



Editors
Joseph Kerry
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Smart Packaging Technologies

for
fast moving
consumer
goods



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Smart Packaging Technologies for Fast Moving Consumer Goods

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Preface

There is no official definition of smart packaging but most would agree that it is packaging that goes beyond the use of simple packaging materials combined with traditional printed features such as alphanumerics, graphics and simple barcodes. It can apply to primary, secondary, or tertiary packaging. In the literature this new type of packaging has been classified in many ways – ‘active’, ‘intelligent’, ‘smart’, ‘diagnostic’, ‘functional’ and ‘enhanced’ are all terms that have been used.

In this book, we prefer to gather all forms of packaging where the package does more than simply protect, store and give information about the product under the all-embracing term ‘smart packaging’. This definition of smart packaging therefore encompasses aspects of packaging design and the incorporation of mechanical, chemical, electrical and electronic forces, or combination of these, within the package. It includes packaging that is active in some way with or without communication to the users and it also includes the most common form of electronic smart packaging, RFID-enabled packaging. Although we have attempted to unify the book around the ‘smart packaging’ terminology, inevitably some of our authors have preferred to stick with their own familiar definitions.

Packaging needs to become smarter in the future for a number of reasons. Up to now, packaging has done an excellent job in preventing waste and getting products to customers in good condition. However, the world of consumer packaged goods is mature and the market saturated, at least in the developed world, so a new paradigm is necessary.

We live in a rapidly changing world where yesterday’s status quo is no longer good enough. At the retail store or supermarket, a sea of coloured noise greets shoppers – row upon row of near identical packaged products that fail to engage the senses, lift the spirits, educate, inspire or entertain. Responsive features are one of the most exciting aspects of smart packaging and present many opportunities to improve the consumer/packaging interface, which has remained unchanged for decades. Future packaging must offer and deliver a more compelling value proposition to the consumer, particularly in terms of convenience and on-the-go support to increasingly hectic lifestyles.

A major part of this book is devoted to the challenges and imperatives for tomorrow's packaging for the food industry. Requirements to improve food product quality and safety, enhance or stabilise food composition and nutrition, extend shelf-life product stability or build confidence, information or consumer convenience into food packs are fast becoming market demands. Future packaging formats must be designed with these requirements in mind. Numerous examples of commercially used smart packaging technologies are provided, along with research presenting current areas that are receiving a lot of attention for potential future commercial usage.

RFID-enabled packaging is a hugely important development area and consequently forms a part of this book but is not treated in great depth. We have chosen to highlight a contribution on the physics of RFID readability, and the strong influences of packaging and product materials, and a real-life successful case study in a retail application. Readers are referred to the many other publications on RFID for further details of this important technology.

Significant smart packaging opportunities exist in non-food market sectors such as pharmaceuticals, beverages, health and beauty, and household products, and these challenges are covered in subsequent chapters. Included as a separate chapter is the new and exciting technology of laser surface authentication – a potentially powerful anti-counterfeiting process for packaging. Finally the important area of legislation as it relates to smart packaging formats is explored.

Consumer benefits will ultimately drive smart packaging developments and must be clearly communicated to the consumer. The strategy of just throwing new products at consumers needs to change, and for real packaging innovation to move up marketing and advertising budgets. Smart packaging can be considered as a natural progression in package innovation for many fast moving consumer goods (FMCGs). After all, competition for shelf space has never been more intense, and the competition arena is increasingly moving from media to the point-of-purchase, making packaging more important than ever before.

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Figure 4.1 Response scale of enzymatic CheckPoint® TTI (Vitsab, Sweden).

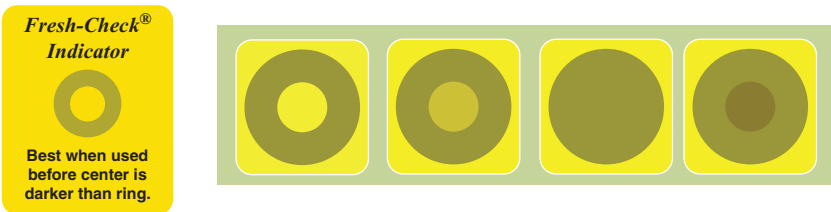


Figure 4.2 Polymer based Fresh-Check® TTI (Temptime Corp.).

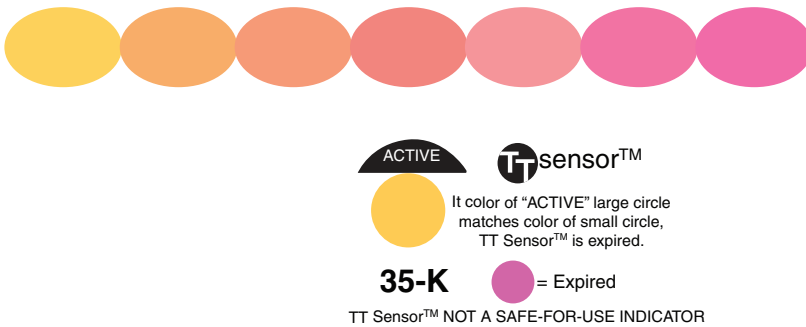


Figure 4.5 TT Sensor™ TTI (Avery Dennison Corp.).

		<u>TAG ORIENTATION</u>				
		OUTWARD	INWARD	FORWARD	UPWARD	DOWNWARD
PRODUCT	Total Tag Read % (Standard Error %)					
	EMPTY	100% (0%)	97.1% (0.8%)	100% (0%)	100% (0%)	97.8% (0.4%)
	FOAM	100% (0%)	98.6% (0.4%)	100% (0%)	100% (0%)	98.0% (0.4%)
	EMPTY BOTTLES	100% (0%)	97.0% (0.5%)	100% (0%)	100% (0%)	99.3% (0.2%)
	RICE	99.7% (0.4%)	60.5% (0.9%)	82.6% (0.6%)	82.3% (0.9%)	78.3% (1.3%)
WATER BOTTLES	67.0% (0.2%)	0.8% (0.3%)	32.3% (0.6%)	25.0% (0%)	0% (0%)	

Notes:
Data in each cell represent percentage of 1200 tag reads (25 trials of 48 cases on a pallet). For example, when the cases contained rice and the tags faced inward (to the center of the pallet rather than out), 60.5% or 726 out of 1200 total tags read correctly. A total of 25 runs (i.e. tags oriented OUT with EMPTY cases) of 25 samples (with each sample comprising a pallet of 48 cases) were made.

Significant Findings:
RED = Product Specific Yellow = Orientation Specific Orange = Both

Figure 10.4 Results of Tazelaar experiment on product/package influence on RFID readability.

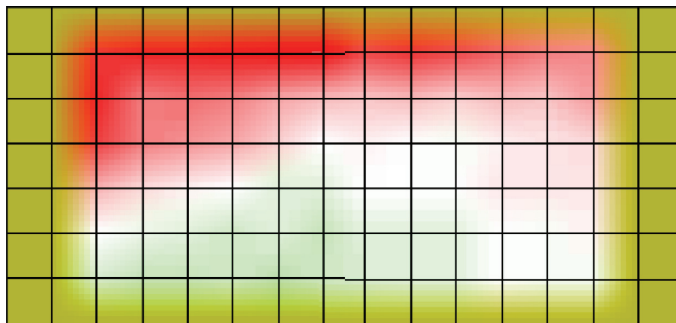


Figure 10.9 Example RFID hotspot result for one side of a case [46].

1

Active Packaging of Food

Brian P. F. Day

1.1 Introduction and Background Information

Active packaging has been variously classified in the literature by a number of differing definitions. Some of these definitions are either so broad as to include many packages that are clearly not active, or so narrow as to exclude important subsets of active packaging (Robertson, 2006). According to previous reviews, active packaging has been classified as a subset of smart packaging and referred to as the incorporation of certain additives into packaging film or within packaging containers with the aim of maintaining and extending product shelf-life (Day, 2001; 2003). However, as pointed out by Robertson (2006), this definition focuses on the additives that make a package active and hence excludes certain categories such as temperature compensating polymeric films for fresh fruit and vegetables. Another definition states that packaging may be termed active when it performs some desired role in food preservation other than providing an inert barrier to external conditions (Rooney, 1995). Robertson (2006) correctly identifies 'desired' and 'inert' as the key words in this definition, since all packaging materials, except glass, are not totally inert and can contribute undesirable components to food or absorb desirable components from food. Consequently, for the purposes of this chapter, active packaging is defined as 'packaging in which subsidiary constituents have been deliberately included in or on either the packaging material or the package headspace to enhance the performance of the package system' (Robertson, 2006). The key words here are 'deliberately' and 'enhance', and implicit in this definition is that performance of the package system includes maintaining the sensory, safety and quality aspects of the food.

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Hence, active packaging includes components of packaging systems that are capable of scavenging oxygen; absorbing carbon dioxide, moisture, ethylene and/or flavour/odour taints; releasing carbon dioxide, ethanol, antioxidants and/or other preservatives; and/or maintaining temperature control and/or compensating for temperature changes. Pira International Ltd estimated the global value of the total active packaging market in 2005 to be worth \$1.558 billion and has forecasted this market in 2010 to be worth \$2.649 billion (Anon., 2005e). Table 1.1 lists examples of active packaging systems, some of which may offer extended shelf-life opportunities for new categories of food products (Day, 2003; Rooney, 1995; Brody, 2005; Robertson, 2006).

Active packaging has been used with many food products and is being tested with numerous others. Table 1.1 lists some of the food applications that have benefited from active packaging technology. It should be noted that all food products have a unique deterioration mechanism that must be understood before applying this technology. The shelf-life of packaged food is dependent on numerous factors such as the intrinsic nature of the food (e.g. pH, water activity, nutrient content, occurrence of antimicrobial compounds, redox potential, respiration rate and biological structure) and extrinsic factors (e.g. storage temperature, relative humidity and the surrounding gaseous composition). These factors will directly influence the chemical, biochemical, physical and microbiological spoilage mechanisms of individual food products and their achievable shelf-lives. By carefully considering all of these factors, it is possible to evaluate existing and developing active packaging technologies and apply them for maintaining the quality and extending the shelf-life of different food products (Day, 2001).

Active packaging is not synonymous with intelligent packaging, which simplistically refers to packaging that senses and informs (Day, 2003). Robertson (2006) defines intelligent packaging as packaging that contains an external or internal indicator to provide information about aspects of the history of the package and/or quality of the food. Intelligent packaging devices are capable of sensing and providing information about the function and properties of packaged food and can provide assurances of pack integrity, tamper evidence, product safety and quality, as well as being utilised in applications such as product authenticity, anti-theft and product traceability. Intelligent packaging devices include time–temperature indicators, gas sensing dyes, microwave doneness indicators, microbial growth indicators, physical shock indicators, and numerous examples of tamper proof, anti-counterfeiting and anti-theft technologies (Day, 2001; Robertson, 2006).

It should be noted that there is a certain grey area with regards to what constitutes active and/or intelligent packaging (Brody, 2005; Robertson, 2006). The vast majority of consumers could not tell the difference and probably do not care so long as the packaging is safe and functional (Kerry, personal communication). Smart packaging can be considered an all-embracing term used to encompass both active and intelligent packaging, as well functional and emotional packaging in addition to clever packaging design (Kerry and Butler, foreword of this book; Robertson, 2006).

The intention of this chapter is to provide an overview of active packaging and to describe briefly the different types of device, the scientific principles behind them, the principal food applications and some of the food safety and regulatory issues that need to be considered by potential users. The major focus of this chapter is on oxygen scavengers but other active packaging technologies are described and some recent developments are highlighted. More detailed information on active packaging can be obtained from some of the other chapters in this book as well as the references listed.

Table 1.1 Selected examples of active packaging systems

Active packaging system	Mechanisms	Food applications
Oxygen scavengers	Iron based Metal/acid Nylon MXD6 Metal (e.g. platinum) catalyst Ascorbate/metallic salts Enzyme based	Bread, cakes, cooked rice, biscuits, pizza, pasta, cheese, cured meats and fish, coffee, snack foods, dried foods and beverages
Carbon dioxide scavengers/emitters	Iron oxide/calcium hydroxide Ferrous carbonate/metal halide Calcium oxide/activated charcoal Ascorbate/sodium bicarbonate	Coffee, fresh meats and fish, nuts and other snack food products and sponge cakes
Ethylene scavengers	Potassium permanganate Activated carbon Activated clays/zeolites	Fruit, vegetables and other horticultural products
Preservative releasers	Organic acids Silver zeolite Spice and herb extracts BHA/BHT antioxidants Vitamin E antioxidant Chlorine dioxide/sulphur dioxide	Cereals, meats, fish, bread, cheese, snack foods, fruit and vegetables
Ethanol emitters	Encapsulated ethanol	Pizza crusts, cakes, bread, biscuits, fish and bakery products
Moisture absorbers	PVA blanket Activated clays and minerals Silica gel	Fish, meats, poultry, snack foods, cereals, dried foods, sandwiches, fruit and vegetables
Flavour/odour absorbers	Cellulose triacetate Acetylated paper Citric acid Ferrous salt/ascorbate Activated carbon/clays/zeolites	Fruit juices, fried snack foods, fish, cereals, poultry, dairy products and fruit
Temperature control packaging	Non-woven plastics Double-walled containers Hydrofluorocarbon gas Quicklime/water Ammonium nitrate/water Calcium chloride/water Super corroding alloys/salt water Potassium permanganate/glycerine	Ready meals, meats, fish, poultry and beverages
Temperature compensating films	Side chain crystallisable polymers	Fruit, vegetables and other horticultural products

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1.2 Oxygen Scavengers

Oxygen can have considerable detrimental effects on foods. Oxygen scavengers (also referred to as oxygen absorbers) can therefore help maintain food product quality by decreasing food metabolism, reducing oxidative rancidity, inhibiting undesirable oxidation of labile pigments and vitamins, controlling enzymic discoloration and inhibiting the growth of aerobic microorganisms (Day, 2001; Rooney, 1995, 2005).

Oxygen scavengers are becoming increasingly attractive to food manufacturers and retailers and the growth outlook for the global market is bullish. Pira International Ltd estimated the global oxygen scavenger market to be 12 billion units in Japan, 500 million in the USA and 300 million in Western Europe in 2001. This market was forecast to grow to 14.4 billion in Japan, 4.5 billion in the USA and 5.7 billion in Western Europe in 2007 (Anon., 2004a). In addition, Pira International Ltd. estimated the global value of this market in 2005 to be worth \$588 million and has forecast this market to be worth \$924 million in 2010 (Anon., 2005e). The increasing popularity of oxygen scavenging polyethylene terephthalate (PET) bottles, bottle caps and crowns for beers and other beverages has greatly contributed to this impressive growth (Anon., 2005e).

Oxygen scavengers are the most commercially important sub-category of active packaging for food products and the most well known take the form of small sachets containing various iron based powders containing an assortment of catalysts. These chemical systems often react with water supplied by the food to produce a reactive hydrated metallic reducing agent that scavenges oxygen within the food package and irreversibly converts it to a stable oxide. The iron powder is separated from the food by keeping it in a small, highly oxygen permeable sachet that is labelled 'Do not eat' and includes a diagram illustrating this warning. The main advantage of using such oxygen scavengers is that they are capable of reducing oxygen levels to less than 0.01 % which is much lower than the typical 0.3–3.0 % residual oxygen levels achievable by modified atmosphere packaging (MAP). Oxygen scavengers can be used alone or in combination with MAP. Their use alone eliminates the need for MAP machinery and can increase packaging speeds. However, it is usually more common commercially to remove most of the atmospheric oxygen by MAP and then use a relatively small and inexpensive scavenger to mop up the residual oxygen remaining within the food package (Day, 2003; Robertson, 2006).

Non-metallic oxygen scavengers have also been developed to alleviate the potential for metallic taints being imparted to food products. The problem of inadvertently setting off in-line metal detectors is also alleviated even though some modern detectors can now be tuned to phase out the scavenger signal whilst retaining high sensitivity for ferrous and non-ferrous metallic contaminants. Non-metallic scavengers include those that use organic reducing agents such as ascorbic acid, ascorbate salts or catechol. They also include enzymic oxygen scavenger systems using either glucose oxidase or ethanol oxidase, which could be incorporated into sachets, adhesive labels or immobilised onto packaging film surfaces (Day, 2003).

Oxygen scavengers were first marketed in Japan in 1976 by the Mitsubishi Gas Chemical Co. Ltd under the trade name Ageless™. Since then, several other Japanese companies, including Toppa Printing Co. Ltd and Toyo Seikan Kaisha Ltd, have entered the market but Mitsubishi still dominates the oxygen scavenger business in Japan (Rooney, 1995; 2005). Oxygen scavenger technology has been successful in Japan for a variety of reasons including

the acceptance by Japanese consumers of innovative packaging and the hot and humid climate in Japan during the summer months, which is conducive to mould spoilage of food products. As pointed out by Robertson (2006), the acceptance of innovative packaging is the most likely reason why oxygen scavengers have been a commercial success in Japan. In contrast to the Japanese market, the acceptance of oxygen scavengers in North America and Europe has been relatively slow, although several manufacturers and distributors of oxygen scavengers are now established in both these continents (Rooney, 1995, 2005; Brody, 2005). Table 1.2 lists selected manufacturers and trade names of oxygen scavengers, including some that are still under development or have been suspended because of regulatory controls (Day, 2003; Rooney, 1995; 1998; 2005).

It should be noted that discrete oxygen scavenging sachets suffer from the disadvantage of possible accidental ingestion of the contents by the consumer and this has hampered their commercial success, particularly in North America and Europe. However, in the last few years, the development of oxygen scavenging adhesive labels that can be adhered to the inside of packages and the incorporation of oxygen scavenging materials into laminated trays and plastic films have enhanced and will help the commercial acceptance of this technology. For example, Marks & Spencer Ltd was the first UK retailer to use oxygen scavenging adhesive labels for a range of sliced cooked and cured meat and poultry products, which are particularly sensitive to deleterious light and oxygen-induced colour changes (Day, 2001). Other UK retailers, distributors and caterers are using these labels for the above food products as well as for coffee, pizzas, speciality bakery goods and dried food ingredients (Hirst, 1998). Other common food applications for oxygen-scavenger labels and sachets include cakes, breads, biscuits, croissants, fresh pastas, cured fish, tea, powdered milk, dried egg, spices, herbs, confectionery and snack food. (Day, 2001). In Japan, Toyo Seikan Kaisha Ltd has marketed a laminate containing an iron based oxygen scavenger which can be thermoformed into an Oxyguard™ tray that has been used commercially for cooked rice.

The use of oxygen scavengers for beer, wine and other beverages is potentially a huge market that has only recently begun to be exploited. Iron-based label and sachet scavengers cannot be used for beverages or high water activity (a_w) foods because when wet, their oxygen scavenging capability is rapidly lost. Instead, various non-metallic reagents and organo-metallic compounds that have an affinity for oxygen have been incorporated into bottle closures, crown and caps or blended into polymer [usually polyester (PET)] materials so that oxygen is scavenged from the bottle headspace and any ingressing oxygen is also scavenged. The PureSeal™ oxygen scavenging bottle crowns (produced by W.R. Grace Co., Inc. USA), oxygen scavenging plastic (PET) beer bottles (manufactured by Continental PET Technologies, USA), OS2000® cobalt catalysed oxygen scavenger films (produced by Cryovac Sealed Air Corporation, USA) and light activated ZrO_2 ® oxygen scavenger materials (developed by Food Science Australia, North Ryde, NSW, Australia) are just four of many oxygen scavenger developments aimed at the beverage market but which are also applicable to other food applications (Rooney, 1995; 1998; 2000; 2005; Scully and Horsham, 2005). However, it should be noted that the speed and capacity of oxygen scavenging plastic films and laminated trays are considerably lower compared with iron-based oxygen scavenger sachets or labels (Hirst, 1998).

More detailed information on the technical requirements (i.e. for low, medium and high a_w foods and beverages; speed of reaction; storage temperature; oxygen scavenging capacity

Table 1.2 *Selected oxygen scavenger systems*

Manufacturer	Country	Trade name	Scavenger mechanism	Packaging form
Mitsubishi Gas Chemical Co. Ltd	Japan	Ageless	Iron based	Sachets and labels
Toppan Printing Co. Ltd	Japan	Freshilizer	Iron based	Sachets
Toagosei Chem. Industry Co. Ltd	Japan	Vitalon	Iron based	Sachets
Nippon Soda Co. Ltd	Japan	Seagul	Iron based	Sachets
Finetec Co. Ltd	Japan	Sanso-Cut	Iron based	Sachets
Toyo Seikan Kaisha Ltd.	Japan	Oxyguard	Iron based	Plastic trays
Ueno Seiyaku Co. Ltd.	Japan	Oxyeater	Iron based	Sachets and labels
Multisorb Technologies, Inc.	USA	FreshMax	Iron based	Labels
		FreshPax	Iron based	Labels
		Fresh Pack	Iron based	Labels
M&G	Italy	ActiTUF	Iron based	Polyester bottles
Ciba Speciality Chemicals	Switzerland	Shelfplus O ₂	PET copolyester	Plastic film, bottles and containers
Chevron Chemicals	USA	N/A	Benzyl acrylate	Plastic film
W.R. Grace Co. Ltd	USA	PureSeal	Ascorbate/ Metallic salts	Bottle crowns
Grace Darex Packaging Technologies	USA	DarExtend	Ascorbate	Bottle crowns
Food Science Australia	Australia	ZerO ₂	Photosensitive dye/organic compound	Plastic film, bottles and containers
CMB Technologies	France	Oxbar	Cobalt catalysed polymer oxidation	Plastic bottles
Cryovac Sealed Air Corporation	USA	OS2000 OS1000	Cobalt catalysed polymer oxidation	Plastic films
Standa Industrie	France	ATCO	Iron based	Sachets
		Oxycap	Iron based	Bottle crowns
EMCO Packaging Systems	UK	ATCO	Iron based	Labels
Johnson Matthey Plc	UK	N/A	Platinum group metal catalyst	Labels
Bioka Ltd	Finland	Bioka	Enzyme based	Sachets
Alcoa CSI Europe	UK	O ₂ -Displacer System	Unknown	Bottle crowns

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and necessary packaging criteria) of the different types of oxygen scavenger can be obtained from the manufacturers and suppliers, as well as Rooney (1995; 1998; 2000), Labuza and Breene (1989) and Brody (2005).

1.2.1 ZerO₂[®] Oxygen Scavenging Materials

As a case study, brief details of the ZerO₂[®] oxygen scavenging development are described here (Rooney, 2000; Scully and Horsham, 2005). ZerO₂[®] is the registered trade name for a range of oxygen scavenging plastic packaging materials that are inactive until activated and thus can be subjected to conventional extrusion-based converting processes in the manufacture of packaging such as film, sheet, coatings, adhesives, lacquers, bottles, closure liners and can coatings. This patented technology is based on research undertaken at Food Science Australia (North Ryde, NSW, Australia).

Packaging problems involving the need for oxygen scavenging may be divided into two classes based on the origin of the oxygen that needs to be removed. Firstly, headspace and dissolved oxygen is present at the time of sealing of most packages of food and beverages. Removal of some or all of this oxygen is required to inhibit the various food degradation processes that occur in such food. A headspace oxygen scavenger is required in this case. Secondly, the oxygen that enters a package by permeation or leakage after package sealing needs to be removed, preferably before contacting the food. The oxygen scavenger required in this case is a chemically enhanced barrier. Prototype ZerO₂[®] headspace scavenging polymer compositions to meet these two requirements have been synthesised from food-grade commercial polymers and extruded into film. Oxygen scavenging from the gas phase can be made to occur within minutes at retort temperatures and within several hours to one or two days at room temperature. Oxygen scavenging to very low levels under refrigeration temperatures can require two or more days, as expected when gas diffusion into the polymer is slowed.

Beverages are particularly susceptible to quality degradation due to oxidation or, in some cases, due to microbial growth. Distribution can require shelf-lives of up to a year under ambient conditions in some cases, resulting in a need for an enhanced oxygen barrier for plastics. The conditions found in liquid paperboard cartons, laminate pouches or multilayer barrier bottles were studied (Rooney, 2000; Zerdin *et al.*, 2003) in collaboration with TNO Food Science and Nutrition (Zeist, The Netherlands). Experimental conditions were chosen using pouches of a laminate including an ethylene vinyl alcohol (EVOH) layer with an experimental ZerO₂[®] layer on the inside (with an EVOH/polyethylene laminate as control). The test beverage was orange juice and, in the control packs, the dissolved oxygen concentration decreased from 8 to 0 ppm, due to reaction with the ascorbic acid (vitamin C), over a month at 25 °C and 75 days at 4 °C. At both temperatures, the ZerO₂[®] laminate removed the oxygen in less than three days and halved the loss of the vitamin C over a storage period of one year. Browning was also reduced by one third after one year at 25 °C (Rooney, 2000; Scully and Horsham, 2005).

Alcoholic beverages, such as beer and white wine, are also susceptible to rapid oxidative degradation. Using ZerO₂[®] materials, shelf life extensions of at least 33 % have been demonstrated for bag-in-box wine. Cheese and processed meats are examples of refrigerated foods that are normally packaged under modified atmospheres. It is the headspace oxygen that severely limits the storage life of these products. Cheese normally requires the

presence of carbon dioxide as well as an oxygen level below 1 %. Results of packaging in laminates with and without a ZrO_2 ® layer have demonstrated that the common spoilage moulds can be inhibited completely with little or no carbon dioxide. Also, discolouring of sliced smoked ham can be inhibited under refrigerated cabinet lighting conditions when the packaging laminate scavenges the initial oxygen concentration of 4 % to very low levels. Development of ZrO_2 ® polymers with 'glass-like' barrier properties is aimed at inhibiting the widest range of oxygen-mediated food degradation processes. Examples studied so far have demonstrated that some fast oxidative degradation reactions can be successfully inhibited. It is likely that the use of such oxygen scavenging packaging materials will influence the consumer trend away from glass and metals towards plastic containers for the packaging of oxygen-sensitive beverages such as beer, wine and juices (Rooney, 2000; Scully and Horsham, 2005).

1.3 Carbon Dioxide Scavengers/Emitters

Many commercial sachet and label devices can be used either to scavenge or emit carbon dioxide. The use of carbon dioxide scavengers is particularly applicable for fresh roasted or ground coffees, which produce significant volumes of carbon dioxide. Fresh roasted or ground coffees cannot be left unpackaged since they will absorb moisture and oxygen and lose desirable volatile aromas and flavours. However, if coffee is hermetically sealed in packs directly after roasting, the carbon dioxide released will build up within the packs and eventually cause them to burst. To circumvent this problem, two solutions are currently used. The first is to use packaging with patented one-way valves that will allow excess carbon dioxide to escape. The second solution is to use a carbon dioxide scavenger or a dual-action oxygen and carbon dioxide scavenger system. A mixture of calcium oxide and activated charcoal has been used in polyethylene-lined coffee pouches to scavenge carbon dioxide but dual-action oxygen and carbon dioxide scavenger sachets and labels are more common and are commercially used for canned and foil pouched coffees in Japan and the USA (Day, 2003; Rooney, 1995). These dual-action sachets and labels typically contain iron powder for scavenging oxygen and calcium hydroxide, which scavenges carbon dioxide when it is converted to calcium carbonate under sufficiently high humidity conditions (Rooney, 1995). Commercially available dual-action oxygen and carbon dioxide scavengers are available from Japanese manufacturers, e.g. Mitsubishi Gas Chemical Co. Ltd (Ageless™ type E and Fresh Lock™) and Toppa Printing Co. Ltd (Freshilizer™ type CV). An innovative dual action carbon dioxide scavenger and oxygen emitter sachet has been developed by EMCO Packaging Systems Ltd (Worth, Kent, UK) to counteract respiration in high oxygen MAP of fresh-cut produce (Anon., 2003e; Hirst, 1998; Parker, 2002).

