients would have been needed to decrease the freezing duration and thus internal water migration. Thus, the duration of the freezing process could have been one of the causes that contributed to the frost formed.

Vacuum packed baby carrots

Table 8 shows the data on ice for the vacuum packed baby cut carrots. The ice formed in vacuum packed carrots in nylon/PE multi-layer bags did not have the frosty appearance as did the rest of the samples (Figure 8). Instead, a glassy-like ice coating developed probably due to product water migration under negative pressure inside the package. A comparison with the data from the rest of the packaging systems could not be done since the measurement procedure (Materials and Methods) was different.

Table 8. Average glassy ice amounts (%) for carrots in bags exposed to air freezer/retail freezer and air freezer sub-treatment after X months

Sub-treatment	Month					
	#1	#2	#3	#4	#5	#6
AF/RF	2.22 (0.14)[s]	2.45 (0.75)	2.79 (0.18)	2.76 (0.17)	2.75 (0.48)	3.03 (0.59)
AF	2.30 (0.17)	2.59 (0.17)	2.67 (0.19)	3.06 (0.23)	2.98 (0.18)	3.05 (0.22)

[s] standard deviation

It is believed that the glassy ice formed due to the combined effect of vacuum and a slow freezing process. Even though the headspace volume was reduced as a result of vacuum packaging, there were still spaces between the loosely packed and rigid carrots. Therefore, water from the core of the product could migrate to the surface even more due to the vacuum. It appears that vacuum packing of loose, relatively large product, creates a headspace of significant nature which allows water migration to occur due to the depressurized space. In this experiment the use of a slow freezing method (Table 1) determined the length of time that the product water was available for migration.

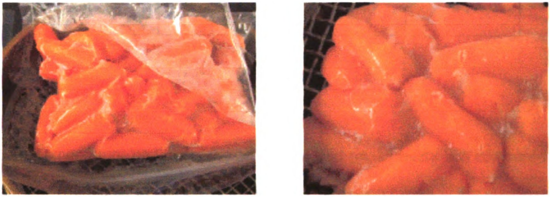

Figure 8. Appearance of glassy ice on vacuum packed samples

<u>Study 4:</u> This study was performed to assess the effect of vacuum packaging, the weight loss of the contents of two bags of carrots was measured. One bag of carrots was placed in a vacuum oven at 23 °C for 5 hours while the other was left in the room at the same temperature for the same time. Weight loss data from the bags is presented in Table 9.

From these results, it is readily noted that vacuum promotes greater weight loss from the carrots than did a larger volume headspace with no vacuum.

Table 9. Weight loss in carrots held in a vacuum oven (≅-14 in of Hg) and at atmospheric conditions

	Initial weight, g	Final Weight, g	Weight loss, g
Vacuum	453.3	440.1	13.2
Ambient	468.1	464.4	3.7

2. Temperature profile

Temperature profiles of the air freezer and retail freezer are compared in Figure 9. The higher peaks correspond to the defrosting cycles of the equipment. For the retail cabinet the defrosting cycle takes longer, and occurs once a day, while the air freezer has an average of 3 defrosting cycles –shorter in length – during the same period.

In the "air freezer" sub-treatment, the packed carrots were exposed only to the air freezer temperatures. In the "air freezer/retail freezer" sub-treatment, the packed carrots were exposed first to air freezer temperatures followed by a week of exposure to the retail freezer cabinet temperatures (Appendix F).

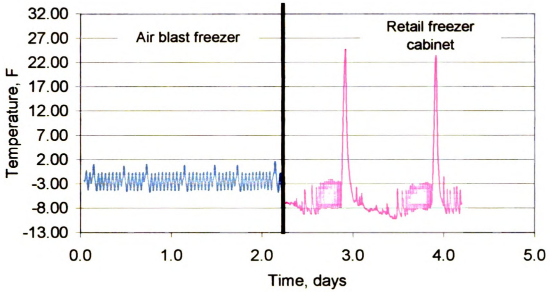

Figure 9. Temperature profile from retail freezer cabinet and air freezer

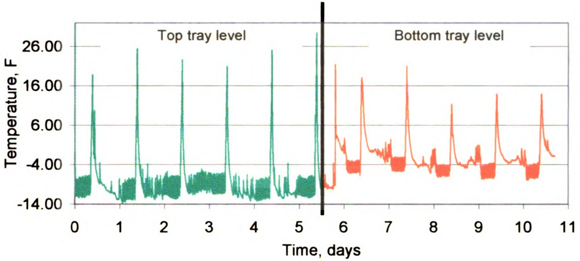

Figure 10. Temperature at top and bottom in retail freezer cabinet

In an additional study to evaluate temperature differences between different tray levels inside the retail cabinet (Figure 10), it was found that the temperature at the top tray level achieved a higher peak during the defrost cycles than that at the bottom tray level. A possible explanation could be that when the evaporators, located on top in this retail freezer cabinet are working, the temperature at the top appears to be fairly low, even lower than at the bottom tray level. During the defrost cycle, the heavier, cold air located on top may displace the warmer bottom air making the temperature at this part consistently lower during the cycle.

Table 10. Average temperatures for air freezer (AF) and air freezer/retail freezer (AF/RF) treatments

Sub-treatments	Month					
	1	2	3	4	5	6
AF	(-2.05 °F) −18.91 °C	(-2.94 °F) −19.41 °C	(-2.97 °F) −19.43 °C	(-2.99 °F) −19.44 °C	(-3.07 °F) −19.49 °C	(-3.07 °F) −19.49 °C
AF/RF	(-1.19 °F) −18.44 °C	(-2.33 °F) −19.07 °C	(-2.66 °F) −19.25 °C	(-2.87 °F) −19.37 °C	(-2.84 °F) −19.35 °C	(-3.14 °F) −19.52 °C

In this study, due to space constraint, the products exposed to the retail freezer cabinet, were placed on the bottom tray. However, it may be that at the top tray level (in this cabinet) the product might have been affected more due to the higher peak temperatures during the defrost cycle.

From the recorded temperature data, it is noted that (except for the last month), the air freezer/retail freezer sub-treatment had consistently higher temperature averages than those of the air freezer sub-treatment (Table 10). These higher averages are mainly due to the higher and longer defrost peak temperatures in the retail cabinet.

3. Moisture content

The moisture content data of the carrots were analyzed using the same non-parametric model used for ice results. Data from vacuum packaged carrots were not included in this analysis. The analysis was performed to determine whether the treatments, sub-treatments, and time had any effect on the moisture content. The data showed that time resulted in statistically significant decreased moisture content ($p<0.05$). The analysis also showed that within different treatments (air freezer and air freezer/retail freezer) frozen carrots packed in perforated LDPE bags had significantly lower moisture content ($p<0.05$) than those packed in the other bags. Differences in the carrot moisture content among the rest of the treatments were not statistically significant. Differences found in the moisture contents were small and were comparable to those predicted in a mass balance calculation using the frost ice results (Appendix D).

In order to assess whether commercial products tend to show this same trend, four bags of a similar brand of frozen baby cut carrots were purchased from a local store and evaluated. All of the bags had the same lot number and were analyzed for frost ice and moisture content using the same procedures described in the methods section. Table 11 summarizes the results.

Table 11. Frost ice and moisture content amounts of commercial packages of frozen baby cut carrots

	Bag #1	Bag #2	Bag #3	Bag #4	Average	Standard Deviation
Frost, g	11.60	9.70	11.40	12.40	10.90	1.04
Frost, %	2.25	2.07	2.50	2.70	2.27	0.21
MC, %	85.20	87.46	86.27	85.58	86.31	1.19

The results clearly show that the frost amounts in commercial packages and carrot moisture content are comparable to amounts in this study (Figures 6 and 7).

4. Color evaluation

The whiteness Index (WI) measures of white discoloration (Bolin and Huxsoll, 1991). The higher the WI score, the more severe the white discoloration. All carrot samples except the vacuum packaged ones were statistically examined using a non-parametric model (Appendix B), to test whether the treatments, sub-treatments, and/or time affected carrot white discoloration.