Carbon dioxide emitting sachet and label devices can either be used alone or combined with an oxygen scavenger. An example of the former is the Verifrais™ package that has been manufactured by SARL Codimer (Paris, France) and used for extending the shelf-life of fresh meats and fish. This innovative package consists of a standard MAP tray that has a perforated false bottom under which a porous sachet containing sodium bicarbonate/ascorbate is positioned. When juice exudate from MA packed meat or fish drips onto the sachet, carbon dioxide is emitted and this antimicrobial gas can replace the carbon dioxide already absorbed by the fresh food, so avoiding pack collapse (Rooney, 1995).

Pack collapse or the development of a partial vacuum can also be a problem for foods packed with an oxygen scavenger. To overcome this problem, dual-action oxygen scavenger/carbon dioxide emitter sachets and labels have been developed that absorb oxygen and generate an equal volume of carbon dioxide. These sachets and labels usually contain ferrous carbonate and a metal halide catalyst although non-ferrous variants, such as ascorbate and sodium hydrogen carbonate, are available. Commercial manufacturers include Mitsubishi Gas Chemical Co. Ltd (Ageless™ type G), and Multisorb Technologies, Inc. (FreshPax® type M). The main food applications for these dual-action oxygen scavenger/carbon dioxide emitter sachets and labels have been with snack food products (e.g. nuts) and sponge cakes (Rooney, 1995; Day, 2003).

Carbon dioxide scavengers and emitters represent a relatively small but growing area of the active packaging market. Pira International Ltd estimated the total global market to be worth \$121 million in 2005 and forecast this market to increase to \$182 million in 2010 (Anon., 2005e). Dual-action combination lines account for the majority of sales. The growth and development of this market is likely to revolve around the development of films that incorporate carbon dioxide scavenger/emitter functionality, although research into this is still in its early stages (Anon., 2003e).

1.4 Ethylene Scavengers

Ethylene is a plant hormone that accelerates the respiration rate and subsequent senescence of horticultural products such as fruit, vegetables and flowers. Many of the effects of ethylene are necessary (e.g. induction of flowering in pineapples and colour development in citrus fruits, bananas and tomatoes) but in most horticultural situations it is desirable to remove ethylene or to suppress its effects. Consequently, much research effort has been undertaken to incorporate ethylene scavengers into fresh produce packaging and storage areas. Some of this effort has met with commercial success, but much of it has not (Rooney, 1995; Day, 2003; Scully and Horsham, 2005). Nevertheless, Pira International Ltd estimated the global value of the ethylene scavenging market in 2005 to be worth \$62 million and has forecast this market in 2010 to be worth \$121 million (Anon., 2005e).

Table 1.3 lists selected ethylene scavenger systems. Effective systems utilise potassium permanganate immobilised on an inert mineral substrate such as alumina or silica gel. Potassium permanganate oxidises ethylene to acetate and ethanol and in the process changes colour from purple to brown, and hence indicates its remaining ethylene scavenging capacity. Potassium permanganate-based ethylene scavengers are available in sachets to be placed inside blankets or tubes that can be placed in produce storage warehouses (Rooney, 1995; Labuza and Breene, 1989; Day, 2003).

Activated carbon-based scavengers with various metal catalysts can also effectively remove ethylene. They have been used to scavenge ethylene from produce warehouses or are incorporated into sachets for inclusion into produce pack, and embedded into paper bags or corrugated board boxes for produce storage. A dual-action ethylene scavenger and moisture absorber has been marketed in Japan by Sekisui Jushi Limited. Neupalon™ sachets contain activated carbon, a metal catalyst and silica gel and are capable of scavenging ethylene as well as acting as a moisture absorber (Rooney, 1995; Labuza and Breene, 1989; Day, 2003).

Table 1.3 *Selected ethylene scavenger systems*

Manufacturer	Country	Trade name	Scavenger mechanism	Packaging form
Air Repair Products, Inc.	USA	N/A	Potassium permanganate	Sachets/blankets
Ethylene Control, Inc.	USA	N/A	Potassium permanganate	Sachets/blankets
Extenda Life Systems	USA	N/A	Potassium permanganate	Sachets/blankets
Kes Irrigations Systems	USA	Bio-Kleen	Titanium dioxide catalyst	Not known
Sekisui Jushi Ltd	Japan	Neupalon	Activated carbon	Sachet
Honshu Paper Ltd	Japan	Hatofresh	Activated carbon	Paper/board
Mitsubishi Gas Chemical Co. Ltd	Japan	Sendo-Mate	Activated carbon	Sachets
Cho Yang Heung San Co. Ltd	Korea	Orega	Activated clays/zeolites	Plastic film
Evert-Fresh Corporation	USA	Evert-Fresh	Activated zeolites	Plastic film
Odja Shoji Co. Ltd	Japan	BO Film	Crysburite ceramic	Plastic film
PEAKfresh Products Ltd	Australia	PEAKfresh	Activated clays/zeolites	Plastic film
Grofit Plastics	Israel	Bio-fresh	Activated clays/zeolites	Plastic film
Food Science Australia	Australia	N/A	Tetrazine derivatives	Plastic film

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In recent years, numerous produce packaging films and bags have appeared on the market place that are based on the putative ability of certain finely ground minerals to scavenge ethylene and to emit antimicrobial far-infrared radiation. However, little direct evidence for these effects has been published in peer-reviewed scientific journals. Typically these activated earth-type minerals include clays, pumice, zeolites, coral, ceramics and even Japanese Oya stone. These minerals are embedded or blended into polyethylene film bags which are then used to package fresh produce. Manufacturers of such bags claim extended shelf-life for fresh produce partly due to the three-dimensional absorption or two-dimensional surface adsorption of ethylene by the minerals dispersed within the bags. The evidence offered in support of this claim is generally based on the extended shelf-life of produce and reduction of headspace ethylene in mineral-filled bags in comparison with common polyethylene bags. However, independent research has shown that the gas permeability of mineral-filled polyethylene bags is much greater and consequently ethylene will diffuse out of these bags much faster, as is also the case for commercially available microperforated film bags. In addition, a more favourable equilibrium modified atmosphere is likely to develop within these bags compared with common polyethylene bags, especially if the produce has a high respiration rate. Therefore, these effects can improve produce shelf-life and reduce headspace ethylene independently of any ethylene absorption or adsorption. In fact, almost any powdered mineral can confer such effects without relying on expensive Oya stone or other speciality minerals (Rooney, 1995; Labuza and Breene, 1989; Day, 2003).

1.5 Ethanol Emitters

Ostensibly, ethanol emitters are a sub-set of preservative releasing technologies although ethanol emitters are usually in sachet forms as opposed to impregnated preservative releasing films. The use of ethanol as an antimicrobial agent is well documented. It is particularly

effective against mould but can also inhibit the growth of yeasts and bacteria. Several reports have demonstrated that the mould-free shelf-life of bakery products can be significantly extended after spraying with 95 % ethanol to give concentrations of 0.5–1.5 % (w/w) in the products. However, a more practical and safer method of generating ethanol is through the use of ethanol emitting sachets (Rooney, 1995; Labuza and Breene, 1989; Day, 2003; Anon., 2003f).

Many applications of ethanol emitting sachets have been patented, primarily by Japanese manufacturers. These include Ethicap™, Antimold 102™ and Negamold™ (Freund Industrial Co. Ltd), Oitech™ (Nippon Kayaku Co. Ltd), ET Pack™ (Ueno Seiyaku Co. Ltd), Oytech L (Ohe Chemicals Co. Ltd) and Ageless™ type SE (Mitsubishi Gas Chemical Co. Ltd). All of these films and sachets contain absorbed or encapsulated ethanol in a carrier material that allows the controlled release of ethanol vapour. For example, Ethicap™, which is the most commercially popular ethanol emitter in Japan, consists of food grade alcohol (55 %) and water (10 %) absorbed onto silicon dioxide powder (35 %) and contained in a sachet made of a paper and ethyl vinyl acetate (EVA) copolymer laminate. To mask the odour of alcohol, some sachets contain traces of vanilla or other flavours. The sachets are labelled 'Do not eat' and include a diagram illustrating this warning. Other ethanol emitters such as Negamould™ and Ageless™ type SE are dual-action sachets that scavenge oxygen as well as emitting ethanol vapour (Rooney, 1995; Labuza and Breene, 1989; Day, 2003; Anon., 2003f).

The size and capacity of the ethanol emitting sachet used depends on the weight of food, the a_w of the food and the desired shelf-life required. When food is packed with an ethanol emitting sachet, moisture is absorbed by the food and ethanol vapour is released and diffuses into the package headspace. Ethanol emitters are used extensively in Japan to extend the mould-free shelf-life of high-ratio cakes and other high moisture bakery products by up to 2000 % (Rooney, 1995; Day, 2003). Research has also shown that such bakery products packed with ethanol emitting sachets did not get as hard as the controls, and results were better than those using an oxygen scavenger alone to inhibit mould growth. Hence, ethanol vapour also appears to exert an anti-staling effect in addition to its anti-mould properties. Ethanol emitting sachets are also widely used in Japan for extending the shelf-life of semi-moist and dry fish products (Rooney, 1995; Day, 2003).

Ethanol emitting sachets are relatively expensive compared with other active packaging technologies and hence their use tends to focus on premium food items. Nevertheless, ethanol emitters represent a relatively small but growing area of the active packaging market. Pira International Ltd estimated the total global market (almost exclusively in Japan currently) to be worth \$37 million in 2005 and forecast this market to increase to \$65 million in 2010 (Anon., 2005e). Developments in this area are likely to involve the incorporation of encapsulated ethanol emitters into closures and packaging films and containers. However, these developments are set to be targeted at consumers in Asia-Pacific markets, given the concerns about product taints and regulatory controls in Europe and the USA (Anon., 2003f).

1.6 Preservative Releasers

In recent years, there has been great interest in the potential use of antimicrobial and antioxidant packaging films that have preservative properties for extending the shelf-life

of a wide range of food products. As with other categories of active packaging, many patents exist and some antimicrobial and antioxidant films have been marketed but the majority have so far failed to be commercialised because of doubts about their effectiveness, adverse secondary effects, narrow spectrum of activity, economic factors and/or regulatory constraints (Rooney, 1995; Day, 2003; Brody, 2005).

The commercial use of antimicrobial films is controversial due to concerns arising from their ability to mask natural spoilage reactions and hence mislead consumers about the condition of packaged food. In addition, the use of antimicrobial additives in packaging films and contact surfaces may give food manufacturers and consumers a false sense of security and undermine traditional cleaning and disinfection practices and possibly lead to the development of resistant microbial strains (Anon., 2003b). Notwithstanding, Pira International Ltd estimated the global value of the antibacterial packaging market in 2005 to be worth \$99 million and has forecast this market in 2010 to be worth \$169 million (Anon., 2005e).

Some commercial antimicrobial films and materials have been introduced, primarily in Japan which is by far the largest market (Anon., 2003a). For example, one widely reported product is a synthetic silver zeolite that has been directly incorporated into food contact packaging film. The purpose of the zeolite is apparently to allow slow release of antimicrobial silver ions into the surface of food products. Many other synthetic and naturally occurring preservatives have been proposed and/or tested for antimicrobial activity in plastic and edible films. These include organic acids (e.g. propionate, benzoate and sorbate), aromatic chloro-organic compounds (e.g. triclosan, the active ingredient in food contact approved Microban™), bacteriocins (e.g. nisin), spice and herb extracts (e.g. from rosemary, basil, cloves, horseradish, mustard, cinnamon, wintergreen oil and thyme), enzymes (e.g. peroxidase, lysozyme and glucose oxidase), chelating agents (e.g. EDTA), volatile inorganic acids (e.g. sulphur dioxide and chlorine dioxide) and antifungal agents (e.g. imazalil and benomyl). The major potential food applications for antimicrobial films include meats, fish, bread, cheese, fruit and vegetables (Rooney, 1995; Day, 2003; Anon., 2003a; 2004b; 2005d; Brody, 2005; Robertson, 2006).

Interest in the use of antioxidant packaging films has been stimulated by two influences. The first of these is the consumer demand for reduced antioxidants and other additives in foods. The second is the interest of plastics manufacturers in using natural and approved food antioxidants (e.g. vitamin E) for polymer stabilisation instead of synthetic antioxidants developed specifically for plastics (Rooney, 1995). The potential for evaporative migration of antioxidants into foods from packaging films has been extensively researched and commercialised in some instances. For example, the cereal industry in the USA has used this approach for the release of butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) antioxidants from waxed paper liners into breakfast cereal and snack food products (Labuza and Breene, 1989). Recently there has been interest in the use of vitamin E as a viable alternative to BHT/BHA-impregnated packaging films since there have been questions raised regarding BHT and BHA's safety (Day, 2003). Hence, the use of packaging films incorporating vitamin E can confer benefits to both film manufacturers and the food industry. Research has shown vitamin E to be as effective as an antioxidant compared with BHT, BHA or other synthetic polymer antioxidants for inhibiting packaging film degradation during film extrusion or blow moulding. Vitamin E is also a safe and effective antioxidant for low to medium a_w cereal and snack food products where development of rancid odours

and flavours is often the shelf-life limiting spoilage mechanism (Rooney, 1995; Labuza and Breene, 1989; Day, 2003).

1.7 Moisture Absorbers

A major cause of food spoilage is excess moisture. Soaking up moisture by using various absorbers or desiccants is very effective at maintaining food quality and extending shelf-life by inhibiting microbial growth and moisture related degradation of texture and flavour. Several companies manufacture moisture absorbers in the form of sachets, pads, sheets or blankets. For packaged dried food applications, desiccants such as silica gel, calcium oxide and activated clays and minerals are typically contained within Tyvek™ (Dupont Chemicals, Wilmington, Delaware, USA) tear-resistant permeable plastic sachets. For dual-action purposes, these sachets may also contain activated carbon for odour adsorption or iron powder for oxygen scavenging (Rooney, 1995). The use of moisture absorber sachets is common place in Japan where popular foods feature a number of dried products that need to be protected from moisture and humidity damage. The use of moisture absorber sachets is also quite common in the USA where the major suppliers include Multisorb Technologies, Inc. (Buffalo, New York), United Desiccants (Louisville, Kentucky) and Baltimore Chemicals (Baltimore, Maryland). These sachets are not only utilised for dried snack foods and cereals but also for a wide array of pharmaceutical, electrical and electronic goods. In the UK, Marks & Spencer Plc has used silica gel-based moisture absorbers sachets for maintaining the crispness of filled ciabatta bread rolls (Day, 2003).

In addition to moisture absorber sachets for humidity control in packaged dried foods, several companies manufacture moisture drip absorbent pads, sheets and blankets for liquid water control in high a_w foods such as meats, fish, poultry, fruit and vegetables. Basically they consist of two layers of a microporous non-woven plastic film, such as polyethylene or polypropylene, between which is placed a superabsorbent polymer that is capable of absorbing up to 500 times its own weight with water. Typical superabsorbent polymers include polyacrylate salts, carboxymethyl cellulose (CMC) and starch copolymers, which have a very strong affinity for water (Day, 2003; Anon., 2003g; Reynolds, 2007). Moisture drip absorber pads are commonly placed under packaged fresh meats, fish and poultry to absorb unsightly tissue drip exudate. Larger sheets and blankets are used for absorption of melted ice from chilled seafood during air freight transportation or for controlling transpiration of horticultural produce (Rooney, 1995). Commercial moisture absorber sheets, blankets and trays include Toppan Sheet™ (Toppan Printing Co. Ltd, Japan), Thermarite™ (Thermarite Pty Ltd, Australia), Luquasorb™ (BASF, Germany) and Fresh-R-Pax™ (Maxwell Chase, Inc., Douglasville, GA, USA).

Another approach for the control of excess moisture in high a_w foods, is to intercept the moisture in the vapour phase. This approach allows food packers or even householders to decrease the water activity on the surface of foods by reducing in-pack relative humidity. This can be done by placing one or more humectants between two layers of water permeable plastic film. For example, the Japanese company Showa Denko Co. Ltd has developed Pitchit™ film, which consists of a layer of humectant carbohydrate and propylene glycol sandwiched between two layers of polyvinyl alcohol (PVA) plastic film. Pitchit™ film is marketed for home use in a roll or single sheet form for wrapping fresh meats, fish

and poultry. After wrapping in this film, the surface of the food is dehydrated by osmotic pressure, resulting in microbial inhibition and shelf-life extension of 3–4 days under chilled storage (Rooney, 1995; Labuza and Breene, 1989). Another example of this approach has been applied in the distribution of horticultural produce. Microporous sachets of desiccant inorganic salts such as sodium chloride have been used for the distribution of tomatoes in the USA (Rooney, 1995). Yet another example is an innovative fibreboard box that functions as a humidity buffer on its own without relying on a desiccant insert. It consists of an integral water vapour barrier on the inner surface of the fibreboard, a paper-like material bonded to the barrier, which acts as a wick, and an unwettable but highly permeable to water vapour layer next to the fruit or vegetables. This multilayered box, patented by CSIRO Plant Industries, Australia, is able to take up water in the vapour state when the temperature drops and the relative humidity rises. Conversely, when the temperature rises, the multilayered box can release water vapour back in response to a lowering of the relative humidity (Day, 1993; Scully and Horsham, 2005).

Moisture absorbers are the best selling active packaging technology for all applications but oxygen scavengers are commercially more valuable for strictly food applications. Pira International Ltd estimated the global value of the moisture absorber market in 2005 to be worth \$722 million (\$454 million for desiccants and \$268 for moisture drip pads) and has forecast this market in 2010 to be worth \$1,286 million (\$823 million for desiccants and \$463 for moisture drip pads) (Anon., 2005e).

1.8 Flavour/Odour Absorbers and Releasers

The commercial use of flavour/odour absorbers and releasers is controversial due to concerns arising from their ability to mask natural spoilage reactions and hence mislead consumers about the condition of packaged food. For this reason, flavour/odour absorbers and releasers have been effectively banned in Europe and the USA (Anon., 2005e; 2006b; 2003c; Brody, 2005). Nevertheless, flavour/odour absorbers and flavour-releasing films are commercially used in Japan and have a number of legitimate applications that cannot be easily dismissed (2003c). For example, in the USA, ScentSational[®] Technologies has developed aroma-releasing packs that have been trialled by the US army to make ready-to-eat meals more appetising (Anon., 2003h). Pira International Ltd estimated the global value of the flavour/odour absorber market in 2005 to be worth \$46 million and has forecast this market in 2010 to be worth \$68 million (Anon., 2005e).

The interaction of packaging with food flavours and aromas has long been recognised, especially through the undesirable flavour scalping of desirable food components. For example, the scalping of a considerable proportion of desirable limonene has been demonstrated after only two weeks storage in aseptic packs of orange juice (Rooney, 1995). Commercially, very few active packaging techniques have been used selectively to remove undesirable flavours and taints, but many potential opportunities exist. An example of such an opportunity is the debittering of pasteurised orange juices. Some varieties of orange, such as Navel, are particularly prone to bitter flavours caused by limonin that is liberated into the juice after orange pressing and subsequent pasteurisation. Processes have been developed for debittering such juices by passing them through columns of cellulose triacetate or nylon beads. A possible active packaging solution would be to include limonin absorbers

(e.g. cellulose triacetate or acetylated paper) into orange juice packaging material (Rooney, 1995).

Two types of taints amenable to removal by active packaging are amines, which are formed from the breakdown of fish muscle proteins, and aldehydes, which are formed from the autoxidation of fats and oils. Unpleasant smelling volatile amines, such as trimethylamine, associated with fish protein breakdown, are alkaline and can be neutralised by various acidic compounds. In Japan, Anico Co. Ltd has marketed Anico™ bags that are made from film containing a ferrous salt and an organic acid such as citrate or ascorbate. These bags are claimed to oxidise amines as they are absorbed by the polymer film (Rooney, 1995).

Removal of aldehydes such as hexanal and heptanal from package headspaces is claimed by Dupont's Odour and Taste Control (OTC) technology that is based upon a molecular sieve with pore sizes of around 5 nanometres. Dupont claims that their OTC technology removes or neutralises aldehydes although evidence for this is lacking. The claimed food applications for this technology are snack foods, cereals, dairy products, fish, poultry and fish (Day, 2003). A similar claim of aldehyde removal has been reported by Swedish company EKA Noble, in collaboration with the Dutch company Akzo, who developed a range of synthetic aluminosilicate zeolites which they claim, absorb odorous gases within their highly porous structure. Their BMH™ powder can be incorporated into packaging materials, especially those that are paper-based, and apparently odorous aldehydes are absorbed in the pore interstices of the powder (Day, 2003).

1.9 Temperature Control Packaging

According to market research by Pira International Ltd, global sales for temperature control packaging was estimated to be a meagre €15.1 million in 2001 but has been predicted to reach €42.4 million in 2007 (Anon., 2002). Self-heating and self-cooling technologies and their associated markers are described in detail by Butler (2005). As with most active packaging markets, Japan's market for temperature control packaging is the largest in the world.

Temperature control active packaging includes the use of innovative insulating materials, self-heating and self-cooling cans. For example, to guard against undue temperature abuse during storage and distribution of chilled foods, special insulating materials have been developed. One such material is Thinsulate™ (3M Company, USA) which is a special non-woven plastic with many air pore spaces. Another approach for maintaining chilled temperatures is to increase the thermal mass of the food package so that it is capable of withstanding temperature rises. The Adenko Company of Japan has developed and marketed a Cool Bowl™ which consists of a double walled PET container in which an insulating gel is deposited in between the walls (Labuza and Breene, 1989).

Self-heating cans and containers have been commercially available for decades and are particularly popular in Japan (Day, 2003; Anon., 2002; 2003d; 2005b; 2006c). Self-heating aluminium and steel cans and containers for sake, coffee, tea and ready meals are heated by an exothermic reaction when quicklime and water positioned in the base are mixed. During 2001 in the UK, Nestlé introduced a range of Nescafé coffees in self-heating insulated cans that used the quicklime and water exothermic reaction. These self-heating cans were

manufactured by Thermotic Developments (UK) but were withdrawn from the market in 2002 because the coffee didn't get hot enough during the winter months. However, Thermotic Developments has revamped its self-heating concept and design and are in further negotiations with interested food manufacturers (Anon., 2005b). Other self-heating technologies, manufacturers and users on the market include HotCan™ (UK), Vitcho (France), Sonoco (USA), Steam to Go™ (UK), KPS Technologies (Korea), Caldo Caldo (Italy), Pressto™ (USA) and Tempra Technologies (USA). The self-heating mechanisms used are most commonly quicklime/water but also include calcium chloride/water, potassium permanganate/glycerol and super corroding alloys/salt water (Anon., 2006c).

Self-cooling cans have also been marketed in Japan for raw sake. The endothermic dissolution of ammonium nitrate and chloride in water is used to cool the product. Another self-cooling can that was introduced briefly into the market was the Chill Can™ (The Joseph Company, USA), which relied on a hydrofluorocarbon (HFC) gas refrigerant. The release of HFC gas was triggered by a button set into the can's base and could cool a drink by 10 °C in 2 minutes. However, concerns about the environmental impact of HFCs curtailed the commercial success of the Chill Can™ (Day, 2003; Anon., 2003d). Another self-cooling can concept that doesn't have the environmental concerns associated with the Chill Can™, has been developed by Tempra Technology in partnership with Crown Cork & Seal (USA). The IC™ (Instant Cool) can relies on the ammonium nitrate/salt water endothermic reaction and can reduce the temperature of ambient drinks by 15 °C within 3 minutes (Anon., 2002).

1.10 Temperature Compensating Films

Commercially available temperature compensating films are manufactured by Landec Corporation (Menlo Park, California, USA). Their patented Intellipac® technology is based on unusual side-chain crystallisable Intellimer® polymers that respond to temperature in a controllable and predictable way. Intellimer® polymers can abruptly change their permeability, adhesion or viscosity when heated or cooled by just a few degrees. These changes are triggered by a built-in temperature switch, which can be set within temperature ranges compatible with most biological applications, particularly the respiration rate of fresh-cut horticultural produce. Moreover, since the process of change involves a physical, and not a chemical change, it can be repeatedly reversed (Robertson, 2006; Scully and Horsham, 2005; Brody, 2005; Anon., 2005a).

Intellimer® polymers help maintain optimal atmospheres within sealed packs of fresh-cut and whole produce during the fluctuations of temperature that can occur during chilled storage and distribution. At elevated temperatures, when respiring produce needs more oxygen, the polymer becomes more permeable, but at lower temperatures, the polymer permeability automatically decreases. Despite their relatively high cost, commercialisation has taken place with Chiquita Brands using Landec's Intellipac® technology for the packaging of single-serve bananas to convenience stores in the USA. Other commercial fresh produce applications include fresh-cut mixed vegetables, broccoli, cauliflower, asparagus and strawberries (Robertson, 2006; Anon., 2005c).

1.11 Conclusions

Active packaging is an emerging and exciting area of food technology that can confer many preservation benefits on a wide range of food products. Active packaging is a technology developing a new trust because of recent advances in packaging, material science, biotechnology and new consumer demands (Ahvenainen and Hurme, 1997). The objectives of this technology are to maintain sensory quality and extend the shelf-life of foods whilst at the same time maintaining nutritional quality and ensuring microbial safety. However, ultimately, active packaging must benefit and be accepted by consumers before it is more widely adopted (Lähteenmäki and Arvola, 2003). Also, active packaging must not be driven by technological possibilities but rather by meeting real market needs (Anon., 2006a).

Oxygen scavengers and moisture absorbers are by far the most commercially important sub-categories of active packaging and the market has been growing steadily for the last ten years and is predicted to grow even further by 2010 (Anon., 2005e). The introduction of oxygen scavenging films and bottle caps will also help stimulate the market in future years and the unit costs of oxygen scavenging technology will drop. All other active packaging technologies are also predicted to be used more in the future, particularly ethylene scavengers, carbon dioxide scavengers and emitters, moisture absorbers and temperature control packaging. Food safety and regulatory issues in the European Union and USA are likely to restrict the use of certain preservative releasers and flavour/odour absorber active packaging technologies (Vermeiren *et al.*, 1999; Brody, 2005). Nevertheless, the use of active packaging is becoming increasingly popular and many new opportunities in the food and non-food industries will open up for utilising this technology in the future.

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2

Active Polymer Packaging of Non-Meat Food Products

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2.1 Introduction

Food products are, in general, highly perishable goods, having a shorter shelf-life than many other consumables. The outer environment being a strong determinant in the spoilage of food, the use of a barrier protection (package) to slow down the deterioration process is essential. In recent decades food packaging has experienced an extraordinary expansion, as most food products, including fresh fruits and vegetables, reach the consumer within some sort of packaging technology. Changes in lifestyle, consumer demands and commercialization trends have made packages a major partner in the preservation of fast moving consumer goods.

Traditionally, food packages have been defined as passive barriers to delay the adverse effect of the environment over the contained product. However, the trends in consumer preferences towards mildly preserved, fresh, and healthy foodstuffs have triggered innovation in food packaging and a considerable amount of research work has been conducted towards the design of packaging materials that, in contrast to the traditional passive barrier concept, interact with the environment and with the food, playing an active role in improving and monitoring food quality and safety [1,2].

Many of these early commercial packaging innovations relied on the inclusion of a small pouch (sachet) containing the active ingredient inserted inside the permeable package. The focus of this chapter however is on smart packaging where the active substances are incorporated within the packaging material wall, rendering a number of advantages such as a reduction in package size, higher effectiveness of the active principles (which is completely surrounding the product), and in many cases higher output in packaging production (since

the incorporation of the sachet means an additional step is eliminated). Plastics are very convenient carriers for this sort of technology, not only as vehicles of the active substance, but also as active participating elements. The large variety of polymeric materials available and the ease of modifying, blending and conforming them into any kind of shape or form, allow for the design of the most convenient smart packaging to suit the specific needs of each food product.

Some precautions and considerations have to be taken into account when applying these active plastics:

- The active agent may change the plastic properties.
- Desorption kinetics are variable and dependent on plastic permeability.
- The active capacity may get shortened by an early reaction if there is no effective triggering mechanism.
- There is a potential undesired migration of active substances or low molecular weight reaction products into the food.

It is important to note that each type of food has a specific spoilage mechanism that must be studied and understood before designing and applying an active technology [3]. In this chapter a general overview of the smart polymer technologies that can be applied to improve the quality, safety and shelf-life of highly perishable food products is presented. Smart polymer packaging technologies that can delay the specific deterioration processes of different groups of food products will be discussed, together with trends in this area and possible future developments (meat products are excluded since these are covered exclusively in Chapter 3). Two smart packaging technologies are described in depth for each food product group according to their specific spoilage mechanism, as summarized in Table 2.1.

2.2 Bread and Bakery Products

Mould spoilage is common in the bakery industry and in many cases mould growth determines the product's shelf-life. There are two main factors determining the growth of mould in bakery products like bread: the presence of oxygen inside the package and the water activity (a_w) of the products, i.e. the availability of water in the food, which in the case of bread is more than 0.9 while mould and yeast are able to grow at a_w as low as 0.62. In the case of drier bakery products, such as breakfast cereals, fat rancidity caused by oxygen is the problem to target. The two main active polymer strategies to delay spoilage of bakery products are: (a) eliminate oxygen from the package headspace, or (b) use substances that inhibit mould growth.

2.2.1 Elimination of Oxygen from Inside the Package: Oxygen Scavengers

Traditionally, oxygen-sensitive foods have been packaged using modified atmosphere packaging (MAP) or vacuum packaging, but these technologies do not always control or remove oxygen completely due to, for instance, the residual presence of the gas and/or permeation

Table 2.1 Summary of the smart packaging systems described for each group of food products according to their specific spoilage mechanism

Food Product	Factors causing spoilage and/or consumer rejection	Smart packaging systems highlighted	'Smart substances' ^a incorporated into the package wall	Other smart systems useful
Bread and bakery products	Mould growth	O ₂ scavenging films	Iron, unsaturated fatty acids, natural antioxidants	Antimicrobial films, aldehyde scavengers
	Fat rancidity	Ethanol emitters	Ethanol entrapped into cyclodextrins	
Fruits and vegetables	Accelerated ripening	Ethylene scavengers	Zeolites, clay, Japanese oya	Humidity absorbers, antimicrobial films
	Mould growth	CO ₂ controllers	Sodium bicarbonate/Zeolites	
Dairy products	Lactose/cholesterol content	Enzymatically active films	Enzymes lactase and cholesterol reductase	Antimicrobial films
Fish and seafood	Microorganism growth	O ₂ scavenging films	Substituted anthraquinone	O ₂ scavenging films, CO ₂ emitters, antimicrobial films
	Aldehyde production	Aldehyde scavengers	Nylon, <i>d</i> -sorbitol and alpha-cyclodextrin	
	Water drip	Humidity absorbers	Superabsorbent polymers, propyleneglycol	

^a Substances that can be used in smart packages and responsible of the desired process aimed at increasing the quality and shelf-life of the food products

through the polymeric packaging materials. The use of oxygen scavengers, which absorb residual O₂ after packaging, may minimize the quality changes undergone by foods. Oxygen scavengers are reducing agents, i.e. substances able to react with oxygen and thus reduce its concentration within the package. These substances can be blended or dispersed in the polymeric materials rendering a smart polymer technology, namely oxygen scavenging films, which ideally should comply with the following characteristics:

- They should be protected from the external oxygen by an external O₂-barrier polymer. Therefore, the use of multilayer structures is preferred.
- The reducing agent (oxygen scavenging substance) should not compromise the processing characteristics or physical properties of the polymeric matrix.

- Release of by-products from the reaction that could affect the sensory or nutritional quality of the food product should be avoided.
- O₂-scavenging films should be stable in air prior to use. This can be achieved using some activation or triggering mechanism.

The most common oxygen absorbers are based on iron oxidation. Although sachets are effective and widely used, several sachet-related disadvantages, such as accidental ingestion or leak from the sachet contaminating the product, have encouraged the development of integrated technologies. Iron powder has been incorporated into polymers such as low density polyethylene, which have been claimed to absorb oxygen effectively at significant rates [4]. However, to activate the reaction in iron-containing films, some humidity is required, which may come from the food product itself or from food preservation processes such as retorting. In Figure 2.1, the kinetics of oxygen scavenging from a polyethylene film containing 40% of a commercial iron-based oxygen scavenging substance is shown as a function of the relative humidity. From the results it could be stated that this technology is only useful for liquid foods and the scavenging rates for walls containing these compounds appear to be unsuitable for many commercial oxygen-scavenging applications, such as those in which sachets are employed [5]. Moreover, incorporation of these substances causes degradation of wall transparency and mechanical properties and these compounds, as well as their oxidation products, can migrate from the container, which can result in the food product failing to meet government standards for human consumption [6]. The application

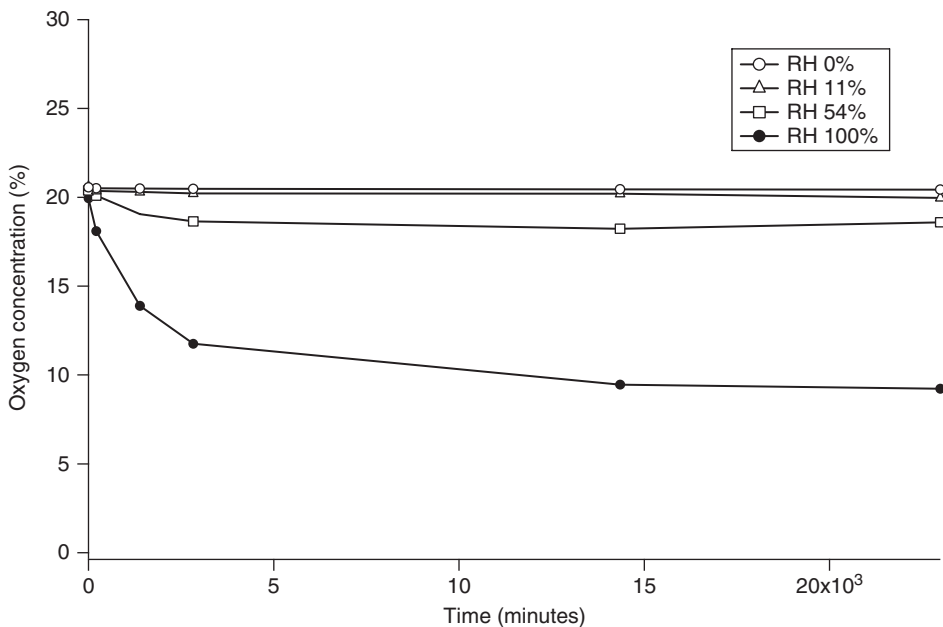


Figure 2.1 Oxygen scavenging kinetics of extruded PE blended with 40% of a commercial iron-based oxygen scavenging material as a function of relative humidity (RH).

of novel nanotechnologies such as nanocomposites can be advantageous in this respect because the nanoparticles can, on the one hand, fixate and/or stabilize the scavenger and, on the other hand, adsorb or delay the diffusion of migrants or off-flavours into the foods. Unsaturated fatty acids can also be used as reducing agents incorporated into polymers. This technology requires a catalyst, a photoinitiator to trigger the reaction by ultraviolet light irradiation, and a functional barrier between the food product and the scavenger layer, to impede migration of undesirable oxidation products [7]. Commercial examples of this smart polymer technology are the Oxygen Scavenging Polymer (Chevron Philips Chemical Company, USA) and Cryovac[®] OS films (Sealed Air Corporation, USA). Other substances that have been incorporated into polymers to reduce the oxygen concentration inside the package are enzymes [1] and entrapped aerobic microorganisms [8]. However, their sensitivity to physical-chemical factors prevents further developments.

In the case of dry food products such as breakfast cereals, a plausible option is the addition of antioxidants into flexible and thermoformable plastic packaging materials [9]. Synthetic antioxidants such as butylated hydroxytoluene (BHT) can be used to prolong the shelf-life of breakfast cereals [10], but due to some health-related concerns derived from the consumption of these substances [11] natural antioxidants are being explored.

There is a number of naturally occurring compounds that have antioxidant properties, including tocopherols, lecithin, organic acids and rosemary extracts. Among them, there is a growing interest in the use of vitamin E (also known as α -tocopherol) and vitamin C being incorporated into polymers. Vitamin E has been marketed as a food-grade odour remover in packaging materials. Added to high density polyethylene (HDPE)-ethylene/vinyl acetate (EVA)-HDPE, vitamin E reduces the 'plastic' taste, thus preserving the fresh taste of breakfast cereals [12]. Incorporation of vitamins E or C into the plastic material would present another advantage when compared to the addition of synthetic antioxidants because the possible migration of these compounds into the food not only does not produce adverse effects, but also improves the nutritional characteristics of the food product. Therefore, this kind of oxygen absorber could be envisaged as the most promising for bread and bakery products.

2.2.2 Inhibition of Mould Growth: Ethanol Emitters

Ethanol is an efficient fungistatic compound that has been widely used to increase the shelf-life of bakery products. The advantage of using a smart technology versus direct incorporation of ethanol is that an even release of the substance during storage time would better prevent the growth of moulds on the surface of the product, while if the ethanol is directly sprayed onto the bakery product, apart from causing a strong flavour, it will migrate from the surface (target for mould growth) into the product [13,14]. However, introducing these highly volatile compounds into the package wall is not simple because the film manufacturing process (solution casting or extrusion) results in the volatilization of the compound and a non-breathable atmosphere in the production plant. A possible solution to this problem consists of using compounds that trap the active molecules and decrease their volatility. Cyclodextrin complexes have been used for these purposes, preserving flavours during extrusion processes [15,16]. Some antimicrobial agents, flavour essences, horseradish essences, and ethanol have been successfully encapsulated in

cyclodextrins [17]. Micro- and nanoencapsulation techniques are being constantly improved in the biomedical and pharmacological areas. Some of the developments designed for the controlled release of drugs could be similarly employed in the design of smart packages. For instance, it has been observed that addition of small amounts of sodium lauryl sulfate can increase the encapsulation efficiency of ethanol, and allow the reduction in the amount of dextrin required to encapsulate ethanol in the preparation of microcapsules [18]. However, it is not a cheap technology and, therefore, it would only be feasible from an economic point of view for certain ingredients in added-value food products. Another technology that has been recently developed includes the entrapment of ethanol or other alcohols within high barrier EVOH copolymers during lamination processes. The controlled release of these systems can be tailored by the material selection or can even be triggered by absorption of different moisture levels [19].

2.2.3 Other Smart Technologies for Bakery Products

Apart from ethanol, other antimicrobial substances have been incorporated into polymeric films to retard the growth of moulds in bakery products. The use of antimicrobial food packaging films can offer advantages compared to the direct addition of preservatives to the food product, as the active agents are applied to the packaging material in a way such that only low levels of preservative come into contact with the food [20]. An example of this technology is a cellulose acetate film containing 4 % of sodium propionate that effectively reduced mould growth in bread [21]. Other volatile antimicrobial substances from spices and herbs have proved efficient in the control of fungal spoilage by common bread spoiling fungi [22]. Through entrapment of these substances in cyclodextrins, as explained above, microbial control through packaging using natural substances could be obtained, but there is a lot of research needed prior to commercialization of these technologies.

Oxidation of fats and oils from some high-fat content bakery products such as snacks, crackers, biscuits and cereal products, can lead to the formation of malodorous aldehyde substances such as hexanal and heptanal, which upon the opening of the package will cause rejection of the product. Aldehyde scavengers incorporated into polymers are another kind of smart packaging technology for this specific problem (see aldehyde scavengers for fish products).

2.3 Fruits and Vegetables

Climatic fruits and vegetables are highly perishable goods as after being collected they continue emitting ethylene, a growth-simulating hormone that accelerates ripening and senescence by increasing their respiration rate, thereby decreasing shelf-life. Ethylene also accelerates the rate of chlorophyll degradation in leafy vegetables and fruits [23]. During ripening, natural acids present in these fresh foods, are metabolically transformed into basic compounds like sugars, increasing the pH and thus favouring the growth of spoilage microorganisms. In order to extend the shelf-life of this fresh produce, the ripening rate has to be slowed down, which can be achieved by reducing the concentration of ethylene as it is being produced, and the gas concentration inside the package needs to be controlled.

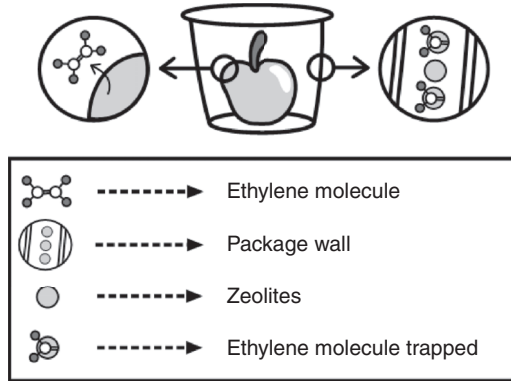


Figure 2.2 Diagram showing how the ethylene molecules generated by fresh produce can be trapped by the zeolites dispersed in the package wall. Figure courtesy of Alberto Bertolin Terradez.

2.3.1 Slowing Down the Ripening Rate: Ethylene Scavengers

Potassium permanganate (KMnO_4) has been traditionally used as an ethylene scavenger contained in sachets and placed inside the package. Nevertheless, products based on potassium permanganate cannot be integrated into food-contact materials because KMnO_4 is toxic and has a purple colour [24]. Several minerals, such as zeolites, clays or nanoclays and Japanese oya, are alternative ethylene scavengers that can be added to the films as finely dispersed powder [25]. Although most of the tested films are opaque and do not absorb as much ethylene as KMnO_4 [26], these films are growing in popularity and several developments have already been commercialized. In Figure 2.2 a diagram of an ethylene scavenging package for fruit is depicted. Some commercial examples of this smart packaging technology are Evert-Fresh (Evert-Fresh Co., USA), Orega plastic film (Cho Yang Heung San Co., Korea), and Peakfresh™ (Peakfresh Products, Australia) [23]. Evert-Fresh is a low-density polyethylene film impregnated with an ethylene-gas-absorbing mineral called oya (very similar to zeolite). Orega consists of a polyethylene film with dispersed zeolite, active carbon and a metallic oxide. This ethylene-absorbing film is used in Korea for packaging fruits and vegetables and it has been used to increase the shelf-life of strawberries, lettuce, broccoli and other ethylene-sensitive products [27]. Nowadays, ethylene scavengers are not widely used, probably because of their insufficient absorbing capacity, but the development of the previously mentioned concepts could contribute, in the near future, to an increased shelf-life of fresh produce, facilitating their commercialization in optimal conditions.

2.3.2 Control of Gas Concentration: CO_2 Controllers

As mentioned before, fresh produce after harvesting is still biologically active. The atmosphere inside the package constantly changes as gases and moisture are produced during metabolic processes. Fruits and vegetables continue to use up O_2 in the headspace of the package and the CO_2 concentration increases. Each fresh food has its own optimal gas composition that needs to be studied for the correct design of the optimal package. Depending

on the respiration rate of the product and on the permeability to CO₂ of the packaging material, either release or absorption of CO₂ will be desirable. Hence, there is a potential field of application for another kind of smart packaging technology—the CO₂ emitters/absorbers. This technology goes beyond the simple modified atmosphere packaging systems that use gas permeability of materials passively, involving the absorption/emission of the specific gas by/from the packaging wall and eventually the control of the gas concentration [28]. To date, most of the technologies for CO₂ control are based on sachet technologies, but some companies are launching novel forms of these smart packages. In the case of CO₂ emitters, sodium bicarbonate is the most common substance used. Recently, CO₂[®] Technologies has commercialized CO₂ emitter pads for use with fresh products such as strawberries [29]. With this technology, a controlled release of the gas is achieved while maintaining the freshness and textural characteristics of the fruit. As with the emitters, CO₂ absorber technologies are mostly in the form of sachets containing calcium hydroxide.

Scavenging films have been developed using the same technology as for ethylene absorbance, i.e. dispersing zeolites in the polymeric material. These substances adsorb gas until equilibrium is achieved, so in the case that the CO₂ concentration in the headspace decreases, then the gas will flow from the absorber into the internal atmosphere. Therefore, they can be called CO₂ controllers [30].

2.3.3 Other Smart Technologies for Fresh Produce

In conjunction with a_w , the relative humidity (RH) of the storage environment is important in determining the growth of microorganisms in foods [31]. The excess water development inside a food package usually occurs due to the respiration of fresh produce. Humidity absorbers, another kind of smart polymer technology that will be further described below, could be used to avoid the presence of water inside the package of fresh produce.

Several antimicrobial films have also been developed specifically for fruit and vegetables. In the case of fruits mainly, the antimicrobial compound can be incorporated into an edible film or coating applied by dipping or spraying onto the fruit [32]. A commercial antifungal coating produced from chitosan is sold as a shelf-life extender for fresh fruit [33].

2.4 Dairy Products

Milk and other dairy foods are important sources of several essential nutrients. However, extensive population studies in the late 1960s and early 1970s showed that much of the world's adult population (approximately 70%) have low levels of the intestinal enzyme lactase [34], leading to gastrointestinal discomfort after the consumption of milk and other dairy products. Apart from the drawback associated with lactose (the main carbohydrate in milk), the cholesterol content of milk is also quite high. Smart packages making use of enzymes can help in solving both problems. Regarding other dairy products such as yoghurts and cheese, the presence of oxygen inside the package and the growth of spoilage microorganisms are the factors to control.

2.4.1 Reducing Lactose and Cholesterol Content: Enzymatically Active Packages

Some immobilized enzymes that were initially applied in food production lines [35] are currently being considered for food packaging applications [36]. The objective of these systems is to catalyse a reaction that is considered beneficial from a nutritional point of view (i.e., decreasing the concentration of a non-desired food constituent and/or producing a food substance attractive for the consumer).

Lactase, for example, can be immobilized by covalent attachment to functionalized surfaces of, for instance, low density polyethylene (LDPE), retaining 10 % of the free enzyme activity [37]. The lactase-active package is meant to reduce the lactose content of milk during storage by splitting this complex sugar into glucose and galactose (see Figure 2.3). Similarly, the enzyme cholesterol reductase could be immobilized into polymers to convert cholesterol into coprostanol and coprosterol. These converted compounds are very poorly absorbed by the digestive system and pass through intact [38]. The use of this type of package allows the production of a value-added product without modifying the manufacturing procedure. UHT milk produced by a conventional process can be packaged in a lactase-active or cholesterol-active package, and through storage, the product arrives at the market as a low/free-lactose or low-cholesterol product respectively. This processing plant inside the package appears to be a very promising technology.

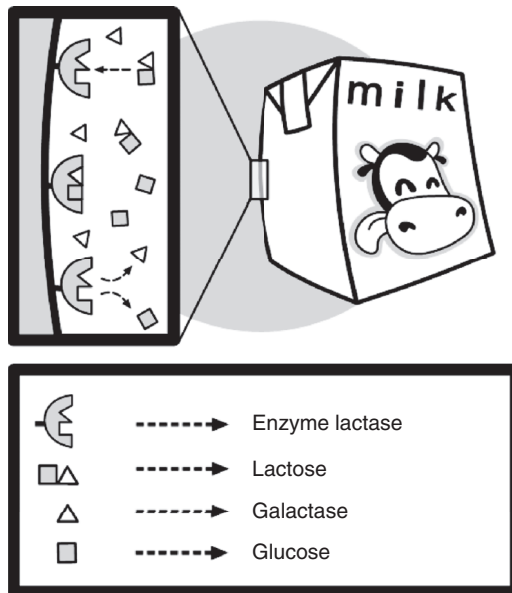


Figure 2.3 Enzymatically active package of milk: lactase enzymes are attached in the inner part of the package transforming lactose ($\square\Delta$) into glucose (\square) and galactose (Δ). Figure courtesy of Alberto Bertolin Terradez.

2.4.2 Oxygen Scavenging Films for Yoghurt

Probiotic bacteria added to yoghurt to impart health benefits require a low oxygen environment for maximum viability. ZerO₂[®] developed by Food Science Australia (CSIRO, Australia) is an oxygen scavenging additive that contains a reducible organic compound, such as substituted anthraquinone, that is incorporated into a polymer for use as a layer in a laminated packaging film. As the oxygen scavenging films described for meat (see Chapter 3), this system is activated by UV light exposure before packaging. It has been observed effectively to reduce the oxygen concentration when used in combination with a high barrier polymer in yoghurt containers [39].

2.4.3 Other Smart Technologies for Dairy Products

Several antimicrobial films have been developed specifically for cheese using bacteriocins such as lactacin or nisin [40]. Attachment of the former compounds to polymeric materials has proved inhibitory both in moulds [41] and lactic acid bacteria [42] on cheese surfaces.

2.5 Fish and Seafood

Fish is an extremely perishable food. It is a very low acid food and therefore is very susceptible to the growth of food poisoning bacteria. The decomposition of fish can be due to enzymatic spoilage, oxidative deterioration and/or bacterial spoilage. Fish is a source of polyunsaturated fatty acids (also known as omega-3 fatty acids) claimed to have protective effects against heart-related diseases. However, they are also highly unstable and upon contacting oxygen, free fatty acids are formed that can be further decomposed into malodorous compounds such as peroxides, ketones and aldehydes. Oxygen scavenging films described before can be used to delay oxidative deterioration, but specific smart polymers can be designed to selectively remove potential decomposition substances. Another problem during the commercialization of fish fillets is the drip of tissue fluid, resulting in water inside the package, causing the quality perception of the product to deteriorate and favouring the growth of food-borne pathogenic microorganisms. There are some smart packaging technologies that could be used to remove malodorous compounds and water from packed fish and fish products.

2.5.1 Removing Malodorous Compounds: Aldehyde or Aroma Scavengers

Most plastic packages adsorb compounds from the food or from the environment, which is commonly known as scalping of substances. This scalping behaviour of polymeric food packages is generally recognized as a negative attribute. However, if the materials are properly designed, selective scalping can be obtained thus improving the flavour profile of food systems [43]. DuPont Polymers (USA) has developed Bynel IXP101, a functionalized ethylene-based copolymer that claims to remove aldehydes. This polyolefin is commercialized as a resin masterbatch intended to be blended with other linear polyethylenes to form an intermediate tie layer in coextrusions [44]. Nylon, *D*-sorbitol and alpha-cyclodextrin incorporated into PET have also demonstrated selective aldehyde scalping [45]. There are several

patents using zeolites and activated carbon dispersed in polymeric materials to attract and trap odour in their porous structure [46]. Nevertheless, a more specific scalping behaviour can be achieved by incorporating acidic compounds into thermoplastic matrixes, as they are susceptible to interaction with the strongly basic compounds (malodorous amines) resulting from protein breakdown in fish muscle [47].

2.5.2 Humidity Absorbers

Desiccants are used in a wide variety of packed products to reduce water activity, inhibiting, in that way, mould, yeast or bacterial growth. Sachets containing silica gel are the typical systems used for this purpose, as addition of the desiccant into the package wall could alter the optical and mechanical properties of the films. Nevertheless, there are some commercial integrated smart packaging technologies with water absorption capacity for fresh fish and shellfish consisting of adsorbent sheets (Thermarite[®], Pty Ltd, Australia; Toppan Sheet[™], Toppan Printing Co., Japan; Peaksorb[®], Peakfresh Products, Australia). These materials are basically a superabsorbent polymer placed between two polyolefin layers (PE or PP). The absorbent sheets are placed under fish or shellfish to absorb water [48]. Some absorbing pads used to soak up the exudates in fish and meat trays, incorporate organic acids and surfactants in order to prevent microbial growth, because the food exudates are rich in nutrients [49].

Another way of intercepting humidity is by including the desiccant agent between two layers of a plastic material highly permeable to water vapour. Pitchit[™] (Showa Denko, Japan) is a commercial desiccant consisting in a layer of propyleneglycol sandwiched between two layers of polyvinyl alcohol (PVOH) [1]. The PVOH is highly permeable to water, but it is impermeable to propyleneglycol. This system is commercialized for home use as a material to wrap meat or fish, reducing the surface water activity of the product [50].

2.5.3 Other Smart Technologies for Fish Products

Oxygen scavenging films could be used to delay oxidative deterioration in fish. However, caution must be taken in applying this technology as pathogenic anaerobic microorganisms, such as *Clostridium botulinum*, could then be able to grow. Instead, as with meat, high concentrations of CO₂ can be used to control the growth of spoilage microorganisms, CO₂ emitters being another smart packaging technology useful for this kind of product [51]. Another way of controlling the growth of pathogens in fish products is through the use of antimicrobial films.

2.6 Outlook and Future Developments

Implementation of some of the existing smart polymer packaging systems can make these technologies a major partner in protection and shelf-life extension of foods. Given the variety of smart concepts and the versatility of polymers, packaging structures can, in principle, be designed to enhance quality and safety while prolonging the shelf-life of potentially any food product in the market. The general trends seem to point towards

the use of natural substances (which, in case of migration, do not pose any health risk), incorporated into biodegradable biomass-derived matrixes. The latter ones, apart from being environmentally friendly and better vehicles for the release of substances, will be a good economical option when the shortage of oil will cause an increase in the prizes of its derived products. Several raw materials originating from agricultural and marine sources can be used to fabricate biodegradable films such as a number of polysaccharides (starch, cellulose and derivatives, alginates, carrageenan, chitosan, etc.), proteins (corn zein, soy protein isolates, wheat gluten, milk proteins, gelatine, etc.) and lipid-based matrixes (waxes or glycerides, seedoils) [40]. Among the active polymer packaging technologies, the area of antimicrobial packaging is probably the one receiving most of the attention and a number of natural substances are being tested against the most common food-borne pathogens. However, looking a step further in what the role of packaging can be in the commercialization of food products, apart from the increasing number of natural substances that can be added to the package walls to exert an active role in preservation, polymeric sustainable and/or biodegradable biomaterials could also be vehicles of functional or bioactive substances, like vitamins, pre- and probiotics, overcoming some of the existing drawbacks in the fabrication of functional foods. This is a new concept in packaging [52], termed bioactive packaging that seeks to transform foods into functional food upon packaging. The future will also see the application of various nanotechnologies, such as the use of nanoclays and electrospun or electrosprayed active or bioactive nanostructured materials [53]. These technologies will offer invisibility within the package (i.e. transparency and required mechanical properties) and will also become excellent carrying systems where the active principle can be better dispersed and, therefore, be more effective. These novel nanotechnologies will also enhance the plastic or bioplastic properties and will act as functional barriers against unintended migration or as scavengers of potential toxic byproducts, thus increasing the quality and safety of fast moving consumer goods.