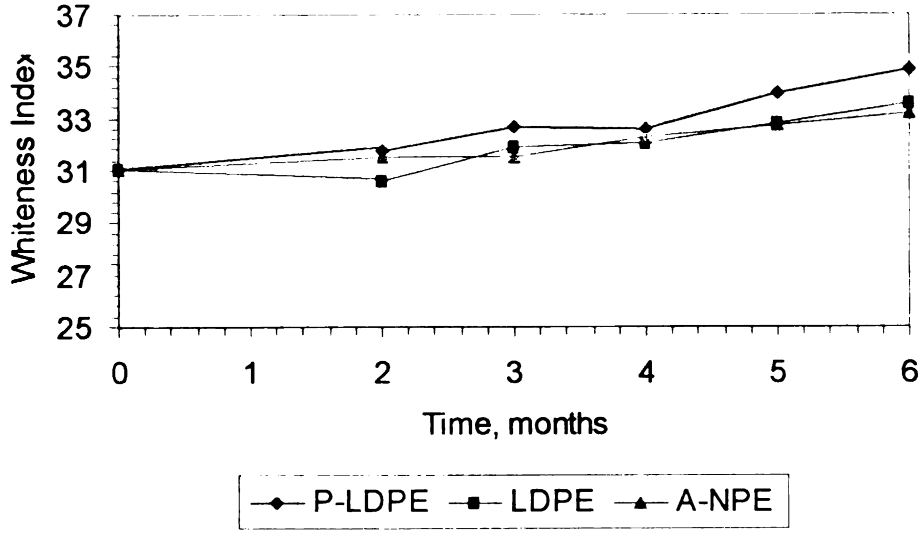

Figure 11. Color change in carrots exposed to air freezer/retail freezer sub-treatment

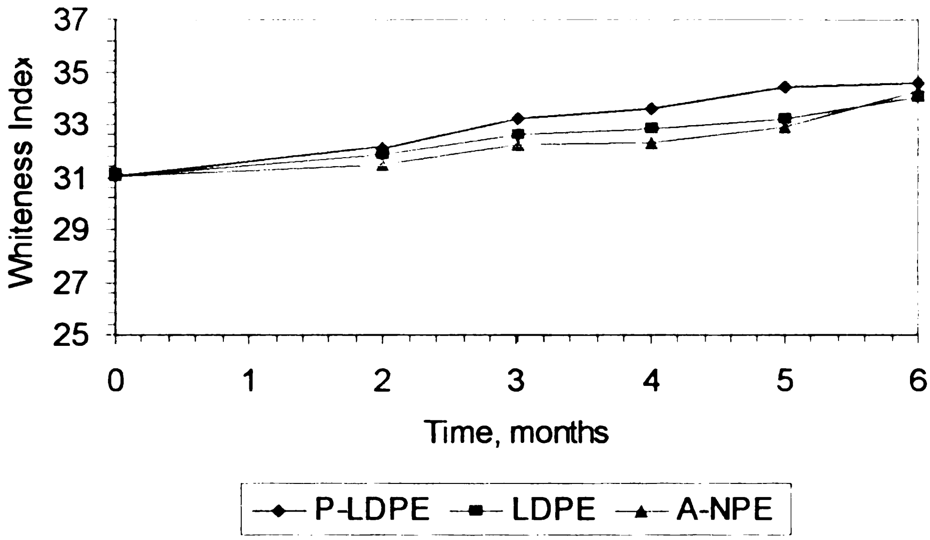

Figure 12. Color change in carrots exposed to air freezer sub-treatment

Figures 11 and 12 show the WI data. The analysis showed that treatments and time had an effect on the white surface discoloration. When the results were sorted out by treatment, it was found that the discoloration was highest ($p<0.05$) in carrots that were packed in perforated LDPE bags regardless of the sub-treatment, followed by those packed in nylon/PE multilayer bags and those packed in non-perforated LDPE bags. The main reason for white discoloration is surface dehydration (Bolin and Huxsoll, 1991). The carrots lost more water due to the presence of perforations and thus became drier and had higher WI values. When the results were sorted by time, it was found that carrots had increasing WI values ($p<0.05$) regardless of treatment or sub-treatment. Though the changes in WI were found to be statistically significant, they were small. A probable reason for this is that the packaging retarded whitening by encasing water (as frost) around the carrots. Thus, frost on the surface of the carrots may have retarded the white discoloration.

5. Appearance – Sensory evaluation

Overall appearance of the carrots (vacuum packaged not included) did not differ significantly ($p>0.05$) (Figure 13). Differences in product discoloration values were low and could have been overlooked by the panel when rating the digital pictures. Appearance differences, assumed to be a combination of product texture, firmness, color and shape, could have been not sensitive enough.

For carrots having frost upon package opening (Figures 14 and 15), it was found those packed in LDPE bags with perforations received significantly higher rating marks than the rest of the frozen packaged carrots ($p<0.05$). The panel perceived that carrots with less frost ice must be better. This is consistent with the frost ice data in this study (Figures 6 and 7) and with similar studies (Méndez Bustabad, 1999; van den Berg, 1966).

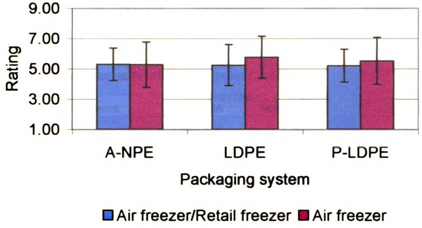

Figure 13. Results of overall appearance of baby cut carrots (after frost ice removed) from packaging systems within the same month (month 6)

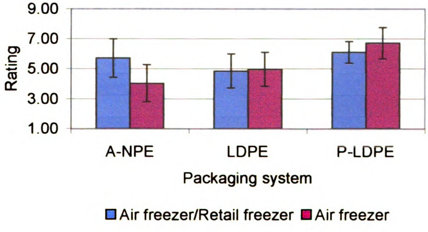

Figure 14. Results of appearance of baby cut carrots upon package opening (frost on product) from packaging systems within the same month (month 6)

The GLM Procedure

Dependent Variable: frostap   frostap

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	19	179.5728333	9.4512018	6.04	<.0001
Error	160	250.2246667	1.5639042		
Corrected Total	179	429.7975000			

R-Square	Coeff Var	Root MSE	frostap Mean
0.417808	23.19434	1.250562	5.391667

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Treatment	2	53.13033333	26.56516667	16.99	<.0001
Subtreatment	1	4.70450000	4.70450000	3.01	0.0848
Treatment*Subtreatme	2	59.27633333	29.63816667	18.95	<.0001
Replicate2	14	62.46166667	4.46154762	2.85	0.0007

Least Squares Means
Adjustment for Multiple Comparisons: Tukey

Treatment	frostap LSMEAN	LSMEAN Number
1	4.86666667	1
2	5.16833333	2
3	6.14000000	3

Least Squares Means for effect Treatment
Pr > |t| for H0: LSMean(i)=LSMean(j)

Dependent Variable: frostap

i/j	1	2	3
1		0.3855	<.0001
2	0.3855		0.0001
3	<.0001	0.0001	

Figure 15. ANOVA and multiple comparison results of baby cut carrots upon package opening (frost on product) from packaging systems within month 6

The panel perceived a difference in the appearance of frozen carrots in the nylon/PE multilayer bags for the air freezer/retail freezer sub-treatment with time as well (Figures 16 and 17). In both determinations those baby cut carrots at month 1 received higher marks than baby cut carrots at month 6. Appearance results for frost on carrots are consistent with frost determination data (Figures 6 and 7).

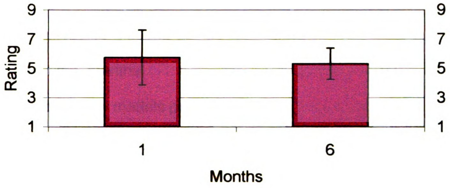

Figure 16.Results of overall appearance of baby cut carrots (after frost ice removed) for A-NPE for two months

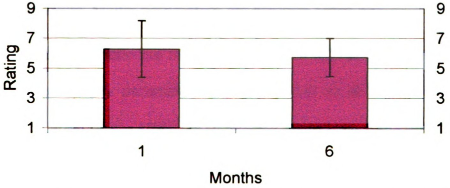

Figure 17. Results of appearance of baby cut carrots upon package opening (frost on product) for A-NPE for two months

6. Model for frost ice formation

Frost ice results were modeled using two relationships: a straight line of the form:

$$y = m\,t + w \qquad (7)$$

and a kinetic-like relationship:

$$y = b + (a-b)\exp(ct) \qquad (8)$$

Where

y = frost ice amount, %

t = time, months

a, b, m, w = models parameters

The results were modeled using a Tablecurve® 2-D V5 curve-fitting program (AISN Software, Mapleton, OR) and their graphs are shown in Appendix E. Comparing the R^2 values of both models (Tables E1 and E2), it can be seen that frost formation was satisfactorily fitted by equation (8) which is plotted in Figures 18 and 19. The more parameters of equation (8) seem to help better fit the experimental data. Model parameters are listed in Table 12.

This first-order kinetic-like model is consistent with previous work used to model other food quality parameter changes (Chen et al., 1989; Lanari and Zaritzky, 1991; Lanari et al., 1993). Both models predict the formation of frost at the beginning of the storage time, probably due in part to the freezing process.

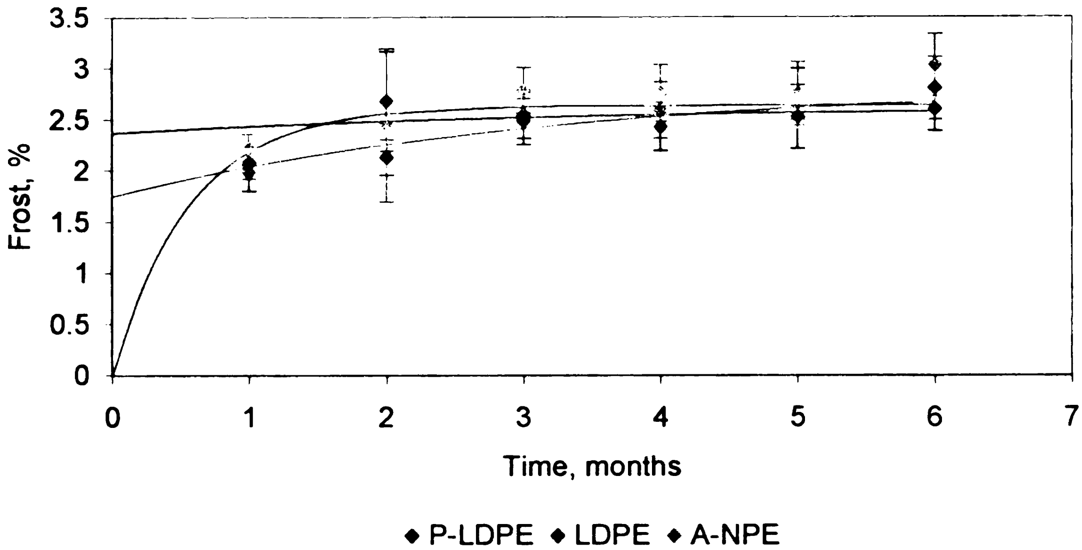

Figure 18. Kinetic-like model for frost formation for bags in air freezer/retail freezer sub-treatment

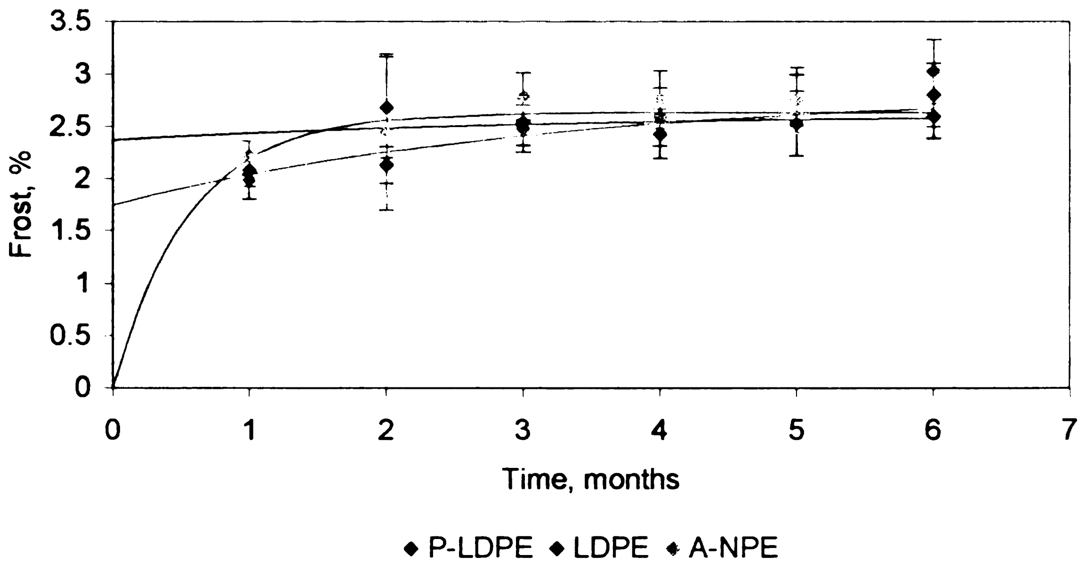

Figure 19. Kinetic-like model for frost formation for bags in air freezer sub-treatment

Table 12. Model parameters for frost formation for packed carrots under air freezer (AF) and air freezer/retail freezer (AF/RF) sub-treatments

Sub-treatment	(AF/RF)			AF		
Treatment	P-LDPE	LDPE	A-NPE	P-LDPE	LDPE	A-NPE
b, %	1.75 (0.42)[s]	1E-12 (7.93)	1.82 (0.37)	0.52 (3.80)	0.90 (1.90)	1.86 (0.33)
a, %	2.84 (0.54)	2.636 (0.11)	3.06 (0.29)	2.73 (0.09)	2.54 (0.13)	3.21 (0.28)
c, % month^{-1}	0.32 (0.43)	1.78 (3.02)	0.39 (0.31)	1.51 (1.71)	1.06 (1.12)	0.38 (0.26)
R^2	0.81	0.70	0.90	0.71	0.70	0.93

[s] Standard deviations are given in parenthesis

The first-order kinetic-like model's parameters appear to be consistent with the experimental data. Frost ice formation on frozen carrots in LDPE bags with perforations, from the air freezer sub-treatment, have a higher c value when compared to similar ones from the air freezer/retail freezer sub-treatment. This seems reasonable when we compare the average temperatures from both sub-treatments (Table 10). At the higher temperatures in the retail freezer, the frost ice tended to evaporate, lowering the c value. This could also be coupled with changes in the relative humidity inside the retail freezer due to the more routine opening of the door. However, this low c value could be misleading since there could be less visible frost ice, even though the product itself may have lost moisture.

The model parameters for carrots in non-perforated LDPE bags did not appear to differ regardless of treatment. Furthermore, it can be noted that their model parameters are not very different from those of LDPE bags with perforations and kept in the air freezer. Thus, the effect of the perforations was only noticeable when the package environment was subjected to higher temperatures and decreases in relative humidity.

Assuming that the freezing process used in this study was related to the initial formation of frost ice, it could be inferred that a different freezing process would yield different initial amounts of frost. However, the c values are probably independent of that process, and by relating them to the temperatures and package permeabilities, could be used to estimate the frost formation.

CHAPTER 4

CONCLUSIONS

The following conclusions could be made:

- With the freezing method used in this study, most of the frost ice was found to be formed at the beginning of the storage time.
- The cooling-warming cycle of a freezer may produce a net migration of moisture towards product surface and package wall that becomes frost.
- Frost ice increased with storage time.Frost decreased with perforated package material, but product dehydration was noticed when stored in these bags.
- When the package material was not perforated, the amount of frost ice in samples stored in air freezer and retail freezer cabinet was not significantly different.
- When the product is frozen inside the package, vacuum packaging promotes the formation of abundant ice with a glassy (not frosty) appearance.
- The less frost ice a package contained, the more positively it was perceived.
- Frost development may be modeled as a quality parameter

Recommendations:

The following recommendations could be made:

- Better methods to determine frost ice and glassy ice amounts should be developed.
- Evaluate the effect of the use of different freezing methods on the frost ice formation. The author believes that a freezing method with a high medium heat transfer coefficient (high freezing rate) produces less frost ice on product. Furthermore, if vacuum packing were used with slow freezing, abundant *glassy* ice would form. In this study, though carrots were uniform in size and shape, their loose, relatively rigid nature left some interstices which under vacuum increased the amount of water migration. The slow freezing process determined the length that the water remained available for migration.
- Earlier data points (immediately after frozen) should be obtained to improve modeling of data.
- The moisture content determination procedure was probably not sensitive enough for samples with such high concentrations of water making this determination difficult. An alternative approach would probably be to measure the water holding capacity of the product.

Future work:

There are many potential avenues that could be taken. If kinetic-like models want to be pursued, data modeling using temperature history would be needed. Thus, model parameters could be studied in terms of temperature changes and added variables (i.e. packaging permeability). If numerical models are of interest, one dimensional heat transfer could be assumed. Temperature history of an entire package unit should be measured. In either case, more experimental data (i.e. thermal characteristics), and improved determinations methods would be needed for the models to be accurate.