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3

Smart Packaging of Meat and Poultry Products

S.A. Hogan and J.P. Kerry

3.1 Introduction

The role of preservative packaging, as applied to meat products, is to maintain acceptable appearance, odour and flavour, stabilise product composition and delay the onset of microbial spoilage. A variety of packaging systems and technologies is currently available for muscle foods, specifically fresh and cooked meats and meat products. Fresh red meats may simply be placed on trays and over-wrapped with an oxygen permeable film or placed within a static gaseous modified atmosphere packaging (MAP) environment containing approximately 70–80 % oxygen and 20–30 % carbon dioxide. Fresh poultry products may again be retailed in an overwrap or a MAP format comprising approximately 65–75 % nitrogen and 25–35 % carbon dioxide. MAP is an extremely important packaging technology used extensively for the distribution, storage and display of meat and poultry products throughout the cold distribution chain (Sivertsvik *et al.*, 2002). While described as static, the atmosphere within an MAP pack is far from being static and gas content levels may alter during storage due to reactions between components of the atmosphere and the product and/or due to transmission of gases in or out of the pack through the packaging film (Stiles, 1991). Processed or cooked meats and poultry or cook-chill convenience-style, muscle-based, foods are described as being oxygen sensitive and for this reason, these products are usually stored under some form of vacuum or in MAP using 60–80 % N₂ : 20–40 % CO₂.

The function of carbon dioxide in MAP is to inhibit growth of spoilage bacteria (Seideman and Durland, 1984). Nitrogen is used in MAP as an inert filler gas in order to reduce the proportions of the other gases or to maintain pack shape (Bell and Bourke, 1996). The

major function of oxygen is to maintain the muscle pigment myoglobin in its oxygenated form, oxymyoglobin, in red meats.

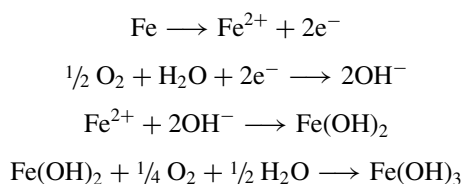
Important properties by which consumers judge meat are appearance, texture and flavour (Faustman and Cassens, 1990). Appearance, specifically colour, is a critical quality attribute in influencing the consumer's decision to purchase. In fresh red meats, myoglobin can exist in one of three chemical forms. Deoxymyoglobin, which is purple, is rapidly oxygenated to cherry red oxymyoglobin on exposure to air. Over time, oxymyoglobin is oxidised to metmyoglobin which results in a brown discoloration associated with a lack of freshness (Faustman and Cassens, 1990). Low oxygen concentrations favour oxidation of oxymyoglobin to metmyoglobin (Ledward, 1970). In order to minimise metmyoglobin formation in fresh red meats, oxygen must be excluded from the packaging environment to below 0.05 % or be present at saturating levels (Faustman and Cassens, 1990). High oxygen levels within MAP also promote oxidation of muscle lipids over time with deleterious effect on fresh meat colour (Kerry *et al.*, 2000). Lipid oxidation is a major quality deteriorative process in meat, resulting in a variety of breakdown products that produce undesirable off-odours and flavours.

In cured, cooked, packaged meat products, factors such as percentage residual oxygen, product to headspace volume ratio, oxygen transmission rate of the packaging material, storage temperature, light intensity and product composition are critical factors affecting colour stability and ultimately consumer acceptance (Møller *et al.*, 2003). Nitrosylmyoglobin, formed from a reaction between myoglobin and nitrite is denatured, upon cooking, to nitrosylmyochrome which gives the characteristic pink colour to cooked, cured ham (Juncher *et al.*, 2003). Exposure to light in combination with oxygen is of critical importance to the colour stability of cooked cured ham as light exposure, even at low oxygen levels, can cause oxidation of nitrosylmyochrome to denatured metmyoglobin, which imposes an undesirable greyness to the meat surface (Møller *et al.*, 2000). Commercially, discoloration in pre-packed, cooked, cured ham is associated with low residual oxygen levels and is overcome with the use of oxygen scavengers or an oxygen scavenging film. Also, with respect to fresh red meats, oxygen scavengers used in conjunction with a carbon dioxide/nitrogen gas mixture extends the colour shelf-life of fresh beef (Allen *et al.*, 1996). Oxygen scavengers are some of the best known examples of smart packaging devices used with oxygen sensitive meat-based products.

3.2 Oxygen Scavengers

High levels of oxygen present in packs containing meat and poultry facilitate microbial growth, off-flavour and off-odour development, colour changes and nutritional losses, thereby causing significant reduction in the quality, safety and overall shelf life stability of these muscle foods. This problem is further compounded in muscle-based food products where clean labelling requirements and minimal processing procedures are being used to satisfy retailer, and ultimately consumer, concerns and demands for fresher and less processed muscle food products. Control of oxygen levels in oxygen-sensitive food packs is critical in order to limit the rate of such deteriorative and spoilage reactions. Oxygen absorbing systems provide an alternative to vacuum and gas flushing technologies as a means of improving product quality and shelf life (Ozdemir and Floros, 2004), while helping

to circumvent problems created by ‘chemical or preservative free’ minimally processed muscle foods. Vacuum packaging and MAP techniques do not always facilitate complete removal of oxygen. Oxygen that permeates through the packaging film or is trapped within the meat or between meat slices cannot be removed by these techniques. Quality changes in oxygen-sensitive foods can be minimised through the use of oxygen scavengers, which absorb residual oxygen following packaging (Vermeiren *et al.*, 1999). Existing oxygen scavenging technologies utilise one or more of the following concepts: iron powder oxidation, ascorbic acid oxidation, photosensitive dye oxidation, enzymatic oxidation (e.g. glucose oxidase and alcohol oxidase), unsaturated fatty acids (e.g. oleic or linolenic acid), rice extract or immobilised yeast on a solid substrate (Floros *et al.*, 1997; Vermeiren *et al.*, 1999). Structurally, the oxygen scavenging component of a package can take the form of a sachet, label, film (incorporation of scavenging agent into packaging film), card, closure liner or concentrate (Suppakul *et al.*, 2003). The majority of commercially available oxygen scavengers are based on the principle of iron oxidation (Smith *et al.*, 1990):



Comprehensive details on a variety of commercially available oxygen scavengers are presented by Suppakul *et al.* (2003). Ageless[®] (Mitsubishi Gas Chemical Co., Japan) is the most common oxygen scavenging system based on iron oxidation (Figure 3.1). These scavengers are designed to reduce oxygen levels to less than 0.1%. Other examples of oxygen absorbing sachets include ATCO[®] (used commercially as oxygen scavengers in pre-packed, cooked and cooked, sliced meat products – Emco Packaging Systems, UK;



Figure 3.1 Ageless[®] Label Mitsubishi Gas Chemical Co. Reproduced with permission from Ageless Sales, Mitsubishi Gas Chemical Co. Japan.

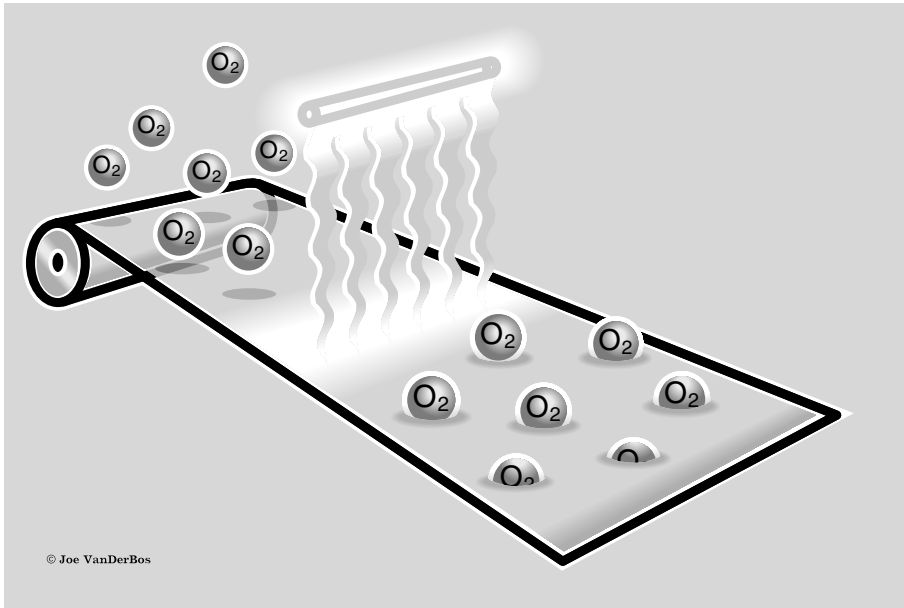


Figure 3.2 Light-activated oxygen scavenging films Cryovac® OS Films. Reproduced with permission from Cryovac Food Packaging, Sealed Air Corporation, USA.

Standa Industrie, France), FreshPax® (Multisorb Technologies, Inc., USA) and Oxysorb® (Pillsbury Co., USA).

The scientific literature contains a number of references to studies that examine the influence of oxygen scavenger sachets on meat quality and these have been reviewed by Kerry *et al.* (2006).

An alternative to sachets involves the incorporation of the oxygen scavenger into the packaging structure itself. This minimizes negative consumer response and offers a potential economic advantage through increased outputs. It also eliminates the risk of accidental rupture of the sachets and inadvertent consumption of their contents (Suppakul *et al.*, 2003). Cryovac® OS2000™ polymer based oxygen scavenging film has been developed by Cryovac Div., Sealed Air Corporation, USA. This UV light-activated oxygen scavenging film (Figure 3.2), composed of an oxygen scavenger layer extruded into a multilayer film, can reduce headspace oxygen levels from 1 % to ppm levels in 4–10 days and is comparable in effectiveness with oxygen scavenging sachets. The OS2000™ scavenging films have applications in a variety of food products including dried or smoked meat products and processed meats (Butler, 2002). A similar UV light-activated oxygen scavenging polymer ZERO₂®, developed by CSIRO, Division of Food Science Australia in collaboration with VisyPak Food Packaging, Visy Industries, Australia, forms a layer in a multilayer package structure and can be used to reduce discoloration of sliced meats. Another successful commercial example for use with meat is the OSP™ system (Chevron Philips Chemical Company, USA). The active substances of OSP™ systems are ethylene methacrylate and cyclohexene methacrylate, which need to be blended with a catalyst or photoinitiator in order to activate the oxygen scavenging mechanism.

3.3 Carbon Dioxide Scavengers and Emitters

As stated previously, the function of carbon dioxide within a packaging environment is to suppress microbial growth. Therefore a carbon dioxide generating system can be viewed as a technique complementary to oxygen scavenging (Suppakul *et al.*, 2003). Since the permeability of carbon dioxide is three-to five-times higher than that of oxygen in most plastic films, it must be continuously generated to maintain desired concentration within the package (Ozdemir and Floros, 2004). High carbon dioxide levels (10–80 %) are desirable for foods such as meat and poultry in order to inhibit surface microbial growth and extend shelf life. Removal of oxygen from the package creates a partial vacuum which may result in the collapse of flexible packaging. Also, when a package is flushed with a mixture of gases including carbon dioxide, the carbon dioxide may dissolve in the product and create a partial vacuum. In such cases, the simultaneous release of carbon dioxide from oxygen-consuming sachets is desirable. Such systems are based on either ferrous carbonate or a mixture of ascorbic acid and sodium bicarbonate (Rooney, 1995). Examples of commercially available dual action combined carbon dioxide generators/oxygen scavengers are Ageless[®] G (Mitsubishi Gas Chemical Co., Japan) and FreshPax[®] M (Multisorb Technologies, Inc, USA). Carbon dioxide emitting sachets or labels can also be used alone. The Verifrais[™] package, manufactured by SARL Codimer (Paris, France), has been used to extend the shelf life of fresh meats. This innovative package consists of a standard MAP tray but has a perforated false bottom under which, a porous sachet containing sodium bicarbonate/ascorbate is positioned. When juice exudates from the packaged meat drips onto the sachet, carbon dioxide is emitted, thus replacing any carbon dioxide absorbed by the meat and preventing package collapse.

The inhibition of spoilage bacteria utilizing active packaging technology may reduce bacterial competition and thus permit growth of toxin producing, non-proteolytic *C. botulinum* or other pathogenic bacteria (Sivertsvik, 2003). Lövenklev *et al.* (2004) reported that while a high concentration of carbon dioxide decreased the growth rate of non-proteolytic *C. botulinum* type B, the expression and production of toxin was greatly increased. As such, the risk of botulism may be increased, rather than reduced, in high carbon dioxide MAP systems. It would appear that further research into the safety risks associated with the use of carbon dioxide in such packaging systems is necessary.

Carbon dioxide absorbers, (sachets) consisting of either calcium hydroxide and sodium hydroxide, or potassium hydroxide, calcium oxide and silica gel, may be used to remove carbon dioxide during storage in order to prevent bursting of packages. Possible applications include use in packs of dehydrated poultry products and beef jerky (Ahvenainen, 2003).

3.4 Moisture Control

The main purpose of liquid water control is to lower the water activity of the product, thereby suppressing microbial growth (Vermeiren *et al.*, 1999). However, as the growth sector in fresh chilled muscle-based foods has evolved, another very good reason to control residual levels of predominantly product-released water in packs is to enhance the visual impact of product at retail level during product–consumer interaction. Temperature cycling



Figure 3.3 *Dri-Loc[®] Absorbent pads, Cryovac[®], Sealed Air Corporation. Reproduced with permission from Cryovac Food Packaging, Sealed Air Corporation, USA.*

of high water activity foods, like meat and poultry products, has led to the use of plastics with an antifog additive that lowers the interfacial tension between the condensate and the film. This promotes film transparency and enables the customer to see clearly the packaged food (Rooney, 1995), although it does not affect the amount of liquid water present inside the package. Several companies manufacture drip absorbent sheets or pads such as Cryovac[®] Dri-Loc[®] (Sealed Air Corporation, USA), Thermarite[®] or Peaksorb[®] (Australia), Toppan[™] (Japan) and Fresh-R-Pax[™] (Maxwell Chase Technologies, LLC, USA) for liquid control in high water activity foods such as meat and poultry. Typically, these systems consist of a super-absorbent polymer located between two layers of a microporous or non-woven polymer (Figure 3.3). Such sheets are used as drip-absorbing pads placed under whole chickens or chicken cuts (Suppakul *et al.*, 2003).

3.5 Antimicrobial Packaging

Microbial contamination and subsequent growth reduces the shelf-life of foods and increases the risk of food borne illness. Traditional methods of preserving foods from the effects of microbial growth include thermal processing, drying, freezing, refrigeration, irradiation, MAP and addition of antimicrobial agents or salts. However some of these techniques cannot be applied to certain products such as fresh meats (Quintavalla

and Vicini, 2002). Antimicrobial packaging is a promising form of active packaging especially for meat and poultry products. Since microbial contamination of muscle-based food products occurs primarily at the surface, attempts have been made to improve safety and to delay spoilage by the use of antibacterial sprays or dips. Limitations of such an approach include neutralisation of antibacterial compounds on contact with the meat surface or diffusion of compounds from the surface into the meat mass. Incorporation of bactericidal agents into meat formulations may result in partial inactivation of the active compounds by meat constituents and therefore exert a limited effect on surface microflora (Quintavalla and Vicini, 2002). Antimicrobial food packaging materials must extend the lag phase and reduce the growth phase of microorganisms in order to extend shelf life and to maintain product quality and safety (Han, 2000). Comprehensive reviews on antimicrobial food packaging have been published by Appendini and Hotchkiss (2002), Suppakul *et al.* (2003), and Coma (2008). To confer antimicrobial activity, antimicrobial agents may be coated, incorporated, immobilised, or surface modified onto package materials (Suppakul *et al.*, 2003). The classes of antimicrobial compound used include acid anhydrides, alcohols, bacteriocins, chelators, enzymes, organic acids and polysaccharides. Examples of commercial antimicrobial materials include concentrates (e.g. AgION™, AgION Technologies LLC, USA), extracts (Nisaplin® (Nisin), Integrated Ingredients, USA) and films (Microgard™ Rhone-Poulenc, USA). Antimicrobial packages have not been commercially successful, with the exception in Japan, of Ag-substituted zeolite, which is the most common antimicrobial agent incorporated into plastics. Ag-ions inhibit a range of metabolic enzymes and have strong antimicrobial activity (Vermeiren *et al.*, 1999). Antimicrobial films can be classified into two types: those that contain an antimicrobial agent that migrates to the surface of the food and, those which are effective against surface growth of microorganisms without migration. Research conducted on the use, application and operation of antimicrobial agents contained within or on meat packaging materials has been reviewed by Kerry *et al.* (2006) and Coma (2008).

3.6 Sensors

The most important (non-inert) gases in MAP products are oxygen and carbon dioxide and their headspace partial pressures serve as useful indicators of the quality status of a meat product. Headspace profiles of oxygen and carbon dioxide can change over time and are influenced by product type, respiration, packaging material, pack size, volume ratios, storage conditions, package integrity, etc. A number of analytical techniques are available to monitor gas phases in MAP products. Instrumental techniques such as GC and GC/MS are not suitable for rapid measurements and are time consuming and expensive. Portable headspace oxygen and/or carbon dioxide gas analysers use 'minimally destructive' techniques (packages can be resealed) but tend not to be applicable to real-time, on-line, control of packaging processes or large scale usage. An optical sensor approach is thought to offer a realistic alternative to such conventional methods.

Many intelligent packaging concepts involve the use of sensors and indicators. For the purposes of clarity the two areas will be discussed separately, although such a distinction is somewhat arbitrary and some overlap is unavoidable. In general, the use of these systems

is envisaged in terms of incorporation into established meat and poultry packaging formats such as MAP and vacuum packaging.

A sensor is defined as a device used to detect, locate or quantify energy or matter, giving a signal for the detection or measurement of a physical or chemical property to which the device responds (Kress-Rogers, 1998a). To qualify as a sensor, a device must provide continuous output of a signal. Most sensors contain two basic functional units : a receptor and a transducer. In the receptor physical or chemical information is transformed into a form of energy that may be measured by the transducer. The transducer is a device capable of transforming the energy carrying the physical or chemical information about the sample into a useful analytical signal.

Research and development of sensor technology has been largely concentrated in biomedical and environmental applications (Demas *et al.*, 1999). The specifications of such sensors are, however, quite different from those required for food packaging applications. The development of improved methods to determine food quality such as freshness, microbial spoilage, oxidative rancidity or oxygen and/or heat induced deterioration is extremely important to food manufacturers. In order to maximise the quality and safety of foodstuffs, a prediction of shelf-life based on standard quality control procedures is normally undertaken. Replacement of such time-consuming and expensive quality measurements with rapid, reliable and inexpensive alternatives has lead to greater efforts being made to identify and measure chemical or physical indicators of food quality. Development of a potential sensor for rapid quantification of such an indicator is known as the marker approach (Kress-Rogers, 2001). Determination of indicator headspace gases provides a means by which the quality of a meat product and the integrity of the packaging in which it is held can be established rapidly and inexpensively. One means of doing so is through the production of intelligent packaging incorporating gas sensor technology.

Chemical sensor and biosensor technology has developed rapidly in recent years. The main types of transducers with potential use in meat packaging systems include electrical, optical, thermal or chemical signal domains. Sensors can be applied as the determinant of a primary measurable variable or, using the marker concept, as the determinant of another physical, chemical or biological variable (Kress-Rogers, 1998a). In the case of headspace gas sensing, accurate measurements are desirable as indicators of meat product quality. Developments in sensor technology has narrowed the gap between the theoretical and the commercially viable, and although practical uses of sensors in the meat industry remain very limited, significant practical steps towards more widespread use have been made (Kerry and Papkovsky, 2002). High development and production costs, strict industry specifications, safety considerations and relatively limited demand (in comparison with the biomedical sector) from industry and consumer alike, have proved the main obstacles to commercial use. Very few systems to date have been able to match exacting industry standards required for successful application. However, developments in materials science, continuous automation processes, signal processing and process control, along with transfer of technology from the biomedical, environmental and chemical sectors all lead toward the likelihood of more universal adoption of sensor technology in food packaging. Greater pressure on food manufacturers to guarantee safety, quality and traceability is also likely to promote the establishment of commercial sensor technology in food packaging.

3.6.1 Gas Sensors

Gas sensors are devices that respond reversibly and quantitatively to the presence of a gaseous analyte by changing the physical parameters of the sensor and are monitored by an external device. Systems presently available for gas detection include amperometric oxygen sensors, potentiometric carbon dioxide sensors, metal oxide semiconductor field effect transistors, organic conducting polymers and piezoelectric crystal sensors (Kress-Rogers, 1998b). Conventional systems for oxygen sensors based on electrochemical methods have a number of limitations (Trettnak *et al.*, 1995) including consumption of analyte (oxygen), cross-sensitivity to carbon dioxide and hydrogen sulfide and fouling of sensor membranes. They also involve destructive analysis of packages.

In recent years, a number of instruments and materials for optical oxygen sensing have been described (Papkovsky *et al.*, 1995; Trettnak *et al.*, 1995). These sensors are usually comprise a solid-state material and operate on the principle of luminescence quenching or absorbance changes caused by direct contact with the analyte. They are chemically inert, do not consume analytes and provide a non-invasive technique for gas analysis through translucent materials.

Approaches to optochemical sensing have included (a) a fluorescence-based system using a pH sensitive indicator (Wolfbeis *et al.*, 1988), (b) absorption-based colourimetric sensing realised through a visual indicator (Mills *et al.*, 1992), and (c) an energy transfer approach using phase fluorimetric detection (Neurater *et al.*, 1999). The latter allows for the possibility of combining oxygen and carbon dioxide measurements in a single sensor through compatibility with previously developed oxygen sensing technology. Most carbon dioxide sensors, however, have been developed for biomedical applications and the use of existing carbon dioxide sensors in food packaging applications is still not feasible (Kerry and Papkovsky, 2002).

3.6.2 Fluorescence-based Oxygen Sensors

Fluorescence-based oxygen sensors represent the most promising systems to date for remote measurement of headspace gases in packaged meat products. Reiniger *et al.* (1996) first introduced the concept of using luminescent dyes quenched by oxygen as non-destructive indicators in food packaging applications. A number of disposable oxygen sensing prototypes has been developed that can be produced at low cost and provide rapid determination of oxygen concentration (Kerry and Papkovsky, 2002).

The active component of a fluorescence-based oxygen sensor normally consists of a long-delay fluorescent or phosphorescent dye encapsulated in a solid polymer matrix. The dye-polymer coating is applied as a thin film coating on a suitable solid support. Molecular oxygen, present in the packaging headspace, penetrates the sensitive coating through simple diffusion and quenches luminescence by a dynamic, i.e. collisional, mechanism. Oxygen is quantified by measuring changes in luminescence parameters against a predetermined calibration. The process is reversible and clean: neither the dye nor oxygen is consumed in the photochemical reactions involved, no by-products are generated and the whole cycle can be repeated.

Materials for oxygen sensors must meet strict sensitivity and working performance requirements if they are to prove suitable for commercial intelligent packaging applications.

They must also have fluorescence characteristics suited to the construction of simple measuring devices. Fluorescence and phosphorescence dyes with lifetimes in the microsecond range are best suited to oxygen sensing in food packaging. Other necessary features include suitable intensity, well resolved excitation and emission longwave bands and good photostability characteristics of the indicator dye. Such features allow sensor compatibility with simple optoelectronic measuring devices (LEDs, photodiodes, etc.), minimise interference by scattering and sample fluorescence, and allow long-term operation without recalibration (Papkovsky *et al.*, 1995). Materials using fluorescent complexes of ruthenium, phosphorescent palladium(II)- and platinum(II)-porphyrin complexes and related structures have shown considerable promise as oxygen sensors (Papkovsky *et al.*, 1991; 1995).

The combination of indicator dye and encapsulating polymer medium determines the sensitivity and effective working range of such sensors. For the purposes of food packaging applications, dyes with relatively long emission lifetimes ($\sim 40\text{--}500\ \mu\text{s}$) such as Pt-porphyrins combined with polystyrene as polymer matrix appear to offer greatest potential (Papkovsky *et al.*, 2000). Other polymers with good gas-barrier properties such as polyamide, polyethylene terephthalate and PVC are not suitable for oxygen sensing as oxygen quenching is slow in such media. The use of plasticised polymers is also unsuitable due to toxicity concerns associated with potential plasticiser migration.

Details relating to sensor fabrication and the criteria that must be considered in order that commercialisation of such technology becomes a reality is described in more detail by Kerry and Papkovsky (2002) and Kerry *et al.* (2006).

Publications on the suitability of fluorescence-based oxygen sensors have provided useful data on their effectiveness in meat packaging applications. Fitzgerald *et al.* (2001) examined the potential of platinum-based disposable oxygen sensors as a quality control instrument for vacuum-packed raw and cooked meat and MA packed sliced ham (Figure 3.4). Direct contact of sensors on the foods provided accurate oxygen profiles over time and correlated well with conventional headspace analysis. Smiddy *et al.* (2002a) used oxygen sensors to examine the effects of residual oxygen concentration on lipid oxidation in both anaerobically packaged MA and vacuum-packed cooked chicken. Similarly, this approach was repeated for raw and cooked beef (Smiddy *et al.*, 2002b). These studies further demonstrated the suitability of such sensors for measuring oxygen levels in commercially used meat packaging and their potential as predictors of quality. Papkovsky *et al.* (2002) used oxygen sensors to measure oxygen content in the headspace of four commercial sliced ham products. Accurate measurements were made under ambient light conditions, in direct contact with the product and under conditions of significant temperature variation. Although the sensor demonstrated minor changes in calibration as a result of direct physical contact with the meat surface over a prolonged period, these effects were minimised through optimisation of the sensor material. It is unlikely in any event, that sensors placed in direct contact with a meat product would be acceptable to producer or consumer alike. O'Mahony *et al.* (2004) used sensors printed directly onto the packaging material of *sous vide* beef lasagne. Although oxygen profiles, microbial growth and lipid oxidation were clearly correlated, further studies appear necessary to investigate issues relating to sensor/packaging material compatibility. Fluorescent oxygen sensors were also useful in detecting a substantial fraction of commercial anaerobic MA or vacuum packed meat products that contained elevated levels of oxygen (Papkovsky *et al.*, 2002; Smiddy *et al.*, 2002c).

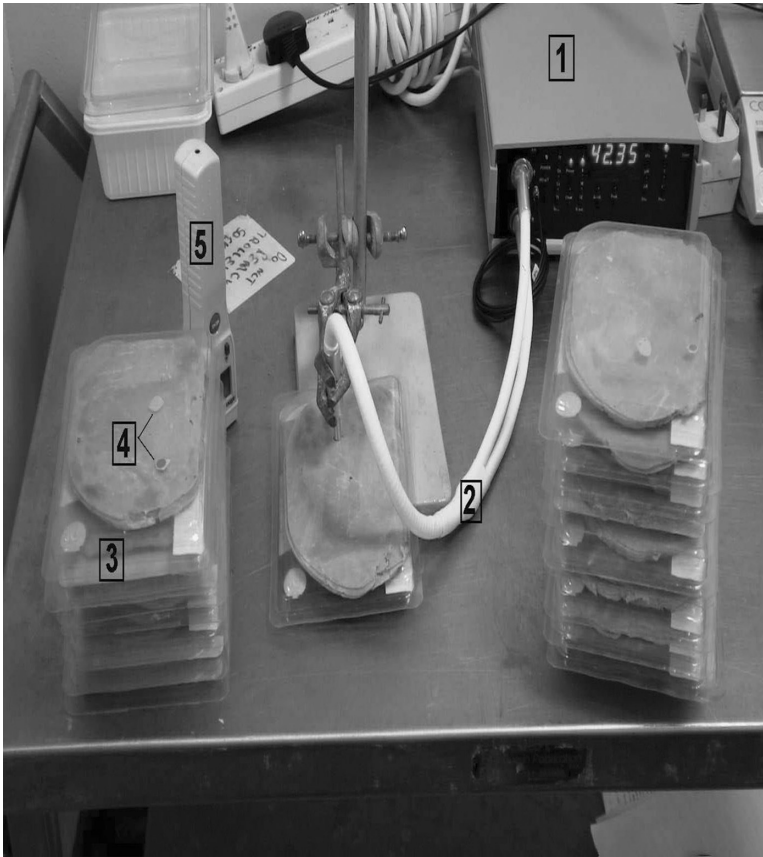


Figure 3.4 Use of platinum fluorescent-based disposable oxygen sensors in MAP packed sliced ham (number 4 in figure indicating as part of this mail).

The development of oxygen sensors is indicative of a move towards commercialisation of indicator-based, intelligent, meat packaging systems. Full commercial realisation might ultimately mean the production of huge numbers of sensors for use throughout the meat distribution chain. It has been estimated that in today's terms, each sensor should cost less than €0.01 to produce (Kerry and Papkovsky, 2002) and impact minimally on packaged meat production costs.

3.6.3 Biosensors

Recently developed biosensor technologies represent another area with considerable potential for application in intelligent meat packaging systems. Biosensors are compact analytical devices that detect, record and transmit information pertaining to biological reactions (Yam *et al.*, 2005). They consist of a bioreceptor specific to a target analyte and a transducer to convert biological signals to a quantifiable electrical response. Bioreceptors are organic

materials such as enzymes, antigens, microbes, hormones and nucleic acids. Transducers may be electrochemical, optical, calorimetric, etc., and are system dependent. Intelligent packaging systems incorporating biosensors have the potential for extreme specificity and reliability. Market analysis of pathogen detection and safety systems for the food packaging industry suggests that biosensors offer considerable promise for future growth (Alocilja and Radke, 2003).

The majority of available biosensor technology is not yet capable of commercial realisation in the food sector. ToxinGuard™ developed by Toxin Alert (Ontario, Canada) is a visual diagnostic system incorporating antibodies printed on polyethylene-based plastic packaging capable of detecting target pathogens such as *Salmonella* sp., *Campylobacter* sp., *Escherichia coli* 0517 and *Listeria* sp. (Bodenhammer, 2002; Bodenhammer *et al.*, 2004). When the food packaging comes into contact with targeted bacteria, a visual signal alerts the consumer or retailer. Toxinguard™ can be targeted to detect freshness degradation, as well as the presence of specific food hazards such as pesticides, or indicators of genetic modification.

Bioett has developed a system based on a biosensor for temperature monitoring. The Bioett System monitors the accumulated effect of temperature on products over time. The system consists of a chipless RF circuit with a built-in biosensor that can be read with a handheld scanner at various points in the supply chain. The information is stored in a database and can be used to analyse the cold chain and validate that the agreed temperature has been maintained. A Time Temperature Biosensor (TTB), attached to 5-kg cases of frozen meat balls, is activated at source. The biosensor registers the accumulated temperatures that the product has been exposed to and this information can be used to optimise and monitor the cold-chain distribution system. A scanner can read the biosensor via radio waves (radio frequency) and also uniquely identifies the goods using a barcode system. The scanner also incorporates a software defined radio subsystem that can also be used for reading of RFID tags. Such systems give some insight into products likely to become more mainstream in the years to come.

3.7 Indicators

Indicators may be defined as a substances that indicate the presence, absence or concentration of another substance, or the degree of reaction between two or more substances by means of a characteristic change, especially in colour. In contrast with sensors, indicators do not comprise receptor and transducer components and communicate information through direct visual change. Numerous forms of indicator exist.

3.7.1 Integrity Indicators

Another alternative approach to established package-destructive techniques for measuring meat quality is the use of non-invasive indicator systems. Such systems usually provide qualitative or semi-quantitative information through visual colorimetric changes or through comparison with standard references. The majority of indicators have been developed to test package integrity. The most common cause of integrity damage in flexible plastic packages is associated with leaking seals (Hurme, 2003). Permanent attachment of a leak

indicator or sensor (i.e. visual or optochemical) to a package holds promise as a means of ensuring package integrity through the distribution chain. A number of studies on package integrity in MAP meat products (Eilamo *et al.*, 1995; Randell *et al.*, 1995; Ahvenainen *et al.*, 1997; Smolander *et al.*, 1997) have established critical leak sizes and associated quality deterioration. Standard (destructive) manual methods for package integrity and leak testing are both laborious and can test only limited numbers of packs (Hurme, 2003). Currently available non-destructive detection systems have other disadvantages such as requirements for specialised equipment, slow sampling time and an inability to detect leakages that are penetrable by pathogens (Stauffer, 1988; Hurme and Ahvenainen, 1998).

Much of the research into integrity detection has focused on visual oxygen indicators for MA packaged products (the oxygen sensors discussed previously are also applicable to integrity testing). With the exception of high oxygen content MA packaging of fresh meat (primarily to enhance colour) many foods are packaged in low (0–2 %) atmospheres. In such cases, leaks normally result in a significant increase in oxygen concentration. Many visual oxygen indicators have been patented and are based mainly on the use of redox dyes (Yoshikawa *et al.*, 1987; Krumhar and Karel, 1992; Mattila-Sandholm *et al.*, 1995; Davies and Gardner, 1996). Such devices have been tested as leak indicators in MA packaged minced steaks and minced meat pizzas and reported as reliable (Eilamo *et al.*, 1995; Ahvenainen *et al.*, 1997). Disadvantages of such devices include high sensitivity (colour change resulting from oxygen concentrations as low as 0.1 % means that many indicators are susceptible to residual oxygen in MA packs) and reversibility (undesirable where leak-induced increases in oxygen are consumed through subsequent microbial growth). Few of these devices have been taken up commercially. One indicator system, specifically designed for MAP foods contains, in addition to an oxygen sensitive dye, an oxygen absorbing component and exemplifies active and intelligent packaging in a single system (Mattila-Sandholm *et al.*, 1998). In-line, non-destructive package leak detection systems are not yet commercially viable due to high costs and a lack of reliability.

A number of companies have produced oxygen indicators, the main application of which has been for the confirmation of proper functioning of oxygen absorbers. Trade names of such devices include Ageless Eye[®] (Figure 3.5), Vitalon[®], and Samso-Checker[®].

A visual carbon dioxide indicator system consisting of calcium hydroxide (carbon dioxide absorber) and a redox indicator dye incorporated in polypropylene resin was described by Hong and Park (2000) and may be applicable to certain meat packaging applications.

3.7.2 Freshness Indicators

The information provided by intelligent packaging systems on the quality of meat products may be either indirect (e.g. changes in oxygen concentration within packs may imply quality deterioration through established correlation) or direct. Freshness indicators provide direct product quality information resulting from microbial growth or chemical changes within a food product. Microbiological quality may be determined through reactions between indicators included within the package and microbial growth metabolites (Smolander, 2003). As yet the number of practical concepts of intelligent package indicators for freshness detection is very limited. Despite this, potential exists for the development of freshness indicators based on established knowledge of quality indicating metabolites. The improved detection of biochemical changes during storage and spoilage of foods (Dainty, 1996; Nychas *et al.*,

AGELESS-EYE® Oxygen Indicator

The AGELESS-EYE is an in-package monitor which indicates the presence of oxygen at a glance.

Magnified

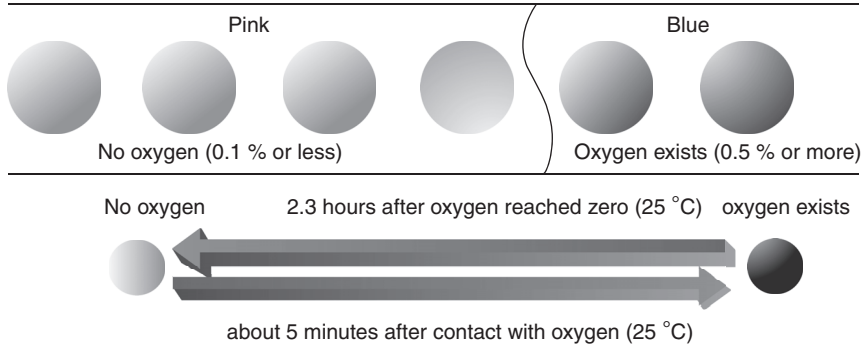


Figure 3.5 Ageless-Eye® by Mitsubishi Gas Chemical Co. used for oxygen detection. Reproduced with permission from Ageless sales, Mitsubishi Gas Chemical Co. Japan.

1998) provide the basis on which freshness indicators may be developed based on target metabolites associated with microbiologically induced deterioration.

The formation of different potential indicator metabolites in meat products is dependent on the interaction between product type, associated spoilage flora, storage conditions and packaging system. A number of marker metabolites associated with muscle food products exist upon which indicator development may be based.

Changes in the concentration of organic acids such as n-butyrate, L-lactic acid, D-lactate and acetic acid during storage offer potential as indicator metabolites for a number of meat products (Shu *et al.*, 1993). Colour based pH indicators offer potential for use as indicators of these microbial metabolites.

Ethanol, like lactic acid and acetic acid, is an important indicator of fermentative metabolism of lactic acid bacteria. Randell *et al.* (1995) reported an increase in the ethanol concentration of anaerobically MA packaged marinated chicken as a function of storage time.

Biogenic amines such as histamine, putrescine, tyramine and cadaverine have been implicated as indicators of meat product decomposition (Okuma *et al.*, 2000; Kaniou *et al.*, 2001; Rokka *et al.*, 2004). Given toxicological concerns associated with these compounds and their lack of impact on sensory quality, the development of effective amine indicators would be of benefit. Detection systems described by Miller *et al.* (1999) and Loughran and Diamond (2000) provide potential for commercial development. In 1999, COX Technologies, USA, launched FreshTag® colourimetric indicator labels that react to volatile amines produced during storage of fish and seafood products.

Carbon dioxide produced during microbial growth can in many instances be indicative of quality deterioration. In MA packaged meat products containing high carbon dioxide concentration (typically 20–80 %), indication of microbial growth by changes in carbon dioxide content is problematical, although application of pH dye indicators may hold promise in other meat packaging systems.

Hydrogen sulfide, a breakdown product of cysteine with intense off-flavours and low threshold levels, is produced during the spoilage of meat and poultry by a number of bacterial species. It forms a green pigment (sulphmyocin) when bound to myoglobin and this pigment formed the basis for the development of an agarose-immobilised, myoglobin-based freshness indicator in unmarinated broiler pieces (Smolander *et al.*, 2002). The indicator was not affected by the presence of nitrogen or carbon dioxide and offers potential.

Freshness indicators based on broad spectrum colour changes have a number of disadvantages that need to be resolved before widespread commercial uptake is likely. A lack of specificity means that colour changes indicating contamination can occur in products free from any significant sensory or quality deterioration. The presence of certain target metabolites is not necessarily an indication of poor quality. More exact correlations need to be established between target metabolite, product type and organoleptic quality and safety. The possibilities of false negatives are likely to dissuade producers from adopting indicators unless specific indication of actual spoilage can be guaranteed.

3.7.3 Time–Temperature Indicators

Among the intelligent packaging solutions available, time–temperature indicators or integrators (TTIs) are expected to witness the sharpest growth in sales in the next 5 years. A time–temperature indicator or integrator (TTI) is defined as a device used to show a measurable, time–temperature dependent change that reflects the full or partial temperature history of the food product to which it is attached (Taoukis and Labuza, 1989). Operation of TTIs is based on mechanical, chemical, electrochemical, enzymatic or microbiological change, usually expressed as a visible response in the form of a mechanical deformation, colour development or colour movement (Taoukis and Labuza, 2003). The visible response thus gives a cumulative indication of the storage temperature to which the TTI has been exposed. TTIs are classified as either partial history or full history indicators, depending on their response mechanism. Partial history indicators do not respond unless a temperature threshold has been exceeded and indicate that a product has been exposed to a temperature sufficient to cause a change in product quality or safety. Full history TTIs give a continuous temperature-dependent response throughout a product's history and constitute the main focus of interest for research and commercial exploitation.

Essentially TTIs are small tags or labels that keep track of time–temperature histories to which a perishable product is exposed from the point of manufacture to the retail outlet or end-consumer. Their use in meat and poultry products, where monitoring of the cold distribution chain, microbial safety and quality are of paramount importance, offers enormous potential.

The basic requirement of an effective TTI is to indicate clear, continuous, irreversible reaction to changes in temperature. Ideally, TTIs should also be low cost, small, reliable, easily integrated into food packaging, have a long pre- and post-activation shelf-life and be unaffected by ambient conditions other than temperature. TTIs should also be flexible to a range of temperatures, robust, pose no toxicological or safety hazard and convey information in a clear manner.

A large number of TTI types have been developed and patented, the principles and applications of which have been reviewed previously (Taoukis and Labuza, 2003). TTIs currently commercially available include a number of diffusion, enzymatic and polymer-based systems, all of which offer potential in meat and poultry products.

Diffusion-based TTIs. The 3M Monitor Mark[®] (3M Company, St Paul, Minnesota, USA) is a non-reversible indicator dependent on the diffusion of a coloured fatty acid ester along a porous wick made of high quality blotting paper. The measurable response is the distance of the advancing diffusion front from the origin. The useful range of temperatures and the response life of the TTI are determined by the type and concentration of ester.

Another diffusion-based TTI, Freshness Check[®], produced by the same company incorporates a viscoelastic material that migrates into a diffusively light-reflective porous matrix at a temperature dependent rate. This causes a progressive change in the light transmissivity of the porous matrix and provides a visual response.

Enzymatic TTIs. The VITSAB[®] TTI (VITSAB A.B., Malmö, Sweden) is based on a colour change induced by a drop in pH resulting from the controlled enzymatic hydrolysis of a lipid substrate. The indicator consists of two separate compartments containing an aqueous solution of lipolytic enzymes and another containing the lipid substrate suspended in an aqueous medium and a pH indicator mix. Different enzyme–substrate combinations are available to give a variety of response lives and temperature dependencies. Activation of the TTI is brought about by mechanical breakage of a seal separating the two compartments and may be done manually or by online automation. Hydrolysis of the substrate causes a drop in pH and a subsequent colour change in the pH indicator from dark green to bright yellow. Visual evaluation of the colour change is made by reference to a five-point colour scale. CheckPoint[®] labels are the latest TTIs developed by VITSAB, which comprise a label type designed to create a better subjective reading response for users and offer direct application to poultry and ground beef products (Figure 3.6).

Cryolog (Gentilly, France) has developed two TTI systems relevant to the food industry. (eO)[®] is an adhesive label TTI in the form of a small gel pad shaped like the petals of a flower that changes from green (good) to red (not good) as shown in Figure 3.7. The colour change represents a pH change due to microbial growth of food microorganisms within the gel itself and its abrupt nature removes any possibility for confusion over whether



Figure 3.6 The TTI CheckPoint[®] system by Vitsab International, Sweden.



Figure 3.7 The TTI Cryolog system from Gentilly, France. Reproduced with permission from Cryolog S.A., Gentilly, France.

the end point has been reached. TRACEO[®] is a transparent adhesive label, designed for use on refrigerated products, placed over the barcode. It uses colouring and opacifying reactions (colourless to red) to indicate when a product is no longer fit for consumption, either because the product has reached its ‘use-by date’, or because it has been subject to a critical accumulation of ruptures in the cold chain. Once the label is red the barcode is rejected by the scanner at check-out.

Polymer-based TTIs. Lifelines Freshness Monitor[®] and Fresh-Check TTIs (Lifelines Technology, Inc., Morris Plains, New Jersey, USA) are based on temperature dependent polymerisation reactions in which diacetylene crystals polymerise via 1,4-addition polymerisation to a highly coloured polymer. Resulting changes in reflectance can be measured by scanning with a laser optic wand. The Fresh-Check[®] consumer version uses a circular label in which the colour of the inner circle is compared to that of an outer circle in order to establish use-by status.

OnVu[™] (Ciba Specialty Chemicals, Inc., Switzerland) produce TTI labels based on organic pigments that change colour with time at rates determined by temperature. The TTI labels consist of a heart shaped ‘apple’ motif containing an inner heart shape. The image is stable until activated by UV light from an LED lamp, when the inner heart changes to a deep blue colour. A filter is then added over the label to prevent it being recharged. The blue inner heart changes to white as a function of time and temperature (Figure 3.8). The system can be applied as a label or printed directly onto the package. Universal Product Codes (UPC) or barcodes, are quintessential to food packaging. Data acquired from barcode readers provides an enormous wealth of information. The Food Sentinel System[™] from SIRA Technologies in the USA uses a modified barcode containing a proprietary thermochromic printing ink which is printed in non-scannable colour. On encountering product abuse, the thermochromic ink changes to an irreversible deep magenta colour which is visible and will

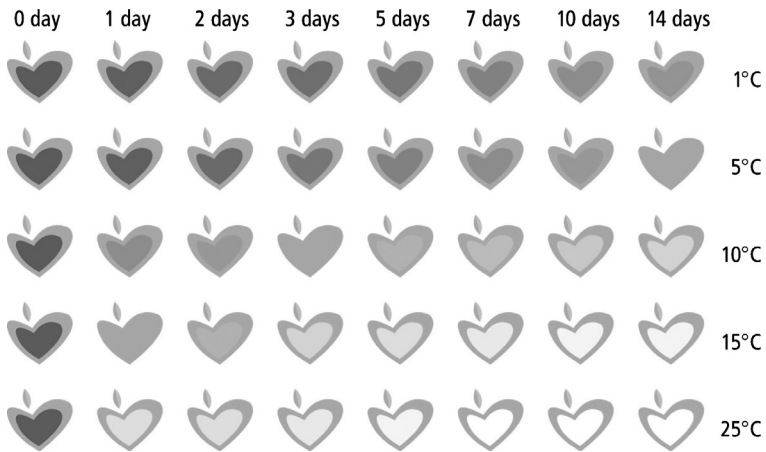


Figure 3.8 The TTI system OnVu™ from Ciba Specialty Chemicals, Inc., Switzerland. Reproduced with permission from Ciba Specialty Chemicals Inc., Switzerland.

be detected during scanning (Figure 3.9). It is therefore capable of adding a temperature and shelf-life monitor to any product barcode, thus preventing the sale of contaminated food and archiving the incident.

A number of TTI systems have their histories read by RFID readers (see next section) rather than by direct visual means. These include Bioett[®], Timestrip[®], KSW Microtec[®] and TempTime[®]. The use of electronic readers allows storage of information and subsequent downloading to local networks and databases.

A number of validation studies has been undertaken in order establish the usefulness of TTIs to food products (Riva *et al.*, 2001; Shimoni *et al.*, 2001; Welt *et al.*, 2003). Yoon *et al.* (1994) showed a positive correlation between oxidative stability and TTI colour change using a phospholipid/phospholipase-based TTI in frozen pork. Smolander *et al.* (2004)

SIRA Food Sentinel System™

Activated Label

PORK LOIN CENTER CUT CHOPS

Bar Code Food Safety Label

-  Keep refrigerated or frozen.
-  Wash working surfaces (including cutting boards), utensils, and hands after touching raw meat or poultry.
-  Cook thoroughly.
-  Keep hot foods hot. Refrigerate leftovers immediately or discard.

FOOD SENTINEL SYSTEM: To assure safe handling, this package is being automatically monitored for proper refrigeration and shelf life by time & temperature-sensitive barcodes. Abused product can also be visually identified by an extra wide, colored bar in the lower bar code.



Ranchers Brand
Sure **2B** Pure

Tare 0.04 lb.	Store No. 3218	Sell By 11/20/06
Net wt/ct 1.29/lb.	Unit Price \$5.69/lb.	Total Price \$7.34

Figure 3.9 The Food Sentinel System™ from SIRA Technologies in the USA. Reproduced with permission from SIRA Technologies Inc., USA.

and Vainionpää *et al.* (2004) determined the applicability of VITSAB®, Fresh-Check® and 3M Monitor® TTIs for monitoring the quality of MA packed broiler cuts at different temperatures and in comparison with several standard analytical methods respectively. In both studies, TTIs were closely correlated with microbiological analyses of spoilage bacteria and were shown to be more effective than certain metabolic quality indices such as spoilage-associated volatiles, biogenic amines and organic acids.

Initial expectations for the potential of TTIs to contribute to improved standards in food distribution, quality and safety have not been realised to date. Factors such as cost, reliability and applicability have all been influential in this regard. The cost of TTIs has been estimated to range from \$0.02 to \$0.20 per unit (Taoukis and Labuza, 2003). Given normal economies of scale, cost-benefit analysis should favour more widespread use of TTIs in due course. The use of thermochromic inks (inks that change colour with temperature) is likely to become more widespread particularly in the light of views that only printing can deliver sophisticated electronic capabilities to packaging at a price that makes next generation TTIs

economically viable. Recent developments in the area of printed electronics make such a scenario a real possibility.

In recent years, TTI systems have achieved high standards of production and quality assurance and can provide reproducible responses according to BSI specifications (BS 7908: 1999). A substantial hurdle to more extensive commercialisation of TTIs has been the question of applicability. Generalisations on the relationship between temperature and quality of food classes have proved insufficient, as even foods of similar type differ markedly in terms of response. For successful application of TTIs to meat and poultry products, and food products in general, there is a requirement that the TTI response matches the behaviour of the food. Whilst the expectation for a TTI to strictly match the behaviour of a foodstuff over a wide temperature range is unfeasible, a thorough knowledge of the shelf-life loss behaviour of a food system based on accurate kinetic models is essential (Taoukis and Labuza, 2003). Advances in food modelling are now making this possible (Taoukis, 2001).

In 1991 a UK survey (Anonymous, 1991) indicated that 95 % of respondents ($n = 511$) considered TTIs to be a good idea but indicated that substantial publicity or an educational campaign would be required for general use. It is likely that such attitudes still apply today. Despite predictions for the full commercial realisation of TTIs, adoption has been limited. However, given technological development and greater consumer appreciation for the need for food safety monitoring (particularly in meat products), analysts believe that TTIs will find widespread commercial application in the food industry. The critical importance of maintaining proper storage temperatures for meat and poultry products throughout the distribution chain means that this sector of the food industry could be a major beneficiary from such a development.

3.8 Radio Frequency Identification

Radio Frequency Identification (RFID) is an electronic, information-based form of intelligent packaging. RFID uses tags affixed to assets (cattle, containers, pallets, etc.) to transmit accurate, real time, information to a user's information system. RFID is one of the many automatic-identification technologies (a group which includes barcodes) and offers a number of potential benefits to the meat production, distribution and retail chain. These include traceability, inventory management, labour saving costs, security and promotion of quality and safety (Mousavi and Sarhadi, 2002). Prevention of product recalls is also considered to be an important role of RFID technology (Kumar and Budin, 2005). RFID technology has been available for approximately 40 years although its broad application in packaging is a relatively recent development.

At its most basic level, an RFID tag contains a tiny transponder and antenna that have a unique number or alphanumeric sequence; the tag responds to signals received from a reader's antenna and transmits its number back to the reader. While the tags are relatively simple, much better inventory information than barcode or human entry systems can be gained through tracking software. RFID tags have the advantage over barcoding in that tags can be embedded within a container or package without adversely affecting the data. RFID tags also provide a non-contact, non-line-of-sight ability to gather real-time data and can penetrate non-metallic materials including bio-matter (Mennecke and Townsend, 2005). Tags can hold simple information (such as identification numbers) for tracking or can carry

more complex information (with storage capacity at present up to about 1 MB) such as temperature and relative humidity data, nutritional information, cooking instructions, etc. Read-only and read/write tags are also available depending on the requirements of the application in question.

Tags are classified according to two types: active tags function with battery power, broadcast a signal to the RFID reader and operate at a distance of up to 50 metres. Passive tags have a shorter reading range (up to about 5 metres) and are powered by the energy supplied by the reader (giving them essentially unlimited life).

Common RFID frequencies range from low (~125 KHz) to UHF (850–900 MHz) and microwave frequencies (~2.45 GHz). Low frequency tags are cheaper, use less power and are better able to penetrate non-metallic objects. These tags are most appropriate for use with meat products, particularly where the tags might be obscured by the product itself and are suitable for close-range scanning of objects with high water content.

The costs of RFID are decreasing as major companies such as Wal-Mart, 7-Eleven and Marks & Spencer adopt the technology. At present, the cost of passive RFID tags ranges from approximately \$0.50 to \$1.00. For the technology to be truly competitive it is estimated that tags must cost less than \$0.05 (others believe tags must be available at less than \$0.01) (Want, 2004). Opinion on possible cost developments differs. Mennecke and Townsend (2005) reported that tags are expected to fall to the \$0.01 per tag level after 2007, although concern remains that tags will be prove too expensive for individual food product monitoring. Initiatives to establish formal standards should serve to reduce further the cost of RFID. The use of organic semiconductor materials, capable of being coated on flexible substrates such as plastics, to create electronic circuits is apparently close to commercial realisation. It is forecast that such printable electronics will be widely available within two or three years. Such a development would see the price of RFID tags drop to that of bar-codes and catalyse the spread of RFID technology.

At present, a number of countries are using RFID to trace individual animals (mainly cattle) from birth to the processing plant. The key to individual animal traceability lies in the ability to transfer animal information sequentially and accurately to sub-parts of the animal during production. RFID-based tracking systems provide an automated method of contributing significantly to that information exchange (Mennecke and Townsend, 2005). At present, individually RFID tagged meat products are not available to the consumer, although the use of RFID tagging of meat cuts has extended to the pig processing industry (Dalehead Foods, Cambridge, UK), where tracking occurs from the individual pig to its subsequent primal pieces, i.e. hams. Although the purpose of this tracking scheme is for quality control, employee accountability and precision cutting, and does not extend beyond the cutting room floor or provide information about the individual animal with the final product, it does exemplify the developing use of RFID technology within the meat industry. In another instance, RFID has been used to track boxed imported beef into the UK from Africa.

The effective use of RFID is extremely specific to the immediate environment in which the technology is applied. Customised system design and trials to minimise localised interferences are necessary to establish properly functioning systems. Such requirements, along with a poorly understood cost efficiencies, are contributing to a slow uptake of this technology in the meat industry. The implementation of RFID technology as an intelligent packaging strategy for meat products is still largely hypothetical. Should the forecasts for an exponential, multi-sector increase in RFID use come to be realised, it is

likely that such an expansion will also be reflected in applications for meat packaging and distribution.

3.9 Potential Future Applications for Smart Packaging with Meat Products

In addition to those packaging techniques already discussed, other packaging technologies more commonly associated with other foodstuffs (Ahvenainen, 2003) may have potential application for meat and meat products. For example, self-heating aluminium or steel cans and containers, currently used by coffee manufacturers (Nescafe, 'hot when you want it'), may find use in the production of ready meals containing various meats. Microwave susceptors typically consist of aluminium or stainless steel metallised polyester films and are used to provide even heating, surface browning and crisping in microwave-oven-heated foods (Ahvenainen, 2003). Incorporation of such susceptors or modifiers into meat product packages may represent a future development for meat and meat-based convenience-style products. Flavour/odour adsorbers also have potential in active packaging technology. Adsorber systems employ mechanisms such as cellulose triacetate, acetylated paper, citric acid, ferrous salt/ascorbate and activated carbon/clays/zeolites. A Swedish company, EKA Noble, in cooperation with a Dutch company Akzo, has developed a range of synthetic aluminosilicate zeolites, which they claim absorbs odorous gases within their highly porous structure. Their BHMTM powder can be incorporated into packaging materials, especially those that are paper based and odorous aldehydes are adsorbed in the pore interstices of the powder. Such technology may prove useful in removing off-odours and flavours generated, for example, as a result of the oxidation of lipids in packaged muscle foods. Similar applications may exist for various flavour emitting polymers (Ahvenainen, 2003).