APPENDIX A

RESULTS

a) Frost ice determination results:

Table A 1. Average frost and glassy ice amounts (%) for carrots in bags exposed to air freezer/retail freezer sub-treatment after X months

Treatment	Month					
	#1	#2	#3	#4	#5	#6
V-NPE (glassy)	2.22 (0.14)[s]	2.45 (0.75)	2.79 (0.18)	2.76 (0.17)	2.75 (0.48)	3.03 (0.59)
A-NPE (frost)	3.63 (1.31)	3.48 (0.15)	5.42 (0.97)	5.91 (0.48)	5.89 (0.97)	4.71 (0.55)
LDPE (frost)	1.99 (0.06)	2.68 (0.48)	2.48 (0.22)	2.59 (0.27)	2.53 (0.31)	2.80 (0.30)
P-LDPE (frost)	2.09 (0.28)	2.13 (0.17)	2.54 (0.22)	2.43 (0.24)	2.75 (0.25)	2.60 (0.21)

[s] standard deviation

Table A 2. Average frost ice amounts (%) for carrots in bags exposed to air freezer sub-treatment after X months

Treatment	Month					
	#1	#2	#3	#4	#5	#6
V-NPE (glassy)	2.30 (0.17)[e]	2.59 (0.17)	2.67 (0.19)	3.06 (0.23)	2.98 (0.18)	3.05 (0.22)
A-NPE (frost)	3.22 (0.97)	4.25 (1.38)	5.64 (1.12)	4.90 (1.03)	4.35 (0.85)	3.67 (0.07)
LDPE (frost)	1.99 (0.13)	2.24 (0.15)	2.51 (0.18)	2.74 (0.55)	2.54 (0.59)	2.33 (0.13)
P-LDPE (frost)	2.25 (0.16)	2.60 (0.10)	2.71 (0.10)	2.91 (0.18)	2.78 (0.15)	2.53 (0.23)

[s] standard deviation

b) Color change results:

Table A 3. Average Whiteness Index values for carrots in bags exposed to air freezer/retail sub-treatment after X months

Treatment	Month					
	Initial	#2	#3	#4	#5	#6
A-NPE	31.08 (1.41)[s]	31.55 (0.77)	31.53 (0.91)	32.29 (0.91)	32.75 (0.40)	33.18 (0.65)
V-NPE	31.08 (1.41)	31.36 (1.21)	32.83 (1.05)	31.95 (1.05)	33.44 (1.09)	34.03 (0.64)
LDPE	31.08 (1.41)	30.65 (0.42)	31.92 (0.61)	32.08 (1.16)	32.81 (0.60)	33.57 (0.58)
P-LDPE	31.08 (1.41)	31.75 (0.40)	32.71 (0.43)	32.59 (0.52)	33.97 (0.28)	34.89 (0.28)

[s] standard deviation

Table A 4. Average Whiteness Index values for carrots in bags exposed to air freezer sub-treatment after X months

Treatment	Month					
	Initial	#2	#3	#4	#5	#6
A-NPE	31.08 (1.41)[s]	31.46 (0.84)	32.27 (0.70)	32.35 (0.36)	32.93 (0.34)	34.31 (0.60)
V-NPE	31.08 (1.41)	32.14 (0.85)	33.33 (0.42)	32.59 (0.88)	33.68 (0.67)	33.77 (0.83)
LDPE	31.08 (1.41)	31.86 (0.85)	32.64 (0.64)	32.87 (1.04)	33.26 (0.60)	34.09 (0.99)
P-LDPE	31.08 (1.41)	32.12 (0.87)	33.19 (0.49)	33.63 (0.74)	34.47 (0.72)	34.62 (0.66)

[s] standard deviation

c) Appearance results

Table A 5. Average rating scores for appearance of carrots upon package opening (frost on them) at month 6

Treatment	Sub-treatment	
	Air freezer/Retail	Air freezer
A-NPE	5.71 (1.29)[s]	4.03 (1.25)
LDPE	4.86 (1.14)	4.96 (1.14)
P-LDPE	6.10 (0.72)	6.70 (1.06)

[s] standard deviation

Table A 6. Average rating scores for overall appearance of carrots at month 6

Treatment	Sub-treatment	
	Air freezer/Retail	Air freezer
A-NPE	5.30 (1.08)[s]	5.27 (1.50)
LDPE	5.24 (1.35)	5.77 (1.39)
P-LDPE	5.19 (1.09)	5.51 (1.56)

[s] standard deviation

Table A 7. Average rating scores for appearance of carrots (A-NPE, air freezer sub-treatment) upon package opening (frost on them) at two different months

Month	
1	6
6.27 (1.89)^s	5.71 (1.29)

^{s} standard deviation

Table A 8. Average rating scores for overall appearance of carrots (A-NPE, air freezer sub-treatment) at two different months

Month	
1	6
5.75 (1.89)^s	5.30 (1.08)

^{s} standard deviation

APPENDIX B

STATISTICAL ANALYSIS

A Wilcoxon non-parametric model with Kruskal-Wallis test was performed for frost ice and color change evaluations. ANOVA results under general linear models were done for appearance studies. The statistical analysis was performed with a SAS 8.02 System for Windows. Tables B1 and B2 describe relate the treatment and sub-treatment code numbers used for all the statistical analyses. Next, the program script used in every case is shown.

Table B 1. Treatment code number and description

Treatment #	Description
1	carrots atmospherically packed in Nylon/PE multilayer bags
2	Carrots atmospherically packed in non-perforated LDPE bags
3	Carrots atmospherically packed in perforated LDPE bags

Table B 2. Sub-treatment code number and description

Sub-treatment #	Description
1	Air freezer/Retail
2	Air freezer

a) SAS 8.02 script for statistical analysis for frost and glassy ice ("wl") data.

```
proc import out=work.book1
   datafile="D:\wonly3.xls"
   dbms=excel2000 replace;
   getnames=yes;
   run;
   proc print;
   run;
Proc glm ;
class  Treatment Subtreatment Month;
model wl = Treatment Subtreatment Month Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/ss3  ;
/*lsmeans Treatment Subtreatment Month  Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/pdiff adjust=tukey
cl;*/
output out=pred r=resid;
run;
Proc mixed ;
class  Treatment Subtreatment Month;
model wl = Treatment Subtreatment Month Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/ddfm=satterth outp=pred
;
/*lsmeans Treatment Subtreatment Month  Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/pdiff adjust=tukey
cl;*/
run;

proc univariate data=pred plot normal;
var resid;
run;

proc print data=pred;
run;
Proc sort;
by subtreatment;
run;

proc npar1way wilcoxon;
class treatment;
by subtreatment;
var wl;
run;
```

Excel file with data in columnwise fashion

To sort by treatment, type "treatment". To sort by months type "months"

Select the class by typing "treatment", "months" or "sub-treatment"

b) SAS 8.02 script for statistical analysis for moisture content ("mc") data.

```
proc import out=work.book1
   datafile="D:\mconly3.xls"
   dbms=excel2000 replace;
   getnames=yes;
   run;
   proc print;
   run;
```

Excel file with data in columnwise fashion

```
Proc glm ;
class  Treatment Subtreatment Month;
model mc = Treatment Subtreatment Month Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/ss3  ;
/*lsmeans Treatment Subtreatment Month  Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/pdiff adjust=tukey
cl;*/
output out=pred r=resid;
run;
Proc mixed ;
class  Treatment Subtreatment Month;
model wl = Treatment Subtreatment Month Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/ddfm=satterth outp=pred
;
/*lsmeans Treatment Subtreatment Month  Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/pdiff adjust=tukey
cl;*/
run;

proc univariate data=pred plot normal;
var resid;
run;

proc print data=pred;
run;
Proc sort;
by subtreatment;
run;
```

To sort by treatment, type "treatment". To sort by months type "months"

```
proc npar1way wilcoxon;
class treatment;
by subtreatment;
var wl;
run;
```

Select the class by typing "treatment", "months" or "sub-treatment"

c) SAS 8.02 script for statistical analysis for color change evaluation (Whiteness Index – "WI")

```
proc import out=work.book1
   datafile="D:\WIonly3.xls"
   dbms=excel2000 replace;
   getnames=yes;
   run;
   proc print;
   run;
Proc glm ;
class  Treatment Subtreatment Month;
model WI = Treatment Subtreatment Month Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/ss3  ;
/*lsmeans Treatment Subtreatment Month  Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/pdiff adjust=tukey
cl;*/
output out=pred r=resid;
run;
Proc mixed ;
class  Treatment Subtreatment Month;
model WI = Treatment Subtreatment Month Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/ddfm=satterth outp=pred
;
/*lsmeans Treatment Subtreatment Month  Treatment*Subtreatment
Treatment*Month
Subtreatment*Month Treatment*Subtreatment*Month/pdiff adjust=tukey
cl;*/
run;

proc univariate data=pred plot normal;
var resid;
run;

proc print data=pred;
run;
Proc sort;
by treatment;
run;

proc npar1way wilcoxon;
class month;
by treatment;
var WI;
run;
```

Excel file with data in columnwise fashion

To sort by subtreatment, type "subtreatment". To sort by months type "months"

Select the class by typing "treatment", "months" or "sub-treatment"

d) SAS 8.02 script for statistical analysis for appearance evaluation

Appearance upon package opening (frost on carrots – "frostap"):

```
proc import out=work.book1
   datafile="D:frostaponly3.xls"
   dbms=excel2000 replace;
   getnames=yes;
   run;
   proc print;
   run;
Proc glm ;
class  Treatment Subtreatment replicate2;
model frostap = Treatment Subtreatment Treatment*Subtreatment
Replicate2/ss3  ;
lsmeans Treatment  subtreatment replicate2/pdiff adjust=tukey cl;
output out=pred r=resid;
run;
proc univariate data=pred plot normal;
var resid;
run;
proc print data=pred;
run;
```