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4

Application of Time–Temperature Integrators for Monitoring and Management of Perishable Product Quality in the Cold Chain

Petros S. Taoukis

4.1 Introduction

Research and industrial data show that chilled or frozen distribution, handling and storage of food and other perishable products frequently deviate from specified temperature conditions. Since temperature is the main determining post-processing parameter for shelf-life under Good Manufacturing Practices, following and managing it to the point of final use of the product is of central importance. This task is very challenging, especially if one considers the potential variation in temperature exposure of single products within batches or transportation subunits. A cost-efficient way would be required to monitor the temperature conditions of the products, individually, and to indicate their real safety and quality throughout the cold chain. Smart, active packaging tags, Time Temperature Integrators (TTI), can be employed (Taoukis and Labuza, 2003). Based on reliable models of product shelf-life and the kinetics of TTI response, the effect of temperature can be monitored, recorded and translated, from production to the final use. A TTI-based system could lead to realistic control of the chill chain, optimization of stock rotation, reduction of waste, and efficient shelf life management. Most of the studies, developed methodology and applications refer to chilled and frozen food products but the same principles would apply for all other perishable consumer goods, provided that the mechanisms of quality degradation of these products are approached thoroughly as in the case of foods.

A novel chill chain management system, coded SMAS, was developed (Koutsoumanis *et al.*, 2005) in order to use the information from the TTI response at designated points of the chill chain, ensuring that the temperature-burdened products reach consumption at an acceptable quality level. The effectiveness of the TTI based SMAS system was evaluated by simulations and field test experiments in order to demonstrate and quantify the improvement in food product quality at the time of consumption in comparison with the conventional First In First Out (FIFO) rule.

4.2 Time–Temperature Integrators

TTI are inexpensive, active ‘smart labels’ that can show an easily measurable, time–temperature dependent change that reflects the full or partial temperature history of a product to which it is attached (Taoukis and Labuza, 1989). The principle of TTI operation is a mechanical, chemical, enzymatic or microbiological irreversible change, usually expressed as a visible response in the form of a mechanical deformation, colour development or colour movement. The rate of change is temperature dependent, increasing at higher temperatures similarly to the deteriorative reactions responsible for product quality deterioration. The visible response of the TTI thus cumulatively reflects the time–temperature history of the product it accompanies.

A number of TTI systems have been proposed in the past, of which few reached the industrial prototype and fewer achieved commercial application. TTI technologies that are currently available and aim to satisfy most of the above requirements are based on different operational principles.

The CheckPoint[®] TTI, (VITSAB A.B., Malmö, Sweden) is an enzymatic system. The TTI is based on a colour change caused by a pH decrease that is the result of a controlled enzymatic hydrolysis of a lipid substrate. Hydrolysis of the substrate causes acid release and the pH drop is translated into a colour change of a pH indicator from deep green to bright yellow to orange red (Figure 4.1). Different combinations of enzyme–substrate types and concentrations can be used to give a variety of response lives and temperature dependencies.

The Fresh-Check[®] TTI (Temptime Corp., Morris Plains, NJ, USA) is based on a solid state polymerization reaction, resulting in a highly coloured polymer. The response of the TTI is the colour change measurable as a decrease in reflectance (Figure 4.2). The colour of the ‘active’ centre of the TTI is compared to the reference colour of a surrounding ring.

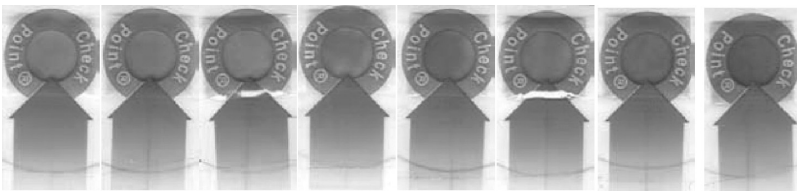


Figure 4.1 Response scale of enzymatic CheckPoint[®] TTI (Vitsab, Sweden).



Figure 4.2 Polymer based Fresh-Check® TTI (Temptime Corp.).

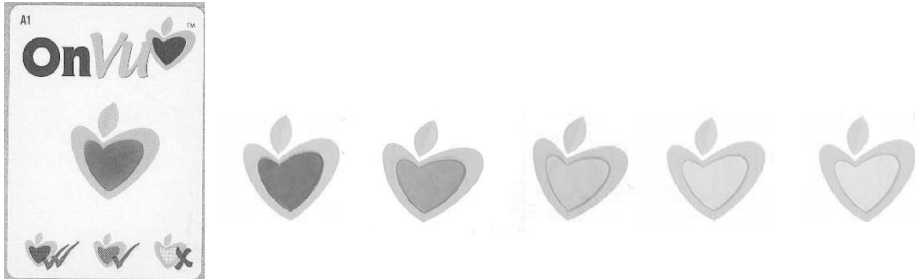


Figure 4.3 Solid state photochromic OnVu™ TTI (Ciba Specialty Chemicals).

Before use the indicators, active from the time of production, have to be stored deep frozen where change is very slow.

The OnVu™ TTI (Ciba Specialty Chemicals & Freshpoint, SW) is a newly introduced solid state reaction TTI (Figure 4.3). It is based on the inherent reproducibility of reactions in crystal phase. Photosensitive compounds are excited and coloured by exposure to low wavelength light. This coloured state reverses to the initial colourless at a temperature depended rate. This TTI can take the form and be applied as a photosensitive ink.

The (eO)® TTI (CRYOLOG, Gentilly, France) is based on a time-temperature depended pH change caused by controlled microbial growth that is expressed to colour change through suitable pH indicators (Figure 4.4).

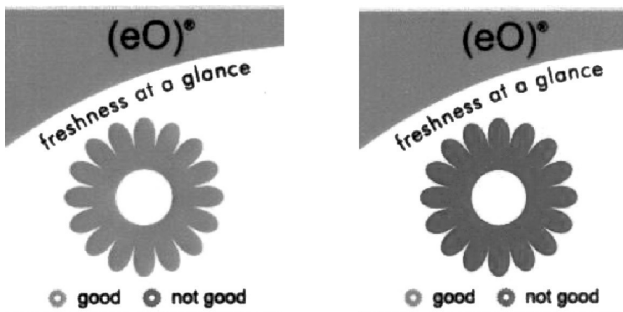


Figure 4.4 Microbial TTI (eO)® (Cryolog, France).

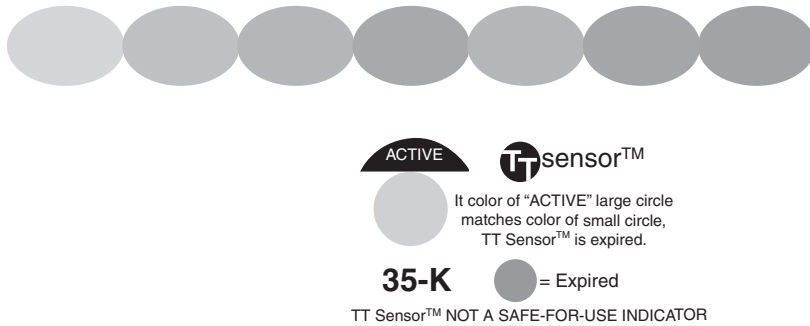


Figure 4.5 TT Sensor™ TTI (Avery Dennison Corp.).

The TT Sensor™ TTI (Avery Dennison Corp., USA) is based on a diffusion–reaction concept. A polar compound diffuses between two polymer layers and the change of its concentration causes the colour change of a fluorescent indicator from yellow to bright pink (Figure 4.5).

The 3M Monitor Mark® (3M Co., St Paul, Minnesota) is based on diffusion of proprietary polymer materials (Figure 4.6). A viscoelastic material migrates into a diffusely light-reflective porous matrix at a temperature dependent rate. The response rate and temperature dependence is controlled by the tag configuration, the diffusing polymer’s concentration and its glass transition temperature and can be set at the desirable range.

Use of TTI can help optimize product distribution, improve shelf life monitoring and management and thus reduce product waste and benefit the consumer by improving shelf life monitoring and management. Cost, reliability, and effective application are criteria for practical success of TTI. The cost is volume dependent, ranging from 2 to 20 cents per unit. Current TTI systems provide reliable and reproducible responses according to their specifications. With regards to effective application of the suitable TTI for the intended perishable product, it has been widely assumed that the response of the TTI should exactly mimic quality deterioration behaviour of the product to be monitored at all temperatures.

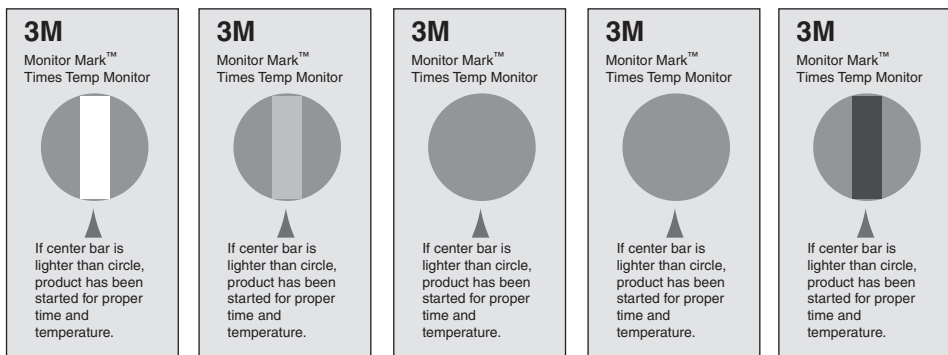


Figure 4.6 Diffusion based 3M Monitor Mark® TTI.

This approach would require an unlimited number of TTI models. Instead, a methodology of translating TTI response to product quality status based on systematic modelling of both the TTI and the food could be used as a tool for product quality monitoring and shelf life management.

Determination and modelling of the shelf life or keeping quality of perishable consumer products is the most important prerequisite for the application of a TTI-based monitoring and management system, usually evaluated by the measurement of the change of one or more characteristic quality indices, A , with time t . The selected indices can be chemical (like development of off flavours or off colours from oxidations or other chemical reactions, loss of an active component like a nutrient, a cosmetic or a therapeutic ingredient), biological (microbial growth, enzymatic deterioration) or physical (texture loss, phase separation). The change of indice A can be expressed as

$$f(A) = k(T)t \quad (1)$$

where $f(A)$ is the *quality function* of the product and k the reaction rate constant.

The rate constant is an exponential function of inverse absolute temperature, T , given by the Arrhenius expression,

$$k = k_{\text{ref}} \exp \left[\frac{-E_A}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \quad (2)$$

where k_{ref} is the reaction rate constant at a reference temperature T_{ref} , E_A is the activation energy of the reaction that controls quality loss and R the universal gas constant. The form of the quality function of the product depends on the reaction order of the phenomenon controlling the deterioration of the product, e.g. $f(A) = \ln(A_0/A_t)$ for $n = 1$ order and $f(A) = [A_t^{1-n} - A_0^{1-n}]/n - 1$ for $n \neq 1$. The activation energy of food related chemical reactions and spoilage or pathogenic microbial growth usually falls within 30–140 kJ/mol (Taoukis *et al.*, 1997).

The value of the quality function, $f(A)_t$, at time t , after exposure of the product at a known variable temperature exposure, $T(t)$, can be found based on Equation (1) by calculating the integral of $k[T(t)] dt$, from 0 to time t . We can define the effective temperature, T_{eff} , as the constant temperature exposure to which for the same time results in the same quality value, $f(A)_t$, as the variable temperature distribution, $T(t)$. The same kinetic approach can be used to model the measurable change X of the TTI. If a *response function* $F(X)$ can be defined such that $F(X) = kt$, with k an Arrhenius function of T , then the effective temperature concept as described above can also be used for the TTI. For an indicator exposed to the same temperature distribution, $T(t)$, as the food product, and corresponding to an effective temperature T_{eff} , the response function can be expressed as

$$F(X)_t = k_{I_{\text{ref}}} \exp \left[\frac{-E_{A_I}}{R} \left(\frac{1}{T_{\text{eff(TTI)}}} - \frac{1}{T_{\text{ref}}} \right) \right] t \quad (3)$$

where $k_{I_{\text{ref}}}$ and E_{A_I} are the Arrhenius parameters of the indicator.

Thus for applying a TTI based product quality monitoring scheme we need to define experimentally the quality function of the product, the response function of the TTI and the respective kinetic parameters. From the measured response X of the TTI at time t the value of the response function is calculated, from which by solving Equation (3), the T_{eff} of the exposure is derived. With the T_{eff} and the kinetic parameters of the product known,

the quality function value is calculated from Equations (2) and (1), and the value of index A is found. This gives the extent of the quality deterioration of the product and allows the calculation of the remaining shelf-life at any reference conditions.

The developed principles give a potential user the ability to select and apply the most appropriate TTI without the need for extensive side-by-side testing of the product and the TTI. A TTI with an activation energy E_{A_i} that differs from the product's E_A by less than 20 kJ/mol would result in a T_{eff} estimation of the product within ± 1 °C.

Based on TTI testing and the described principles, the response function and the response rate of different TTIs has been reported (Taoukis *et al.*, 1999; Taoukis, 2001; Mendoza *et al.*, 2004; Giannakourou and Taoukis, 2002; Giannakourou *et al.*, 2005). More recent testing has been conducted by the author's research group (Taoukis, 2007, unpublished data). The Arrhenius parameters that describe the temperature dependence of the response were obtained by plotting the logarithm of the response rate constant versus temperature ($1/T$) and calculating the best statistical fit.

All tested TTIs can be tuned with regards their total response time from few hours to several weeks and thus cover the required monitoring time for the different perishable products. Most TTIs have to be manufactured with different specifications to achieve this (e.g. use different enzyme or chemical concentration). The OnVu TTI has the flexibility to set the response length by selection of activation time.

The second requirement is that the temperature dependence of the quality of the products expressed by the E_A value should be similar to the E_A of the TTI response. The TTIs fall in the useful range with the Checkpoint and the OnVu showing the widest range and flexibility of setting the E_A value. The Fresh Check and TT Sensor basically have fixed E_A value in the middle of the range, where most but not all products fall.

The response signal is the parameter that determines the ease of reading of the TTI. The Checkpoint and eO TTIs change from green to red, a change that is understandable and discernible by the consumer. The TTsensor changes from yellow to bright pink. The Fresh-Check change is from transparent to dark blue and the OnVu from dark blue to white. All configurations are easy to read visually and translated if the correct message follows the TTI and if the appropriate training is provided to the chill chain personnel.

Other aspects that can be considered when evaluating a TTI have to do with their applicability. All tested TTIs come as shelf adhesive labels suitable for high speed application on the food product packages. Additionally the OnVu TTI can be pre-applied on the packaging material as a temperature sensitive ink.

Another issue concerns the TTI stability before application. The Fresh-Check and eO TTIs are active from the time of production and have to be stored and transported frozen. At these temperatures the rate of change is practically zero. The other three types are activated at application. The Checkpoint has two separate compartments with the enzyme and substrate. The separating seal is broken by pressure at the time of application, and enzyme and substrate are mixed to start the reaction, which translates into the colour response of the TTI. The Checkpoint before use is cold stored to assure stability and full activity of the enzyme. However this TTI can be also stored in ambient temperature for short times, e.g. during transportation. The TT Sensor and OnVu TTI can be stored at ambient conditions before activation for long times. TT sensor is activated by attaching the top polymer layer so that diffusion starts. The OnVu is activated by exposure to a UV source for a preset time (5–30 s) that will also determine the total response time.

Another practical index is of course cost. Cost per TTI unit depends on the TTI technology but also very much on the production volume. At this moment no TTI is produced in high enough volumes so only estimates can be obtained. Based on these estimates and indicative quotes from the TTI developers cost could range from 1 to 15 Euro cents.

The characteristics of all the tested TTIs are summarized in Table 4.1.

4.3 Cold Chain Management

The information provided by the TTI smart labels, translated to remaining shelf life at any point of the cold chain, can be used to manage shelf-life by improving distribution control and stock rotation practices. The approach currently used is the First-In/First-Out (FIFO) system according to which, products received first and/or with the closest expiration date on the label are shipped, displayed and sold first. This approach aims at establishing a ‘steady state’ with all products being sold at the same quality level. The assumption is that all products have gone through uniform handling, thus quality is basically a function of time. The use of the indicators can help to establish a system that does not depend on this unrealistic assumption. The objective is again a ‘steady state’ situation with the least remaining shelf life products being sold first. This approach was coded LSFO (Least Shelf-life First Out). The LSFO reduces the number of rejected products and largely eliminates consumer dissatisfaction since the fraction of product with unacceptable quality at the time of use or consumption is minimized. LSFO aims at reducing the rejected products at the consumer end, by promoting, at selected decision making points of the product life cycle, those product units with the shorter shelf-life, according to the response of the attached TTI (Taoukis *et al.*, 1998; Giannakourou and Taoukis, 2002). LSFO allows the calculation of the actual remaining shelf life of individual product units at strategic control points of the chill chain. Based on the distribution of the remaining shelf life, decisions can be made for improved handling, shipping destination and stock rotation. A further improvement of the LSFO approach, is a chill chain management system coded SLDS (Shelf-Life Decision System) (Giannakourou and Taoukis, 2003). Compared with LSFO, SLDS policy additionally takes into account the realistic variability of the initial quality state A_0 of the product.

The state of the TTI technology and of the scientific approach with regard to the quantitative safety risk assessment in foods allows the undertaking of the next important step, i.e. the study and development of a TTI-based management system that will assure both safety and quality in the food chill chain (Koutsoumanis *et al.*, 2005). The development and application of such a system, coded with the acronym SMAS, was the target of the multinational European research project ‘Development and Modeling of a TTI based Safety Monitoring and Assurance System (SMAS) for chilled Meat Products’ (project QLK1-CT2002-02545, 2003-2006; <http://smas.chemeng.ntua.gr>). SMAS uses the information from the TTI response at designated points of the chill chain, ensuring that the temperature-burdened products reach consumption at acceptable quality level. Although SMAS is developed for meat products the same principles can be effectively applied to the management of the chill chain of all chilled food or non-food perishable products.

The effectiveness of the TTI based SMAS system was evaluated by running a large number of chill chain scenarios using a Monte Carlo simulation approach. Field test experiments

Table 4.1 TTI properties

Type of TTI	Operation principle	Response type	Response range	E_A range (kJ/mol)	Activatable	Cost ^a
CheckPoint® Types M, L	Enzymatic	Tricolour Green to yellow to red	Hours to weeks at 4 °C	70–170	Y	B
Fresh-Check®	Polymeric	Colourless to blue	Hours to weeks at 4 °C	80–90	N	A
OnVu™	Photochemical	Dark blue to colourless	Hours to weeks at 4 °C	90–150	Y	A
TT Sensor™	Diffusion-reaction	Yellow to pink	Hours to weeks at 4 °C	115–125	Y	B
eO	Microbiological	Green to red	Hours to weeks at 4 °C	100–110	N	B

^a A: 1–5 cents, B: 5–15 cents

to demonstrate and quantify the improvement at the time of consumption in comparison to the conventional First-In/First-Out (FIFO) rule, were also conducted.

The SMAS decision making routine at a specified control point of the chill chain is based on the microbial growth that has potentially occurred within the period between production and arrival of the product at the control point. The growth is estimated based on the product’s characteristics and the time–temperature history of the product using the appropriate predictive model. The above elements form the programme core of an integrated software that allows the calculation of growth in individual product units (e.g. small pallets, 5–10 kg boxes or single packs) at strategic control points of the chill chain. Based on the relative growth, it is possible to make decisions for optimal handling, shipping destination and stock rotation, aiming to obtain a narrow distribution of quality at the point of consumption. At a certain point of the chill chain, e.g. at a distribution centre, product from the same initial shipment is split in half and forwarded to two different retail markets, one close and a distant one that requires long transportation. The split could be random according to conventional, currently used FIFO practice or it can be based on the actual microbial growth of the product units and the developed decision system. For all units, the time–temperature history of the product, monitored by TTI, is input. This information directly fed into a portable unit with the SMAS software, is translated to microbial status, N_t , based on the growth models of the pathogen of concern. Having calculated N_t for all the n product units, a microbial load distribution for the products at the decision point is constructed. Based on the load of each product unit relative to this distribution, decisions about its further handling are made (Figure 4.7).

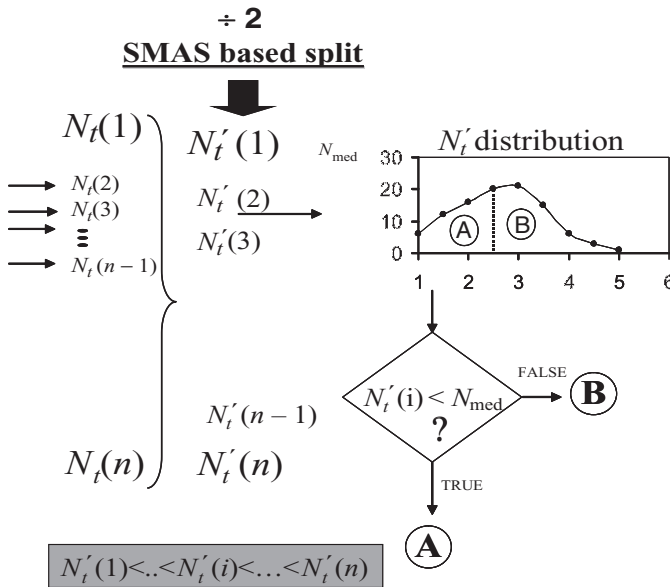


Figure 4.7 Classification of products based on their microbial load and rationale of SMAS based split at the decision point (where A and B are the two possible destinations, the distant and the local market).

In order to simulate the results of the application of the developed SMAS system and quantitatively prove its effectiveness the Monte Carlo method can be applied (Koutsoumanis *et al.*, 2005). By taking into account the status of the product after production and various temperature distributions at different steps and alternative storage conditions, the distribution of the quality of the studied set of products at the final stage of consumption can be estimated.

To confirm the SMAS effectiveness appropriate experiments were also designed and conducted. One such experiment is described below to demonstrate the SMAS approach and the kind of information required for its application.

Modified-atmosphere-packed fresh pork cuts, were used in the experimental chill chain simulation. Two sets of experiments were conducted. The first was used to model the growth of the natural spoilage microflora of the products and the second for the 'field test' experiment. Fifty 600-g MA packaged pork cuts (60 % CO₂, 40 % air) were stored under controlled isothermal conditions (0, 5 and 10 °C) in high-precision (± 0.2 °C) low-temperature incubators. Samples were taken at appropriate time intervals to allow for efficient kinetic analysis of microbial growth. Total plate count and lactic acid bacteria, the dominant spoilage flora at these conditions were measured. Sensory evaluation was also conducted at each sampling time.

Lactic acid bacteria were the dominant organisms at all temperatures in MAP samples. The growth data of spoilage bacteria of pork cuts stored at different isothermal conditions (0, 5, 10 °C) were modelled as a function of time using the Baranyi model, and the kinetic parameters (exponential growth rate constant k , lag phase) were estimated. The temperature dependence of the kinetic parameters was modelled using the Arrhenius equation. The Arrhenius model sufficiently described the temperature dependence of the growth of spoilage lactic acid bacteria. At all temperatures, growth of lactic acid bacteria, which is a well established spoilage index for MAP chilled meat, followed closely the decrease of sensory quality. End of shelf-life coincided with an average level of log 7.2 of lactic acid bacteria within the studied range of temperatures.

For the field test the same major meat packer supplied 72 MAP units of packed pork cuts. The transportation of the products from production site in the island of Crete to Athens (NTUA) took 18 hours. They were distributed in different trucks and at different locations within the trucks. Electronic data loggers recorded the temperature for all 72 products during the transportation. On half of the products, TTIs were attached to be handled with the SMAS approach, the rest were handled according to the FIFO approach. Two different enzymatic TTI tags were used for each package at time of production; M4-10 and L5-8 (CheckPoint® TTI). The M4-10 was designed to expire within 10 days at 4 °C, thus serving as a shelf life indicator at the end of the storage ($E_A = 88$ kJ/mol). L5-8 having a higher activation energy ($E_A = 200$ kJ/mol), and being more temperature sensitive, expire within 2 days at 10 °C, serving as indicator at the time of split (decision point).

Simulated testing of distribution and storage of MAP packed pork cuts was conducted. All products were stored in programmable cabinets simulating the conditions of the real chill chain to the point of consumption. The simulated chill chain conditions consisted of six different time-temperature scenarios (including the 18 hours' storage during the transfer from the meat producer and packer to the laboratory) that were conducted in programmable controlled temperature cabinets (Figure 4.8).

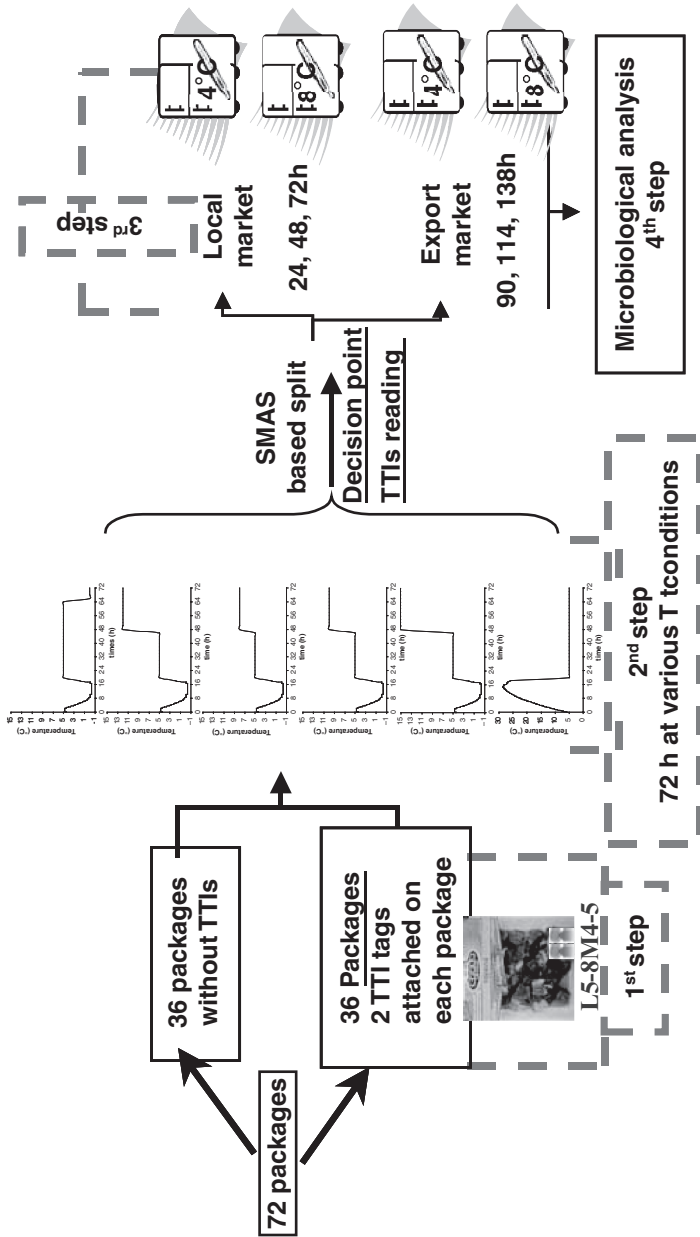


Figure 4.8 Design of the field test for pork cuts products.

Colour change readings of the attached TTIs were taken throughout the field test at appropriate times corresponding to critical stages of the actual transportation process at a designated decision time simulated to be the distribution centre, 72 hours after meat production and packaging TTI visual reading was conducted with an eight-stage TTI colour reference scale (Figure 4.1).

According to TTI colour scores and using the SMAS Decision Maker Software all SMAS products (36) were sorted according to their actual temperature history as obtained by the TTIs. After sorting, the products were split into two groups, products for 'local' market and products for 'distant' market, for further handling. The 36 samples that had no TTI attached were split randomly. After split at the decision point, samples were split and stored at 4 °C and 8 °C.

Microbiological analyses of the meat products were conducted at six different stages. Products that belonged to the local market group were microbiologically analysed at three stages; 24, 48 and 72 hours after the split. Products coded as products for the distant market were microbiologically analysed 90, 114 and 138 hours after the split.