Excel file with data in columnwise fashion

Overall appearance (after frost removed):

```
proc import out=work.book1
   datafile="D:overapponly3.xls"
   dbms=excel2000 replace;
   getnames=yes;
   run;
   proc print;
   run;
Proc glm ;
class  Treatment Subtreatment replicate2;
model overapp = Treatment Subtreatment Treatment*Subtreatment
Replicate2/ss3  ;
lsmeans Treatment  subtreatment replicate2/pdiff adjust=tukey cl;
output out=pred r=resid;
run;
Proc mixed ;
proc univariate data=pred plot normal;
var resid;
run;
proc print data=pred;
run;
```

Excel file with data in columnwise fashion

Appearance upon package opening (frost on carrots) "frostap" vs. time:

```
proc import out=work.book1
   datafile="D:frostapptime.xls"
   dbms=excel2000 replace;
   getnames=yes;
   run;
   proc print;
   run;
Proc glm ;
class month Subtreatment replicate2 replicate1;
model frostap = month Replicate1(month) replicate2 /ss3;
random Replicate1(month)/ test;
lsmeans month/pdiff adjust=tukey cl
                    e=Replicate1(month);
output out=pred r=resid;
run;
proc univariate data=pred plot normal;
var resid;
run;
proc print data=pred;
run;;
```

Excel file with data in columnwise fashion

Overall appearance (after frost removed) "overap" vs. time:

```
proc import out=work.book1
   datafile="D:overapptime.xls"
   dbms=excel2000 replace;
   getnames=yes;
   run;
   proc print;
   run;
Proc glm ;
class month Subtreatment replicate2 replicate1;
model overapp = month Replicate1(month) replicate2 /ss3;
random Replicate1(month)/ test;
lsmeans month/pdiff adjust=tukey cl
                    e=Replicate1(month);
output out=pred r=resid;
run;
proc univariate data=pred plot normal;
var resid;
run;
proc print data=pred;
run;;
```

Excel file with data in columnwise fashion

APPENDIX C

PERMEABILITY STUDIES

Tables C1 and C2 show the WVTR values (two replicates) of each film at 20, 15 and 10 °C.

Table C 1. Water vapor transmission rate (WVTR) data for the LDPE material at three temperatures: 20, 15 and 10 °C

Readings at equilibrium	Temperature (°C)					
	20.0		15.0		10.0	
	WVTR, g/(m^2 day)		WVTR, g/(m^2 day)		WVTR, g/(m^2 day)	
	Cell A	Cell B	Cell A	Cell B	Cell A	Cell B
1	1.429	1.435	0.5597	0.5697	0.5438	0.5447
2	1.426	1.425	0.5956	0.5472	0.5847	0.5397
3	1.440	1.435	0.5847	0.5255	0.5430	0.5380
4	1.390	1.419	0.5897	0.5372	0.5363	0.5347
5	1.440	1.411	0.5171	0.5205	0.5205	0.5171
6	1.424	1.452	0.5213	0.5413	0.5197	0.5338
7	1.451	1.427	0.5096	0.5472	0.5247	0.5213
8	1.461	1.472	0.5697	0.5322	0.5372	0.5413
9	1.476	1.490	0.5213	0.5163	0.5071	0.5096
10	1.457	1.472	0.5322	0.5313	0.5113	0.5205
11	1.476	1.472	0.5397	0.5639	0.5180	0.5238
12			0.5280	0.5030		
13			0.5255	0.5347		
14			0.5672	0.5280		
15			0.5664	0.5305		
16			0.5730	0.5096		
Average	1.443	1.446	0.5500	0.5336	0.5315	0.5295
Std. Deviation	0.025	0.026	0.0233	0.0171	0.0216	0.0115

Table C 2. Water vapor transmission rate (WVTR) data for the nylon/PE multiplayer material at three temperatures: 20, 15 and 10 °C

Readings at equilibrium	Temperature (°C)					
	20.0		15.0		10.0	
	WVTR, g/(m^2 day)		WVTR, g/(m^2 day)		WVTR, g/(m^2 day)	
	Cell A	Cell B	Cell A	Cell B	Cell A	Cell B
1	4.164	3.832	2.676	2.517	1.996	1.774
2	4.147	3.812	2.721	2.542	1.952	1.722
3	4.192	3.837	2.731	2.522	1.893	1.735
4	4.176	3.869	2.701	2.512	1.893	1.676
5	4.136	3.854	2.672	2.524	1.837	1.682
6	4.137	3.885	2.708	2.514	1.846	1.634
7	4.227	3.879	2.710	2.504	1.798	1.706
8	4.181	3.840	2.728	2.523	1.802	1.692
9	4.180	3.829	2.682	2.537	1.723	1.643
10	4.149	3.910	2.709	2.531	1.757	1.665
11	4.151	3.812	2.749	2.502	1.788	
12	4.202	3.853	2.732	2.521	1.749	
13	4.145	3.843	2.740	2.552	1.757	
14	4.146	3.796	2.724	2.510		
15	4.176	3.851	2.700	2.527		
16	4.179	3.871	2.699			
17	4.137	3.873	2.698			
18	4.223	3.855				
19		3.888				
Average	4.169	3.852	2.711	2.523	1.830	1.693
Std. Deviation	0.029	0.029	0.022	0.014	0.083	0.043

Tables C3 and C5 show the permeability values (average of two replicates) of each film at 20, 15 and 10 °C. Permeability values were calculated using the following equation:

$$P = \left(\frac{q}{t \times A}\right) \cdot \frac{l}{\Delta p} = WVTR \cdot \frac{l}{\Delta p} \qquad (C1)$$

Where,

WVTR = water vapor transmission rate, g/(m^2 day)

l = film thickness (both, nylon/PE multilayer and LDPE films: 3 mils)

Δp = water vapor pressure difference between the sides of the film (p_1) and (p_2), of which, p_2 = 0 mmHg (at 0%RH), and $p_1 = p_s$ (at 100% RH), where p_s is the saturated water vapor pressure at 20, 15 or 10 °C listed in tables C4 and C6. Then, $\Delta p = p_s$

Table C 3. Average permeability values for the Nylon/PE multilayer material at three temperatures: 20, 15 and 10 °C

	Temperature (°C)		
	20.0	15.0	10.0
Replicate	P, g mil/ (m^2 day mmHg)	P, g mil/ (m^2 day mmHg)	P, g mil/ (m^2 day mmHg)
A	0.713	0.636	0.596
B	0.659	0.592	0.551
Average	0.686	0.614	0.574

Table C 4. Permeability data for the Nylon/PE multilayer material at 100% RH

Temperature, °C	1/T, K^{-1}	p_s (mmHg)*	P, g mil/ (m^2 day mmHg)	ln P
10.0	0.004	9.209	0.574	-0.5554
15.0	0.003	12.788	0.614	-0.4880
20.0	0.003	17.535	0.686	-0.3766

* From Perry's chemical engineers handbook (1984)

Table C 5. Permeability values for the LDPE material at three temperatures: 20, 15 and 10 °C

	Temperature (°C)		
	20.0	15.0	10.0
Replicate	P, g mil/ (m^2 day mmHg)	P, g mil/ (m^2 day mmHg)	P, g mil/ (m^2 day mmHg)
A	0.247	0.1290	0.1731
B	0.247	0.1252	0.1725
Average	0.247	0.1271	0.1728

Table C 6. Permeability data for the LDPE material at 100% RH

Temperature, °C	1/T, K^{-1}	p_s (mmHg)*	P, g mil/ (m^2 day mmHg)	ln P
10.0	0.004	9.209	0.173	-1.7555
15.0	0.003	12.788	0.127	-2.0627
20.0	0.003	17.535	0.247	-1.3978

* From Perry's chemical engineers handbook (1984)

To calculate the activation energies for water permeation (Ep) through each film, the Arrhenius relationship listed next was used. Tables C4 and C6 show the values of ln P and 1/T plotted in graph C1 as y = m x + b.

$$\ln P = \ln P_0 \cdot + \frac{Ep}{R}\left(\frac{1}{T}\right) \qquad \text{(C2)}$$

Where,

T = temperature, K

P = film permeability, g mil/ (m^2 day mmHg)

Ep = activation energy, cal/(mol K)

R = ideal gas law constant, 1.987 cal/(mol K)

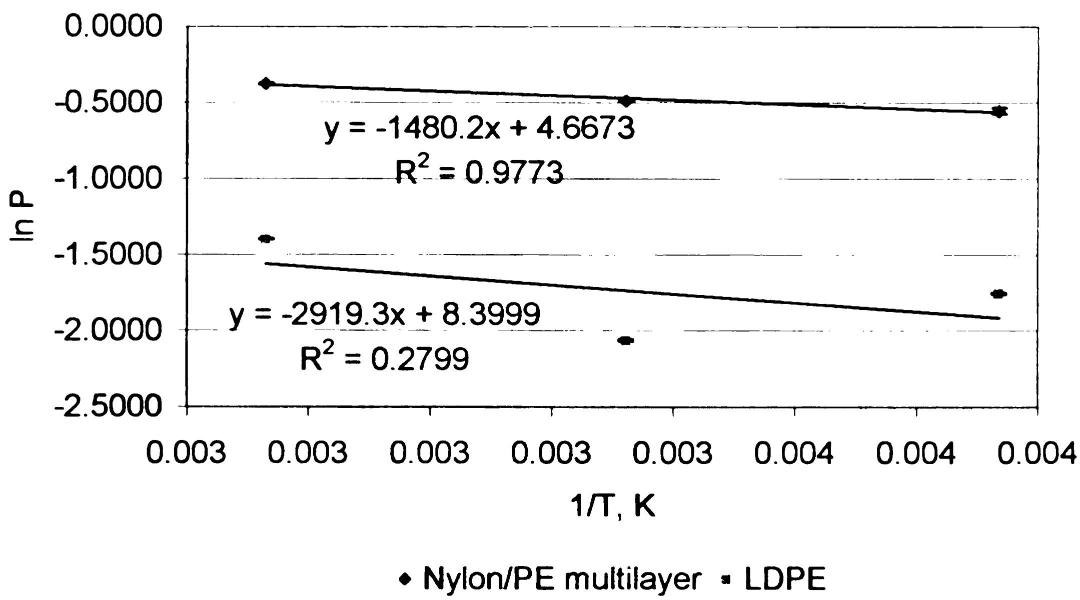

Figure C 1. ln P at 100% RH vs. 1/T

Table C7 lists the activation energy for permeation of each film, and their extrapolated water vapor permeabilities from 10 °C to 0 °C using a variation of the Arrhenius relationship

$$\ln P_2 = \ln P_1 \cdot + \frac{Ep}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{(C3)}$$

Where,

T_1 = 283.15 K

T_2 = 273.15 K

P_1 = film permeability at T_1, g mil/ (m^2 day mmHg)

P_2 = film permeability at T_2, g mil/ (m^2 day mmHg)

Ep = activation energy, cal/(mol K)

R = ideal gas law constant, 1.987 cal/(mol K)

Table C 7. Activation energies and permeability values for plastic films at 0 °C and 100% RH

Films	Slope	Ep, cal/mol	P, g mil/ (m^2 day mmHg)
LDPE	2919.3	5800.6	0.1184
Nylon/PE multilayer	1480.2	2941.2	0.4738

Table C8 show the maximum predicted amount of moisture transported through each film up to 6 months. Values of this table were calculated using the following relationship

$$q = \frac{P \cdot t \cdot A \cdot \Delta p}{l} \qquad \text{(C4)}$$

Where,

t = time, days

A = package area (both, nylon/PE multilayer and LDPE films: 0.0528 m^2)

q = amount of water permeated, g

P = film permeability at 0 °C, g mil/ (m^2 day mmHg)

l = film thickness (both, nylon/PE multilayer and LDPE films: 3 mils)

Δp = water vapor pressure difference between the sides of the film (p_1) and (p_2), of which, p_2 = 0 mmHg (at 0%RH), and $p_1 = p_s$ (at 100% RH), where p_s is the saturated water vapor pressure at 20, 15 or 10 °C listed in tables C4 and C6. Then, $\Delta p = p_s$

Table C 8. Maximum predicted amount of moisture transported through package at 100% RH and 0 °C after X months

	Month					
	1	2	3	4	5	6
q (non-perforated LDPE), g	0.2863	0.5727	0.8590	1.1454	1.4317	1.7181
q (Nylon/PE multilayer), g	1.1455	2.2910	3.4364	4.5819	5.7274	6.8729

APPENDIX D

MASS BALANCE CALCULATION AND MOISTURE CONTENT RESULTS

Notation:

W_f = frost weight, g

W_d= calculated dry matter weight, g

W_n= net weight, g

W_{wo} = calculated initial weight of water in carrots, g

W_{wf} = predicted final water weight in carrots, g

M_{Ci} = experimental initial moisture content, 87.5 %

M_{Cf}= predicted final moisture content, %

Equations for mass balance:

To calculate the initial amount of water in carrots:

$$W_{wo} = M_{Ci} * W_n$$

To calculate the final amount of water in carrots:

$$W_{wf} = W_{wo} - W_f$$

To calculate the dry matter amount:

$$W_d = W_n - W_{wo}$$

To calculate the predicted final moisture content:

$$M_{Cf} = W_{wf} * 100 / (W_{wf} + W_d)$$

Table D 1. Average frost and glassy weight values (grams) for air freezer sub-treatment for different months

	#1	#2	#3	#4	#5	#6
A-NPE	10.36	11.96	12.17	14.06	13.82	14.04
V-NPE	14.76	19.29	25.36	22.72	20.22	17.00
LDPE	8.90	10.09	11.18	12.27	11.43	10.74
P-LDPE	10.10	12.02	12.22	12.67	12.51	10.79

Table D 2. Average net weight values (grams) for air freezer sub-treatment for different months

A-NPE	450.55	462.08	455.38	459.00	464.25	460.93
V-NPE	458.43	454.05	449.38	464.00	465.08	463.30
LDPE	447.45	449.63	446.00	447.65	450.13	461.75
P-LDPE	449.33	462.25	451.38	435.70	450.70	426.48

Table D 3. Average calculated initial water amounts in carrots (grams) for air freezer sub-treatment for different months

A-NPE	394.23	404.32	398.45	401.63	406.22	403.31
V-NPE	401.12	397.29	393.20	406.00	406.94	405.39
LDPE	391.52	393.42	390.25	391.69	393.86	404.03
P-LDPE	393.16	404.47	394.95	381.24	394.36	373.17

Table D 4. Average calculated final water amounts in carrots (grams) for air freezer sub-treatment for different months

A-NPE	383.88	392.36	386.28	387.57	392.40	389.27
V-NPE	386.36	378.01	367.85	383.28	386.72	388.39
LDPE	382.62	383.33	379.07	379.43	382.43	393.29
P-LDPE	383.06	392.45	382.74	368.57	381.85	362.38

Table D 5. Average calculated dry matter weight in carrots (grams) for air freezer sub-treatment for different months

A-NPE	56.32	57.76	56.92	57.38	58.03	57.62
V-NPE	57.30	56.76	56.17	58.00	58.13	57.91
LDPE	55.93	56.20	55.75	55.96	56.27	57.72
P-LDPE	56.17	57.78	56.42	54.46	56.34	53.31

Table D 6. Average calculated final moisture content in carrots (in %) for air freezer sub-treatment for different months

A-NPE	87.21	87.17	87.16	87.11	87.12	87.11
V-NPE	87.08	86.95	86.75	86.86	86.93	87.02
LDPE	87.25	87.21	87.18	87.15	87.17	87.20
P-LDPE	87.21	87.17	87.15	87.13	87.14	87.18

Table D 7. Average experimental final moisture content in carrots (in %) for air freezer sub-treatment for different months

	#1	#2	#3	#4	#5	#6
A-NPE	85.91	84.23	85.70	85.45	85.73	84.93
V-NPE	86.37	85.20	85.41	85.00	85.63	84.51
LDPE	85.67	84.98	86.32	85.50	85.67	85.48
P-LDPE	85.87	85.28	85.50	85.44	85.76	85.13

Table D 8. Average frost weight values (grams) for air freezer/retail sub-treatment for different months

	#1	#2	#3	#4	#5	#6
A-NPE	9.99	11.23	12.85	12.50	12.75	14.36
V-NPE	16.22	15.86	24.57	27.21	27.01	21.14
LDPE	8.83	12.02	10.97	11.69	11.34	12.44
P-LDPE	8.97	9.27	11.53	10.95	12.53	10.93

Table D 9. Average net weight values (grams) for air freezer/retail sub-treatment for different months

A-NPE	449.73	458.65	460.60	452.85	463.10	474.10
V-NPE	446.43	456.03	453.23	460.58	458.80	448.53
LDPE	443.68	447.93	441.98	450.98	448.73	443.75
P-LDPE	430.00	434.50	453.60	450.43	455.53	420.78

Table D 10. Average calculated initial water amounts in carrots (grams) for air freezer/retail sub-treatment for different months

A-NPE	393.51	401.32	403.03	396.24	405.21	414.84
V-NPE	390.62	399.03	396.57	403.00	401.45	392.46
LDPE	388.22	391.93	386.73	394.60	392.63	388.28
P-LDPE	376.25	380.19	396.90	394.12	398.58	368.18

Table D 11. Average calculated final water amounts in carrots (grams) for air freezer/retail sub-treatment at different months

A-NPE	383.52	390.09	390.18	383.75	392.47	400.48
V-NPE	374.40	383.17	372.00	375.79	374.44	371.32
LDPE	379.39	379.91	375.76	382.91	381.29	375.84
P-LDPE	367.28	370.91	385.37	383.17	386.06	357.24