For the field test microbiological results after storage (at 4 and 8 °C) at different times following the split are shown in Figure 4.9.

According to the field test results as illustrated in Figure 4.8, 33 % of samples reach the spoilage level of $\log 7.2$ with the FIFO approach and 16 % when the SMAS split is applied. Similar results are obtained by Monte Carlo calculations using the above microbial growth model.

The overall results from this and other field tests with a variety of meat products and the Monte Carlo simulation showed that the SMAS sorting at a decision point worked satisfactorily thus demonstrating the usefulness of TTI monitoring and the applicability of SMAS.

In summary, SMAS uses the information from the TTI, at appropriate points of the cold chain (e.g at a central distribution centre), to make decisions for the further management of products based on their temperature history and hence quality and safety status. The

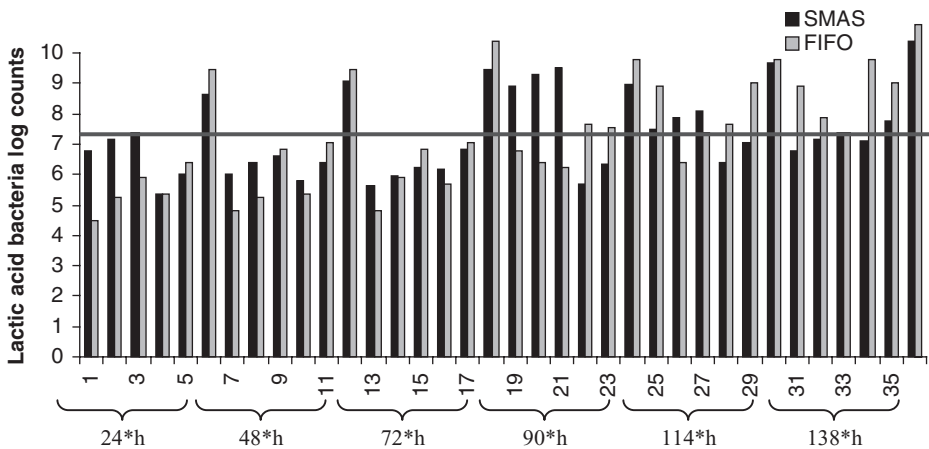


Figure 4.9 Measured lactic acid bacteria log counts for each date of microbiological analysis for all 72 samples (* hours after the split).

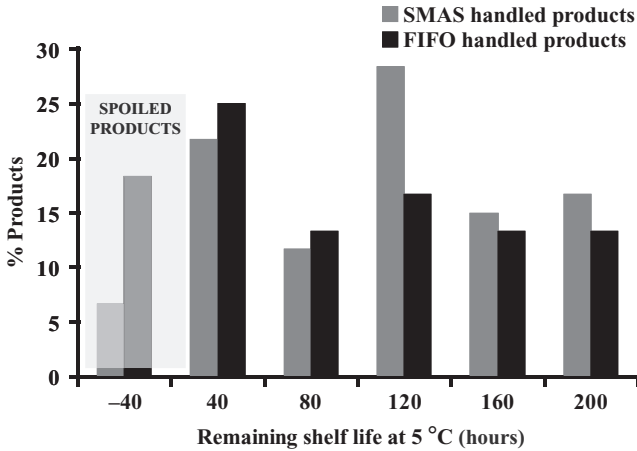


Figure 4.10 Distribution of the remaining shelf-life of meat products at the time of ‘consumption’ with FIFO and SMAS approach.

conducted work established the applicability of the TTI based SMAS approach in improving the meat chill chain. The overall work showed that the SMAS based sorting at a decision point resulted in substantially reducing the spoiled products at the time of consumption in comparison with the conventional FIFO approach (Figure 4.10). Similarly the risk factor (i.e. the probability that the pathogen might exceed a specified level) was significantly reduced (Koutsoumanis *et al.*, 2005).

Cold chain optimization and effective management will be a central issue in striving for food and other perishable consumer products of higher quality, in the coming years, both in research, industrial practice and regulatory efforts. Integrated systems, like the proposed SMAS based on the availability of quality data and temperature history of individual product units will be applied and validated in practice. TTIs will be combined with RFID technology and all will supplement and benefit from the traceability requirements that are being currently put in place by regulation and by industry initiative.

Acknowledgements

Part of the information contained in this chapter stems from research supported from the Commission of the European Communities, FP5 Quality of life RTD Project SMAS, QLK1-CT-2002-02545 (<http://smas.chemeng.ntua.gr>) and the FP6 Collective Research Project FRESHLABEL COLL-CT-2005-012371.

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5

Smart Packaging Technologies for Fish and Seafood Products

Alexis Pacquit, Karl Crowley and Dermot Diamond

5.1 Introduction

Latest figures show that busy consumers are increasingly seeking quick and easy to prepare, fresh chilled or frozen prepacked fish products [1]. Demand for home consumption products is heavily influenced by the limited time available for meal preparation in today's busy lifestyles. Furthermore, coupled with economic, social affluence and lifestyle choices in terms of disposable income, an increasing number of consumers are moving toward healthier semi-processed refrigerated prepacked options. Increased awareness of the health benefits of seafood (high protein, low fat and high omega-3 fatty acids) is certainly a key driver behind this trend.

The seafood processing industry in Europe was worth approximately €18 billion per year in 2003; roughly twice the value of landings and aquaculture combined [2]. Although this industry has benefited from a trend toward healthier eating, it faces mounting problems largely stemming from dwindling stocks and diminishing returns. This has resulted in a need to diversify from familiar though threatened species such as cod into what are termed 'under utilised species' – fish species that up until now have been seen as having little commercial value. While this opens new opportunities for fishermen and suppliers alike, the need to educate and supply information to consumers poses some interesting challenges that may be met with emergent technologies – including smart packaging.

One area being driven by legislators in Europe and elsewhere is in the area of food traceability – requiring much more information to be available to the consumer and forcing the establishment of a chain of responsibility throughout the whole food chain [3, 4]. The

seafood industry is unique in food production in that a large quantity of fish are both farmed and caught wild. One common differentiation, often expressed by consumers is the desire for wild fish over aquaculture produce – particularly in the case of salmon – a preference that a recent British advertising campaign for wild salmon controversially exploited [5], thus demonstrating the power of consumer demand for information. Some of these traceability requirements can be covered by merely stating the additional detail (e.g. harvest date and location, species, etc.) on the label although others potentially require more advanced methods, such as RFID tags. Such tags are already being employed on pallets of fish exported from Alaska as a means of verifying the origin in addition to guaranteeing proper storage conditions [6]. This quality assurance facet is another area becoming increasingly important to both suppliers and consumers. There is consequently great interest, within the fisheries industries, retailers, consumer's rights watchdogs and food safety controlling bodies in developing accurate, rapid, cost effective and non-destructive methods to evaluate real-time freshness of fish and seafood products. Emphasis is on methods that account for the products history and their storage conditions from 'harvest-to-home'.

Seafood, particularly fish, has the advantage of being seen largely free from health issues such as the bird flu, BSE and foot and mouth crises that have affected the poultry and meat industry over the past few years. Some sectors may have even seen an increase in fish consumption as a direct result of these crises. Nevertheless, seafood, both fish and shellfish, are particularly prone to spoilage and the need to minimise the risk to the consumer's health – not to mention the supplier's reputation – is another powerful driving force behind new smart packaging technologies.

In this chapter, the applications of smart packaging to seafood will be discussed with reference to current and developing technology, covering both the application and scientific background of this diverse area.

5.2 What are the Parameters of Fish Quality?

Fish quality is a complex concept involving many factors. The importance of some of these may vary with markets, geographical location and cultures. The common physical attributes such as appearance, size, species, colour, odour and taste are of direct concern to the consumers. However, safety, feeding habits, sexual maturity, fishing ground and depth of living also affect the quality of the catch. Nonetheless, freshness is by far the most important factor in fish quality assessment no matter which market or part of the world one is focusing on.

It is a well known fact that the quality of fish is irregular. Seafood in general may be available virtually all year round but no two harvests are the same. At present, the judgement of fish and seafood freshness largely relies on sensory assessment of freshness attributes, such as appearance (eyes, skin, and gills), texture, odour and colour, by a trained panel of assessors at fish auctions who assign scores indicating quality and remaining shelf life. These scores are the basis of a grading scheme, the Quality Index Method (QIM), produced from the compiled characteristics of various common European fish species [7, 8]. Additional methods include microbiological (total viable count or TVC), physical (texture, electrical properties) and chemical (*K* and *K1* values, Total Volatile Basic Nitrogen or TVB-N, lipid oxidation). The *K* and *K1* values reflect the extent of adenosine

triphosphate (ATP) degradation after death and they have been extensively used as freshness indicators [9, 10]. An excellent review of these methods has been provided by Olafsdottir *et al.* [11]. The possibility of developing a multisensor device to measure fish freshness was investigated in an European project called ‘MUSTEC/FAIR 98-4076’ (Multisensor Techniques for Monitoring the Quality of Fish) [12].

5.3 Mechanisms of Fish Spoilage

Figure 5.1 shows the post-mortem changes occurring in fish muscle [13]. The initial quality loss in fish is primarily caused by autolytic changes (enzymatic digestion and degradation of flesh) and is unrelated to microbial activity [14, 15]. The loss of the intermediate nucleotide inosine monophosphate (IMP) is responsible for the loss of fresh fish flavour, but apart from this, the autolytic changes contribute to spoilage by making catabolites, such as nucleotides and other ATP-related compounds, available for bacterial growth.

Food microbiology may be separated in two key aspects, safety and freshness, as they concern two different types of foodborne microorganism. Safety in food products often refers to the risk of hazardous pathogen outbreak (i.e. *Listeria monocytogenes*, *Clostridium*

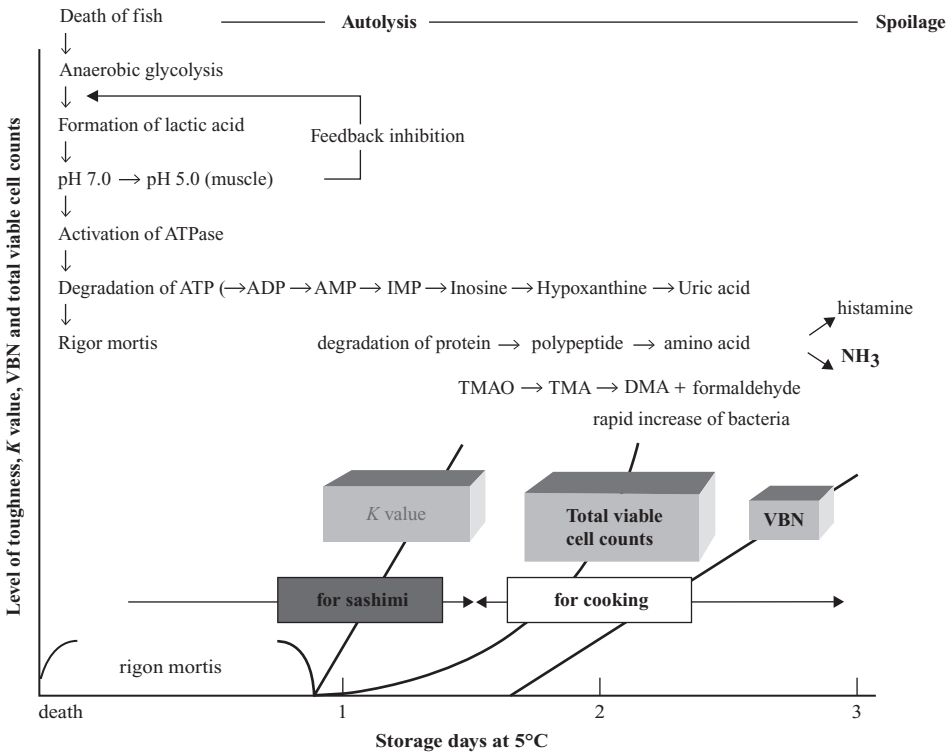


Figure 5.1 Post-mortem changes in fish meat. Reproduced from [13] with permission from Elsevier.

botulinum, *Vibrio* spp.) which can cause infection with very low numbers of live cells, and/or the production of biotoxins (e.g. intoxication), both of which can result in food-borne diseases with serious human pathology. These pathogens may represent part of the natural flora of fish or maybe are introduced through subsequent processing, storage or transport [14,16]. On the other hand the study of freshness often refers to the growth of spoilage microorganisms (*Pseudomonas* spp., *Shewanella putrefaciens*, *Photobacterium phosphoreum*) that lead to the generation of off-odours, off-flavours and other metabolic breakdown products. It is however important to note that oxidation of tissues and oils also results in off-odours and flavours (rancidity in oily fish) [14]. Odour is undoubtedly the most common index of fish freshness. Indeed, the customer, with no knowledge or training of fish quality evaluation, is generally assessing the freshness and safety of his/her fish product upon opening the food pack based on its odour or scent. Since most household kitchen refrigerators are not at the correct temperature and the yearly average kitchen temperature is 18 to 19 °C, fish product packs only presenting 'use by date' information potentially represent a health and safety issue. However, if such a device as a time temperature integrator (TTI) or an amine sensor were added on the same pack, it may provide a real-time assessment of the product quality and assist the customer in his/her decision.

Seafood, both fish and shellfish, are highly perishable goods and, in general, food commodities have their own structural specificities [pH, water activity (a_w), be part of a bigger biological system (meat), whole system (fruit) or processed system (cheese, bread)] and thus have their own distinctive microbiology. In fish, original microbial flora is influenced by the species, habitat geography (fresh or saltwater, tropical or arctic water, pelagic swimmers or bottom dwellers) and even harvest season. Thus, fish harbour quite a heterogeneous flora when fresh and, aside from temperature, the spoilage characteristics of packaged seafood will depend upon a number of additional variables such as the subsequent processing steps (fresh or frozen, whole or filleted, loose or prepacked) as well as the type of packaging (modified atmosphere, vacuum or air) [16]. After death and during storage, the number of microorganisms on the skin and gill surfaces increases gradually and spreads within the various tissues. Generally, one or more species, referred to as specific spoilage organisms (SSO), will outgrow the others depending on the surrounding conditions and the product composition, giving off a range of breakdown and metabolic compounds [9]. Examples of SSOs and typical spoilage compounds of some fish products are presented in Table 5.1.

European guidelines for microbiological criteria in respect of many foodstuffs have not yet been established. Microbiological guidelines exist for shelled and shucked products of cooked crustaceans and molluscan shellfish, live bivalve molluscs and live echinoderms, tunicates and gastropods but no guidelines have been established for fresh uncooked fish products [18]. The reason for this is related to the variety of natural microbial flora per fishing ground, habitat geography and species, as outlined above, across the extensive diversity of countries and climate.

In the past 50–60 years, basic microbial analysis methods have remained essentially unchanged. Technological advancements have made them relatively faster and easier to complete, but they still require sample treatment, agar plate preparation and rely on trained operators for bacteria colony screening. Conventional measurements of bacterial populations based on plate count procedures typically require several incubation days before results are available, which then entail backward corrective actions. The products may be retained in suitable storage conditions before delivery clearance. This causes delays in the

Table 5.1 SSO and typical spoilage compounds in groups of fresh and lightly preserved seafoods [16, 17]

Product	Typical SSO	Number at rejection ^a	Typical volatile compounds
Fresh chilled products stored in air	<i>Shewanella putrefaciens</i> ^b <i>Pseudomonas</i> spp. ^c	10 ⁸ –10 ⁹ 10 ⁸ –10 ⁹	TMA, H ₂ S and other sulphur compounds, Hx (hypoxanthine). NH ₃ , esters, non-H ₂ S sulfides
Fresh fish, chilled, MA packed	<i>P. phosphoreum</i> ^b Lactic acid bacteria ^c	>10 ⁷ >10 ⁸	TMA, Hx, alcohols and ketones. Acetic acid, NH ₃ , H ₂ S, diacetyl, tyramine.
Fresh fish, >10 °C	<i>Vibrionaceae</i> , <i>Aeromonas</i> spp.	10 ⁷ –10 ⁸	TMA, volatile sulfides
<i>Sous vide</i> cooked fish	<i>Clostridium</i> spp.	>10 ⁶	Strong faecal, sulfydryl odours
Sugar-salted herring	Halophilic, anaerobes ^d osmotolerant yeast	10 ⁷ –10 ⁸ 10 ⁴ –10 ⁵	Indole, H ₂ S, acids fruity

^a numbers in cfu g⁻¹, ^b typical of marine, temperature water fish, ^c typical of freshwater fish and fish from warmer waters, ^d not identified

production chain, loss of optimal product freshness, reduction in product ‘display–time’, thus product shelf-life and ultimately financial loss.

Some spoilage metabolites can be used as quality indices [19] such as the volatile compounds trimethylamine (TMA), dimethylamine (DMA) and ammonia, collectively known as TVB-N, or the biogenic amines hypoxanthine and histamine. Their content in freshly caught marine fish investigated immediately after hauling is normally found to be relatively constant [20]. Over time and depending on the fish species, temperature and general storage conditions (atmosphere, *a_w*, microbial cross-contamination, etc.), the TVB-N level increases as a result of bacterial metabolism. Hence, it is a potential indicator of fish spoilage and figures within current EU legislation as an additional tool for fish quality assessment [21]. The current method for TVBN analysis involves extracting the volatiles bases using a perchloric acid solution followed by steam distillation of the extract which is then collected in boric acid and titrated against standard HCl. Although accurate when performed by experienced analysts, the method is nonetheless destructive and time consuming.

It is time, therefore, to move beyond conventional existing techniques to emerging technologies for low-cost, real-time, assessment of food quality and safety. Scientists are now looking at finished products, studying the biodegradation processes under the industry specific conditions (frozen, chilled, loose, prepacked, in air, in modified air packaging (MAP), vacuumed, etc.) and making inventories of the changes in appearance, colour, texture, scent, pH and moisture as well as of the consumption/release of certain compounds. Low cost devices and non-invasive methods can now be employed to monitor these changes in the product rapidly and relate them to quality. They can ultimately be integrated within smart packaging.

5.4 On-pack Quality Indicators

For packed produce, often the only assurance of quality is the use-by date assigned on packing. For highly perishable foodstuffs such as fish and shellfish this is highly problematic as it assumes proper maintenance of temperature and other conditions during storage and transport before and after packaging. In this case, the only direct means of testing whether the seafood has spoiled is to breach the package, rendering the produce unfit for resale.

Another possibility is to incorporate a device on, or even within, the pack that will allow a non-destructive assessment of quality. Two main possibilities for non-invasive quality indicators are:

- (i) time-temperature Integrators (TTIs),
- (ii) food quality indicators.

In both cases, the indication given by the sensors is generally (though not exclusively) colorimetric: a highly visual change in colour of the indicator allowing for a rapid assessment of the quality of the packed seafood. The two types of indicator are chemical based but they utilise two different approaches: TTIs displaying a colour change dependent on the ambient temperature effects on a chemical reaction within the indicator. Food quality indicators react to changes – usually chemical or biological – occurring within the packaging headspace as the seafood spoils. In this section, the operation, relative merits and issues associated with these quality indicators will be discussed.

5.5 Time–Temperature Integrators

The spoilage of perishable foodstuffs is almost always heavily dependent on storage temperature. Traditionally, temperature was manually checked at various intervals to ensure suitable conditions were maintained though this method was time-consuming and did not provide a complete and verifiable temperature record. In recent times, the use of automated temperature loggers has allowed a complete archive of data to be collected, verifying storage temperatures and providing information on possible weaknesses in the supply chain [22, 23]. As noted earlier, battery-powered RFID tags have also been used to monitor temperature for bulk containers of fish transported from Alaska [6]. Although this technology is useful for storage and transport of bulk produce it is presently too expensive and overly complicated for single packs of goods – a low-cost and easily read alternative fits the requirement for smart packaging applications. Temperature–time integrators are an example of this technology and have already found a variety of applications in many areas, including pharmaceuticals and perishable foods including meat, dairy and seafood [24, 25].

Although TTI technology had been present for several decades [26, 27], it is only in the last 15 years that it has been considered reliable enough to be employed in these applications [4]. Since then there has been a steady uptake from suppliers and supermarkets throughout the world. This uptake is being driven by the consumers desire for quality assurance coupled with increasing demands from legislators, particularly in the United States – a good example of this is the Import Alert No. 16-125 issued in 2002 by the United States Food and Drug

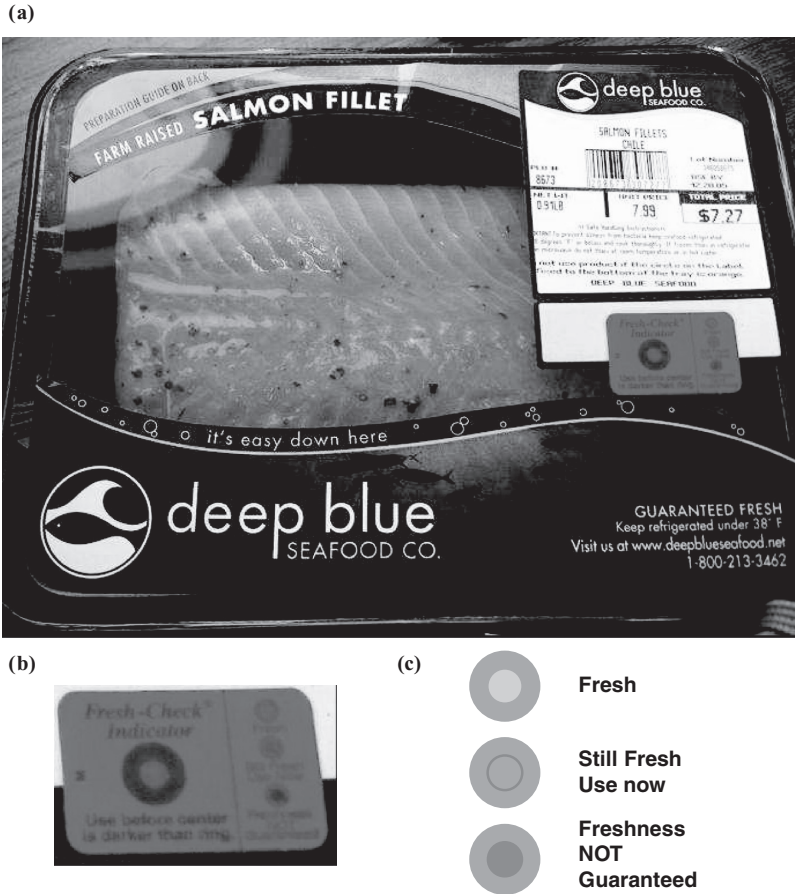


Figure 5.2 An example of smart packaging application of TTIs. Fresh-Check[®] indicator employed on packaged salmon fillet (a); Detail of the sensor; (b), and change in sensor over time (c). Used with kind permission of Fresher Than Fresh/TEMPTIME.

Administration [28]. This alert stipulates that refrigerated, modified air packaged (MAP) fish must be verifiably fit for consumption and refers to TTIs (on each pack of fish) as one means of fulfilling this requirement. Commercial examples of TTIs employed in smart packaging seafood are shown in Figures 5.2 and 5.3 (salmon in both cases). In Figure 5.2(a), the Fresh-Check[®] TTI (detail, Figure 5.2b) is seen to be affixed to the pack in much the same way as a normal label and it remains on the pack all the way through to the consumer. The active part of the sensor can be read by a handheld colorimeter for a quantitative result or can be compared with the reference ring allowing a quick visual inspection to ascertain quality (Figure 5.2c). The design of the TT-Sensor[™] is slightly different, as can be seen in Figure 5.3. The active circle undergoes a distinctive yellow to pink colour change on expiry. An example of some of the commercially available TTIs employed for seafood packaging and their mechanisms are given in Table 5.2.

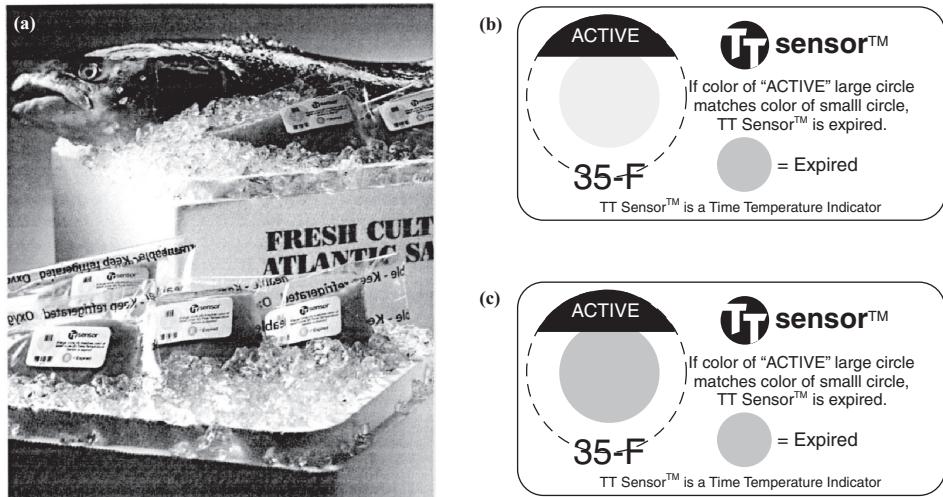


Figure 5.3 TT-Sensor™ on packs of fresh salmon (a), detail of the sensor before (b) and after expiry (c). Used with kind permission of Avery Dennison.

The TT Sensor™ is initiated by applying an activator label over the sensor window, an example of a TT-Sensor™ label applicator is given in Figure 5.4. The main label is applied by the wheel on the bottom right while the transparent activator labels are applied from the spindle visible at top left – both are applied simultaneously to the freshly packed produce. This approach allows storage of the tabs under normal conditions and a specified start time for the reaction. The Fresh-Check® sensors are ready activated which makes for easy application – though the sensors must be kept in cold storage prior to use. The various brands of TTI come in variety of different models, depending on the nature of the food product to be monitored. The success of a particular TTI will depend on whether its reaction kinetics matches those of the dominant spoilage mechanisms. Selection of the correct type of TTI is essential as an indicator that changes too fast will result in wastage of safe seafood while a slow responding indicator may result in the sale and consumption of spoiled seafood. For optimal use, both the kinetics of the TTI and the spoilage mechanisms of the produce need to be understood [27, 29].

Shellfish are especially sensitive with many species, e.g. whelk and oysters, undergoing rapid spoilage after death, and hence they require immediate cooking or live transport. This

Table 5.2 An example of some commercially available TTIs, which have been employed for smart packaging of seafood

Company	TTI name	Mechanism
Avery Dennison	TT Sensor™	pH change due to diffusion of acidic species.
TempTime	Fresh-Check®	Darkening due to polymerisation reaction.
Vitsab	Checkpoint®	Enzymatic or diffusive mechanism leading to pH change.