Table D 12. Average calculated dry matter weight in carrots (grams) for air freezer/retail sub-treatment for different months

A-NPE	56.22	57.33	57.58	56.61	57.89	59.26
V-NPE	55.80	57.00	56.65	57.57	57.35	56.07
LDPE	55.46	55.99	55.25	56.37	56.09	55.47
P-LDPE	53.75	54.31	56.70	56.30	56.94	52.60

Table D 13. Average calculated final moisture content in carrots (in %) for air freezer/retail sub-treatment for different months

A-NPE	87.22	87.19	87.14	87.15	87.15	87.11
V-NPE	87.03	87.05	86.78	86.72	86.72	86.88
LDPE	87.25	87.16	87.18	87.17	87.18	87.14
P-LDPE	87.23	87.23	87.17	87.19	87.15	87.17

Table D 14. Average experimental final moisture content in carrots (in %) for air freezer/retail sub-treatment for different months

	#1	#2	#3	#4	#5	#6
A-NPE	86.44	85.80	85.70	85.45	85.84	85.64
V-NPE	85.79	85.20	85.41	85.00	85.33	85.21
LDPE	86.50	85.20	86.32	85.50	86.20	85.81
P-LDPE	86.03	84.89	85.50	85.44	85.80	84.60

APPENDIX E

MODELS FOR FROST FORMATION

a) Model: y = m t + w

Table E 1. Model parameters for frost formation for packed carrots under air freezer and air freezer/retail sub-treatments (straight line)

Sub-treatment	Air freezer/Retail			Air freezer		
Treatment	P-LDPE	LDPE	A-NPE	P-LDPE	LDPE	A-NPE
w, %	1.99 (0.14)	2.14 (0.21)	2.18 (0.12)	2.41 (0.21)	2.11 (0.22)	2.24 (0.12)
m, % month^{-1}	0.12 (0.03)	0.11 (0.05)	0.14 (0.03)	0.06 (0.05)	0.08 (0.06)	0.15 (0.03)
R^2	0.75	0.50	0.85	0.25	0.33	0.85

[e] standard deviation

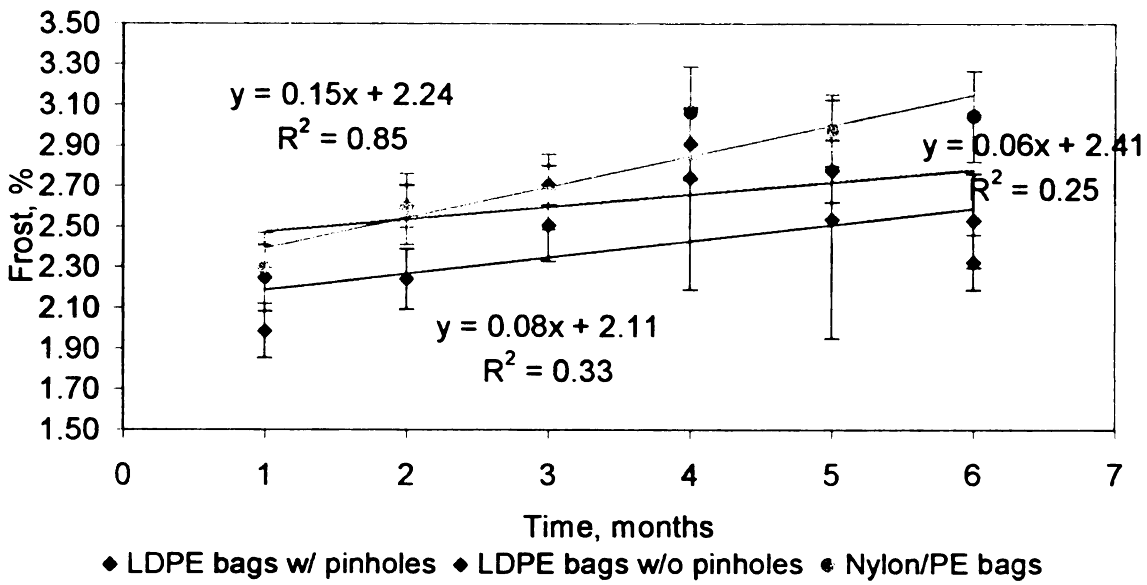

Figure E 1. Straight-line model for samples exposed to air freezer/retail sub-treatment

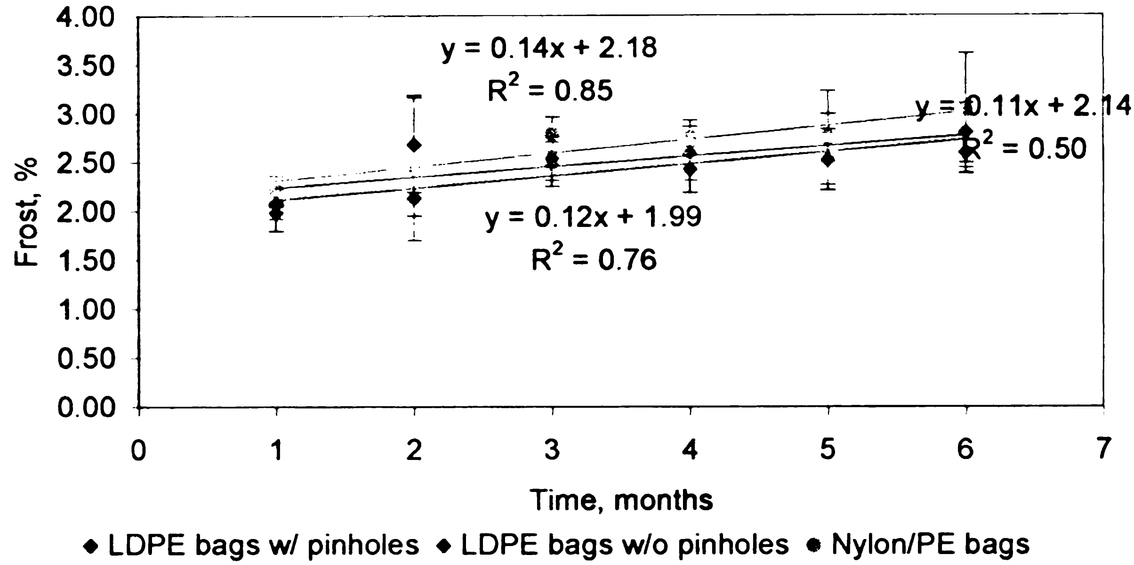

Figure E 2. Straight-line model for samples exposed to air freezer sub-treatment

b) Model: $y = b + (a-b) \exp(-ct)$

Table E 2. Model parameters for frost formation for packed carrots under air freezer and air freezer/retail sub-treatments

Sub-treatment	Air freezer/Retail			Air freezer		
Treatment	P-LDPE	LDPE	A-NPE	P-LDPE	LDPE	A-NPE
b, %	1.75 (0.42)[e]	1E-12 (7.93)	1.82 (0.37)	0.52 (3.80)	0.90 (1.90)	1.86 (0.33)
a, %	2.84 (0.54)	2.636 (0.11)	3.06 (0.29)	2.73 (0.09)	2.54 (0.13)	3.21 (0.28)
c, % month^{-1}	0.32 (0.43)	1.78 (3.02)	0.39 (0.31)	1.51 (1.71)	1.06 (1.12)	0.38 (0.26)
R^2	0.81	0.70	0.90	0.71	0.70	0.93

[e] standard deviation

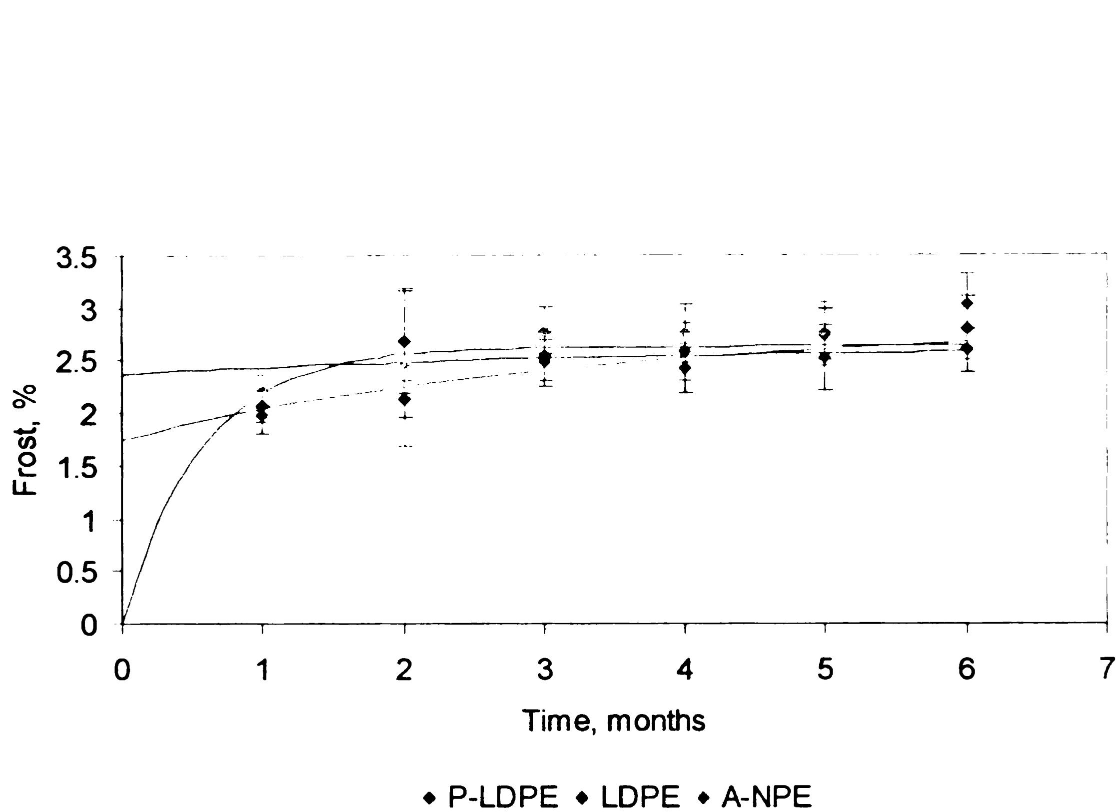

Figure E 3. Models for frost formation for bags in air freezer/retail sub-treatment

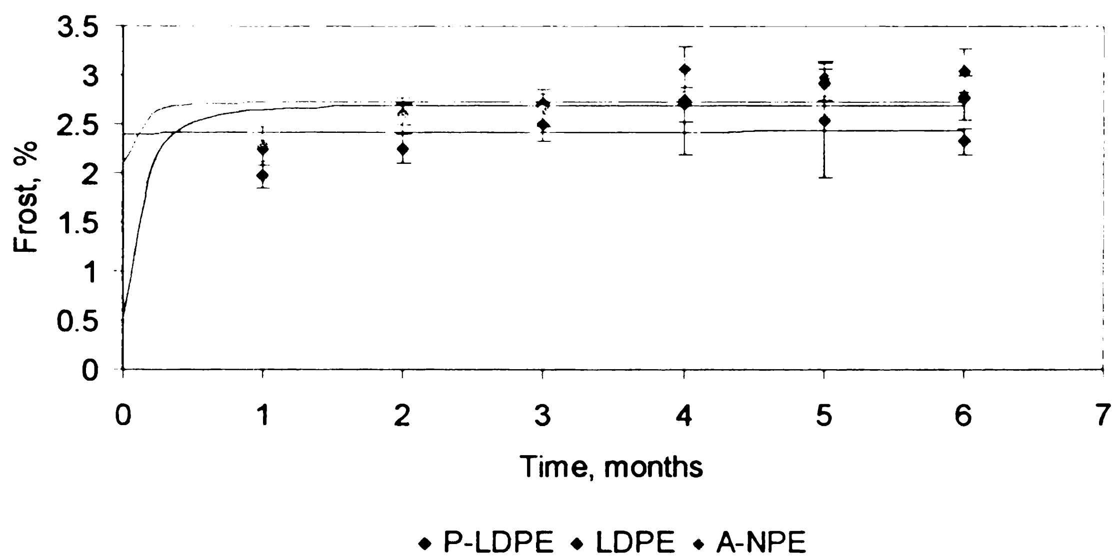

Figure E 4. Models for frost formation for bags in air freezer sub-treatment

APPENDIX F

Temperature profiles of the different sub-treatments are shown next. Figure F1 contains all the 6-month data for the air freezer sub-treatment. Figures F2 to F7 show the data for every month for the air freezer/retail freezer sub-treatment.

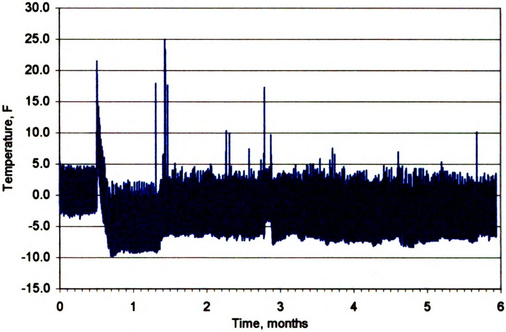

Figure F1. Temperature profile of Air freezer sub-treatment - All 6 Months

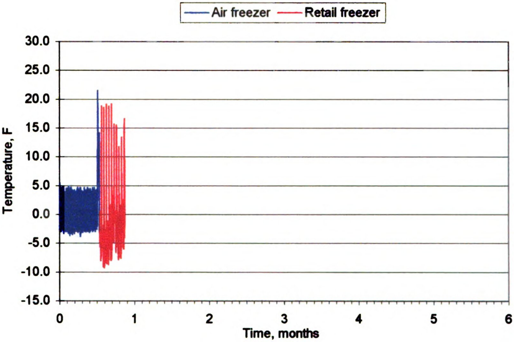

Figure F2. Temperature profile of Air freezer/Retail freezer sub-treatment - Month 1

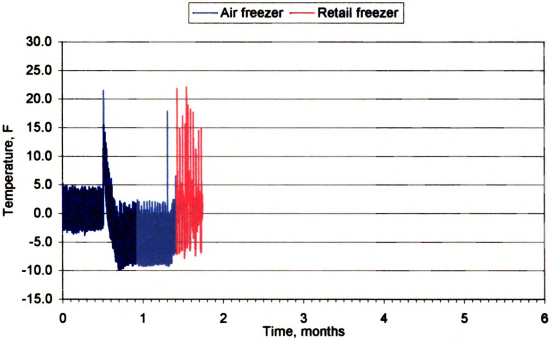

Figure F3. Temperature profile of Air freezer/Retail freezer sub-treatment - Month 2

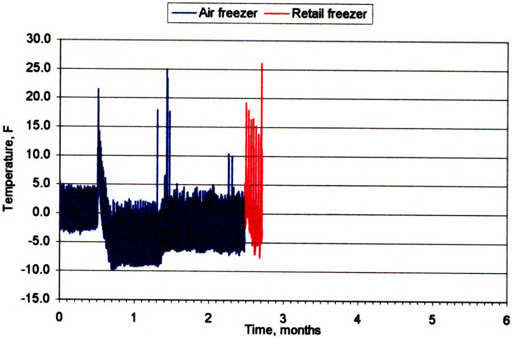

Figure F4. Temperature profile of Air freezer/Retail freezer sub-treatment - Month 3

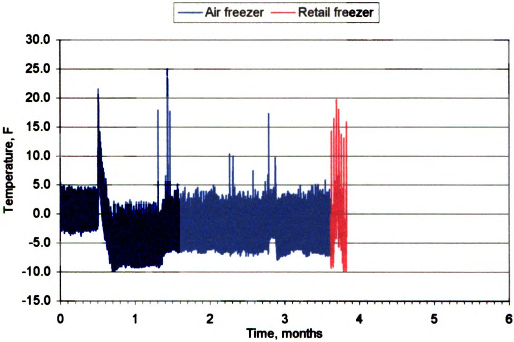

Figure F5. Temperature profile of Air freezer/Retail freezer sub-treatment - Month 4

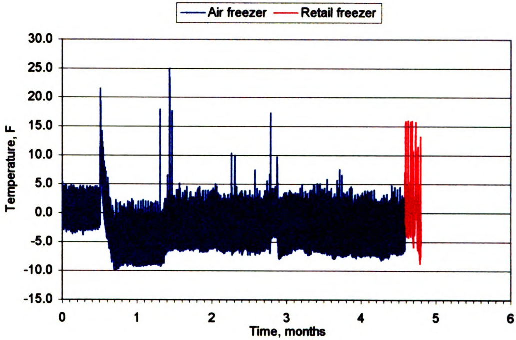

Figure F6. Temperature profile of Air freezer/Retail freezer sub-treatment - Month 5

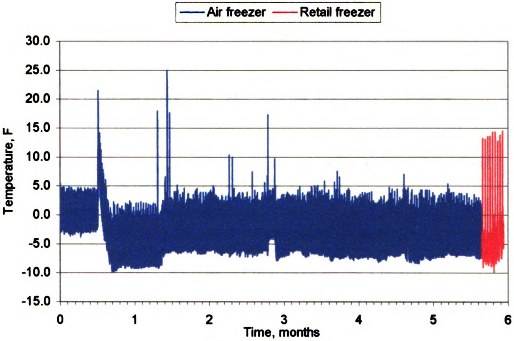

Figure F7. Temperature profile of Air freezer/Retail freezer sub-treatment - Month 6

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