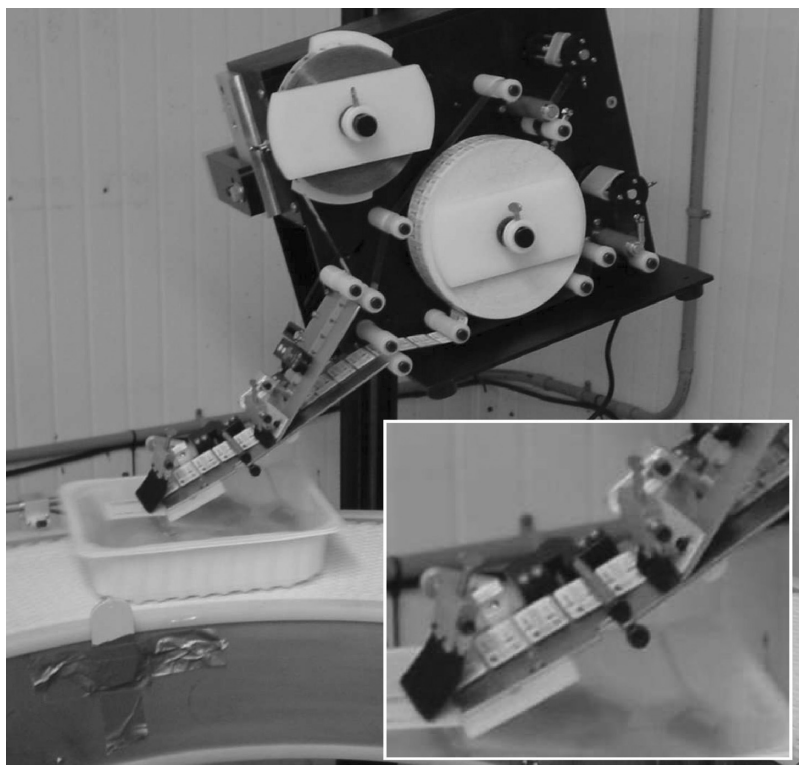


Figure 5.4 TT-Sensor™ label applier in operation. Upper spindle holds transparent activator tabs and lower spindle holds the main label. Inset shows detail of applicator arm. Used with kind permission of Avery Dennison.

makes TTIs unsuitable as a means of monitoring live/fresh shellfish species. According to TempTime, their TTIs are not used for live shellfish – however they can be applied to cooked and processed shellfish produce. Fish species, on the other hand, generally display a much longer lag time between death and complete spoilage.

The kinetic behaviour of TTIs may be explained through the Arrhenius equation [30], in which the activation energy is a critical parameter. Some examples of activation energies for a variety of seafood spoilage mechanisms are given in Table 5.3.

Another important parameter is the order of the reaction kinetics of the TTI: for example, zero order and first order reactions under isothermal conditions display linear and exponential changes with time, respectively. Though first order kinetics are generally observed in nature, it is zero order (or pseudo-zero order) kinetics that have largely been applied in TTIs for seafood applications. An example of pseudo-zero order TTI response is given in Figure 5.5 for a Fresh-Check® TJ2 indicator [31]. In this case, the measured colour change of the indicator has been converted to a percentage (starting at 100 %) and plotted against time. Over long timescales – well past expiry of the TTI – first order kinetics were detected. However, over the indicator lifetime, linear responses were obtained for each of the temperatures

Table 5.3 Activation energies for different spoilage mechanisms for seafood

Species	Mechanism	E_a (kJ mol ⁻¹)
Fresh fish fillets ^a	Spoilage	~84 – 125 ^b [24]
Fresh fish fillets ^a	Toxins	~50 – 84 ^b [24]
Boque	Microbial (<i>Pseudomonas</i> spp.)	81.6 ± 11.6 [29]
Boque	Microbial (<i>Shewanella putrefaciens</i>)	82.7 ± 11.1 [29]
Cod fillet	Spoilage	42.3 ^b [25, 32]
Cod fillet	Toxin	60.7 ^b [25, 32]
Whiting fillet	Spoilage	29.3 ^b [25, 32]
Whiting	Toxin	48.6 ^b [25, 32]

^a Species not specified^b Converted from kcal mol⁻¹ to kJ mol⁻¹

studied – as can be seen for the R^2 values for each of the trends. The expected faster response for increasing temperatures can be readily observed – changes of 0.211 %/h observed at 0 °C compared with 0.923 %/h at 10 °C; almost four times faster.

It would be a mistake, however, to assume that all spoilage mechanisms proceed in such a simplistic manner; the effect of temperature on fish spoilage can often be non-linear, as detailed in the following example. As noted earlier, assurances of proper temperature storage for fish packaged in modified atmospheres are required in the US. Although MAP can

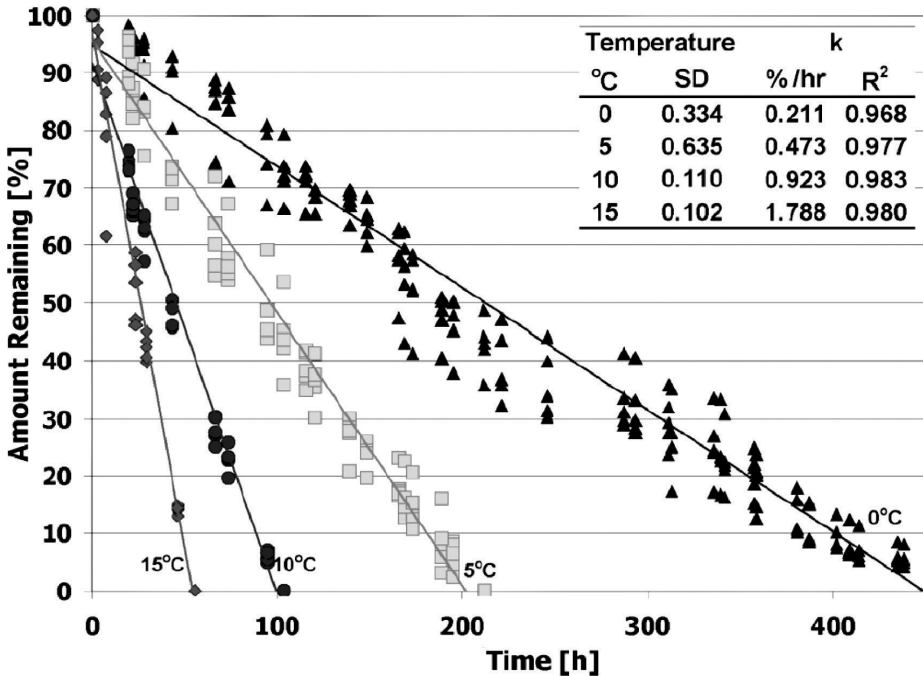


Figure 5.5 The response obtained for Fresh-Check[®] Tj2 indicators at different temperatures over time. Reproduced from T.F. Mendoza, et al., *Journal of Food Science*, Vol. 69, (3), pp. FMS90–FMS96. Copyright (2004), with permission of Blackwell Publishing.

reduce the growth of aerobic bacteria, packs containing reduced oxygen content can result in apparently unspoiled fish containing dangerous levels of a toxin produced by *Clostridium botulinum*, the bacterium responsible for causing botulism. Therefore, to ensure MAP fish is fit for consumption, researchers have focused on trying to understand the effects of temperature on *C. botulinum* growth. From earlier work by Baker and Genigeorgis [33], Skinner and Larkin developed a simple model to predict conservatively the temperature dependent time before the *C. botulinum* toxin breached acceptable limits [34]:

$$\log L = 0.65 - 0.525 T + 2.74 \left(\frac{1}{T} \right) \tag{1}$$

where L is the lag-time (days) for *C. botulinum* toxin formation and T is temperature ($^{\circ}\text{C}$). Welt *et al.* developed a theoretical means for determining optimal TTI behaviour (for pseudo-zero order kinetics) based on this curve [35]. Following on from this Mendoza and coworkers compared the behaviour of a number commercially available and prototype TTIs to determine the most suitable for use in seafood packaging [31]. To this end, they characterised the response of the TTIs under dynamic and isothermal conditions (see Fig 5.5) and compared the results against the Skinner-Larkin relationship. A visual example of this is given in Figure 5.6 which shows an Arrhenius plot (i.e. $\ln k$ against $1/T$, see Equation 2) of the Skinner–Larkin curve and three commercial TTIs. Where a TTI line cuts below the SL curve (e.g. the C2-10 and TJ2), it is responding slower than the *C. botulinum*

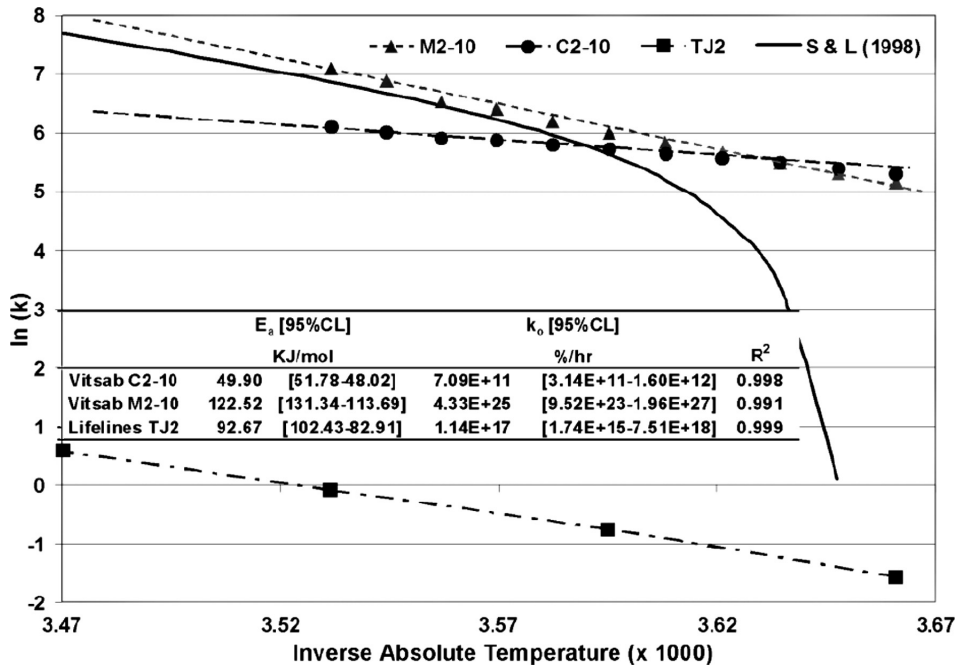


Figure 5.6 An Arrhenius plot of the Skinner–Larkin curve (S & L) and the response of three commercial TTIs (Vistab M2-10, C2-10 and Lifelines TJ2). Reproduced from T.F. Mendoza *et al.*, *Journal of Food Science*, Vol. 69 (3), pp. FMS90–FMS96. Copyright (2004) with permission of Blackwell Publishing.

lag time, i.e. indicating spoilage too late. To be effective, the TTI line must approach the SL curve from above, as the M2-10 in this example. Even so, the non-linear SL curve displays increasing deviation from the M2-10 line from approximately 3 to -1°C (i.e. 3.62 to 3.67 on the x -axis), resulting in the sensor giving a false positive for fish that is still safe. Although this scenario is by far the lesser of two evils, it is still wasteful and further research is required to develop TTIs that provide a more accurate fit to spoilage profiles.

Nevertheless, the future for TTI smart packaging appears to be in a very healthy state. The science of both seafood spoilage and TTI behaviour is now well understood with further improvements and refinements occurring continuously. This improving reliability, coupled with low unit cost (2–4¢ unit cost for Fresh-Check[®] indicators, according to TempTime) makes TTIs an attractive means of improving confidence in quality. The acceptance of TTIs as fulfilling the USFDA regulatory requirement for MAP seafood cannot be overstated as this is driving the adoption of the technology in the United States. In Europe, adoption is being driven more on the supermarket/marketing side, with stores such as Monoprix in France using, since 1991, the Fresh-Check[®] TTI – ‘La puce fraîcheur’ from Temptime (formerly LifeLines Technology, USA) as a guarantee of freshness to the consumer and to obtain, in the process, a competitive advantage [36].

5.6 Food Quality Indicators

While TTIs provide an excellent means of indicating shelf life and flagging temperature abuses, they do not provide an indication of actual quality of the produce. Temperature abuses prior to packaging (e.g. on board the trawler, improper storage of fillets at processor, etc.) will not be taken into account by the TTIs. Therefore, a true food quality indicator (FQI) will flag the reduction in quality as a direct result of a process that occurs during spoilage. Use of quality assessment for seafood is common regarding fresh, unpacked produce, though to our knowledge no commercially available FQI exists for packaged seafood produce. To determine possible means of devising an FQI for smart packaging, it is useful to give a brief overview of quality assessment of unpackaged seafood produce.

As noted earlier, faster, automated sensory techniques were investigated in the recent EU project, FAIR CT98-4076 to develop an artificial quality index (AQI) [12]. The wide variety of changes in terms of texture, colour, electrical properties and odour observed during spoilage of cod and hake suggested a range of possibilities for directly assessing quality. Unfortunately, many of these techniques are not suited to implementation in smart packaging due to technical and cost issues. Aside from unit cost, the design and implementation of FQIs into packaging is more problematic than externally placed TTI labels. In this case, the FQIs will have to be within the pack or at the very least have contact with the interior atmosphere (or headspace) of the pack, requiring the sensor and its ingredients to comply with stringent regulations governing food packaging, covered by in the US by the Code of Federal Regulations – Title 21 [37].

Even so, a number of promising avenues of research exist for FQIs in seafood. One of the most promising is the development of sensors that respond to changes in the packaging headspace as the fish spoils. Many of the spoilage mechanisms discussed in the previous section result in the release of different volatile gases over time. Duflos *et al.* employed mass spectroscopy techniques to determine the differences in the gases emitted by cod,

Table 5.4 Volatile amines commonly emitted during seafood spoilage

Compound	Formula	Boiling point	Density	pK _a
Ammonia	NH ₃	-33.4 °C	0.68 g/L	9.25
Dimethylamine	N(CH ₃) ₂ H	7 °C	1.5 g/L	10.73
Trimethylamine	N(CH ₃) ₃	2.9 °C	0.67 g/L	9.81

mackerel and whiting after 0 and 10 days of storage at 4 °C [38]. In a thorough study they identified 20 volatile compounds common to the three species that increased over time. Of particular interest are the volatile amines, responsible for the pungent smell of spoiled fish. These compounds are related to ammonia and some examples of those emitted during seafood spoilage are given in Table 5.4. The pK_a is a property related to pH and in this case indicates that the amines are relatively basic.

The measurement of amines in fish flesh, TVB-N (Total Volatile Basic Nitrogen) analysis, is already widely used as a laboratory-based assessment of quality [21]. On-flesh pH measurements are also employed, the pH of the flesh increasing as the amine content increases. This change in pH allows the possibility of employing pH indicator dyes as means to provide a colorimetric indication of quality. An early device proposed as a seafood indicator involved wooden skewers permeated with a dye that changed colour if inserted into spoiled seafood [39]. More recently, colorimetric membranes have been developed for detecting a variety of gases such as carbon dioxide [40] and ammonia [41]. These sensors are generally non-specific, responding to the pH change brought about due to a build up of the target gas. This lack of specificity limits the uses of these sensors to a few specific well-defined situations. Fortunately, seafood FQI technology shows strong potential as an application for these simple sensors.

As noted earlier, no commercial implementations of the technology appear to exist at present. However around the year 2000, the National Centre for Toxicological Research (NCTR, affiliated with the USFDA) was developing an FQI called a Fresh-Tag, licensed to Cox Technologies [24, 42]. The Fresh-Tag was designed to respond to the volatile amines that build up during seafood spoilage. The original device was in the form of a rectangular plastic tag with a hollow barb for piercing the pack [43]. As amines build up in the packaging headspace, they proceed through the barb to the active sensor, consisting of a wick that progressively changes colour as the amines build up. At time of writing the exact status of the Fresh-Tag is unclear. The original license holder, Cox Technologies, was acquired by Sensitech in 2004 who were in turn acquired by Carrier Corp – neither Sensitech or Carrier Corp make reference to the device on their respective web pages. On the development side, the NCTR and consultant partners are currently engaged in market exploration to develop a viable device based on the original Fresh-Tag technology.

The Adaptive Sensor Group in Dublin City University has also been developing FQI technology for seafood and a brief overview of our research in this area follows.

The sensors consist of pH indicator dyes immobilised within a cellulose-based polymer membrane. An example of some of these dyes is given in Figure 5.7. These sensors can be cast onto substrates as diverse as PET (polyethylene terephthalate) or filter paper, through drop coating or mass production techniques such as screen printing. A schematic diagram outlining how the sensor works is given Figure 5.8. Initially, when the fillets

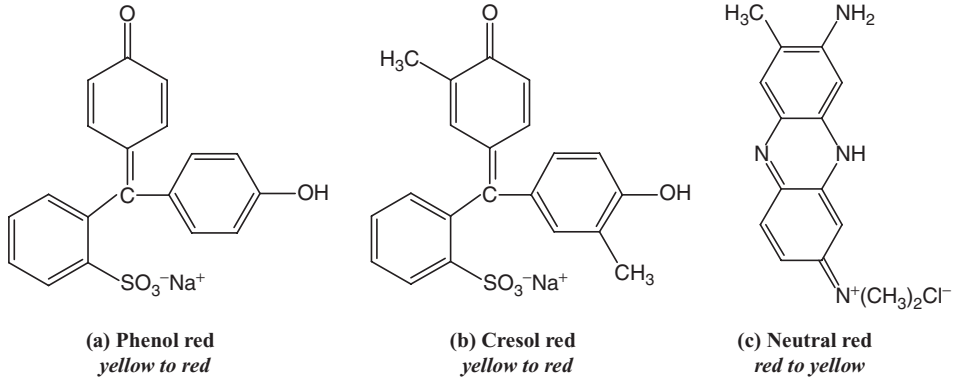


Figure 5.7 Structural formulas of some of the colorimetric indicators being investigated for food quality indicators. The acid to base colour change is also given.

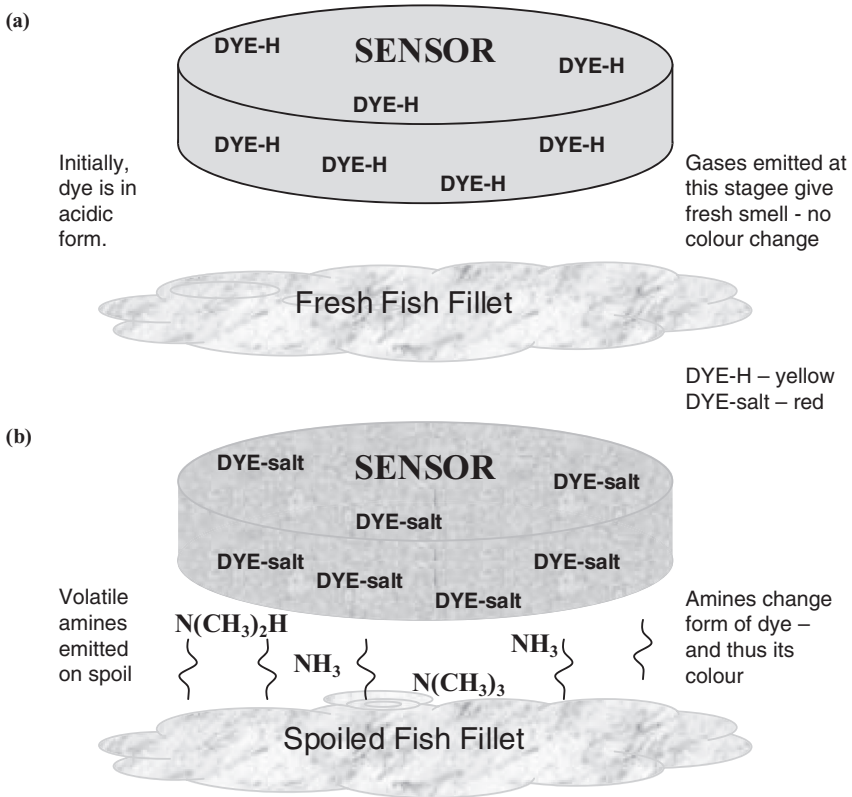


Figure 5.8 Schematic showing the basic operation of the food quality indicator before (a) and after (b) spoilage.

are freshly packed, the dye within the sensor is in its acidic form (usually yellow in colour). As the fish spoils, the volatile amines detailed in Table 5.4 are increasingly released and the dye is changed to a new form (basic), usually red or blue in colour depending on the dye used. The sensor response is colorimetric and can therefore be observed with the human eye through the use of a reference ring in a similar way to the TTI sensors (Figure 5.2c). A more quantitative means of measuring and recording the colour change is possible through the use of a colorimeter. The custom-built colorimeter employed in this study has been described previously [44]. In brief, two LEDs at a 45° configuration illuminate the area of interest and the reflected light is measured by a photodiode.

Although the concept appears simple, a number of challenges exist. As the volatile amines are released during spoilage are produced by microbial action on the flesh, there is often a lag between the increase in microbial populations and the increase in amine concentration. An example of this is given in Figure 5.9 which shows the response of a bromocresol green sensor to cod fillets stored at room temperature. Both the TVC and *Pseudomonas* populations show a gradual increase more or less from the start, which then rapidly accelerates, reaching the 10^7 cfu/g spoilage threshold after about 18 hours. This is also the time at which the bromocresol green sensor begins to change colour after initially displaying little change. Therefore in the case of this sensor, the point of spoilage can therefore be taken as once the colour change has begun [44, 45].

There are a number of options regarding sensor formulation and preparation to reduce this lag time and improve the response of the sensor; e.g. membrane thickness, choice of

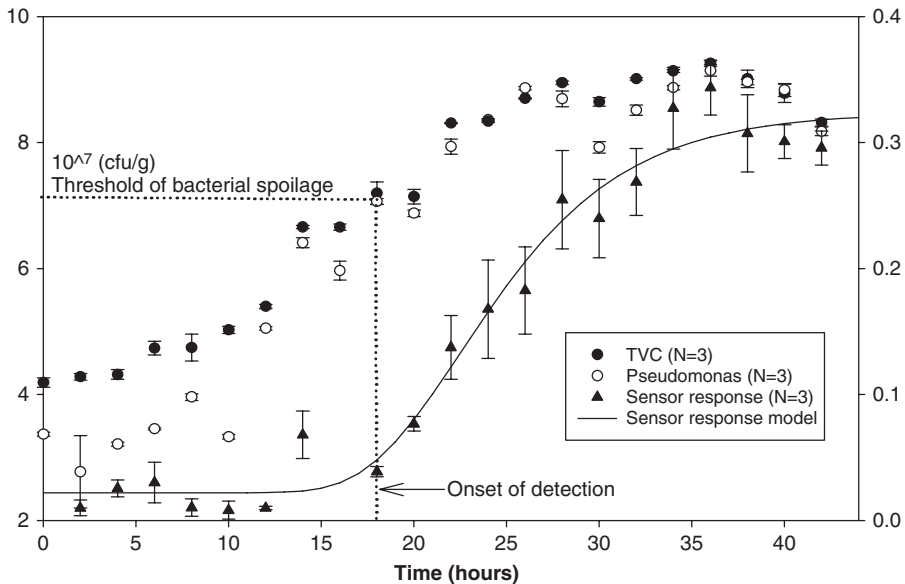


Figure 5.9 Correlation of sensor response and changes in bacterial population of fresh cod kept at 20°C over time. Bacterial data are averages of two replicates while sensor data are average of 15 measurements. The error bars are standard error of the mean values. Reprinted from Pacquite et al., *Talanta*, Vol. 69, pp. 512–520. Copyright (2006) with permission from Elsevier.

substrate, etc. However choice of dye remains by far the most dominant factor. In this case, the dyes considered generally belong to the sulfonphthalein family, whose basic structure is composed of three aromatic rings connected to a carbon – see Figure 5.7(a) and (b) for two examples. This family of dyes more or less covers the full range of pH, potentially allowing a sensor to be tailored – or tuned – to respond to a particular concentration of amines. Dyes with pK_a values just below (≤ 1.5 units) or above the amine pK_a values (see Table 5.4) cannot be used as no change in colour will be observed. Therefore, the lower the pK_a of the dye, the more responsive it will be to lower concentrations of volatile amines. There is, however, a limiting factor; large quantities of water are always present with a pack of seafood and the headspace humidity is in the region of 100%. For dyes of pK_a values around or below 7, the water can result in a colour change – potentially masking the amine response. To combat this, the sensor can be ‘waterproofed’, e.g. by using hydrophobic enclosures, though this may also adversely affect the amine response while adding greatly to the unit cost of a sensor. Therefore, a relatively narrow pK_a range exists for suitable dyes (~ 7.5 – 8.5). Evaluation of sensor behaviour has been conducted through packaging trials – where the sensor response to fish fillets of known history (packaged in the same manner as commercially packaged fish) is checked against conventional freshness tests. An example of these packaged fillets and the colorimeter used in the trials (described previously) is given in Figure 5.10. The results of sensor formulations composed of three potential candidate dyes are given in Figure 5.11.



Figure 5.10 Examples of cod fillets packaged with three internal spoilage indicators (three different sensor formulations in each pack). The colorimeter and probe used for measuring the colour change are also shown.

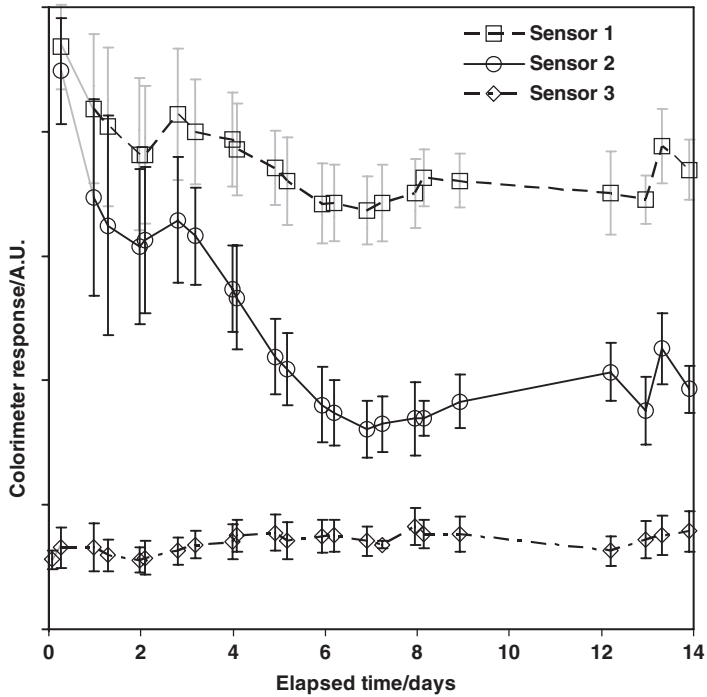


Figure 5.11 Measured responses for sensor formulations incorporating three different dyes. Three packs: 250 g cod fillets stored at 4 °C. Error bars display standard deviation ($n = 6$; sensors 1 and 2, $n = 3$; sensor 3).

Sensor 1 contained cresol red; a dye with pK_a of *ca* 8.1, sensor 2 incorporated phenol red with a pK_a of ~ 7.8 , while sensor 3 contained neutral red, a non-sulfonphthalein dye also with a pK_a of ~ 7.8 . The structure of the three dyes is given in Figure 5.7. After preparation, sensors 1 and 2 appear light yellow in colour while sensor 3 appears red – indicating that the dyes are in the protonated (acidic) form. In the deprotonated (basic) form, sensors 1 and 2 appear red (causing a drop in response) and sensor 3 turns yellow (yielding an increase in response). The sensors are affixed to the transparent packaging film prior to sealing the film and tray. The cod fillets used in this study had been landed on the morning of the trial, and time zero was taken as the moment the packs were sealed. Throughout the duration of the trial the packs were stored in a refrigerator (4 °C). The supplier generally predicts a shelf life of between 6 and 8 days for the fish under these conditions. The three response curves for the sensors in Figure 5.11 are shown to scale relative to each other. Sensors 1 and 2 can be seen to display varying responses over time while sensor 3 displays only a very slight increase over the entire trial. On the first day, sensors 1 and 2 display a rapid drop before levelling off as they equilibrate to the conditions within the pack. Between day 3 and 7 both these sensors darken steadily before again levelling off – this endpoint corresponding to spoilage of the fish. Sensors 1 and 2 both display similar levels of relatively large scatter, however the increased response of sensor 2 means the response is easier to distinguish. Therefore, the pK_a of sensor 2 appears to yield an indicator that displays a good trade off between amine response and effects due to water within the pack.

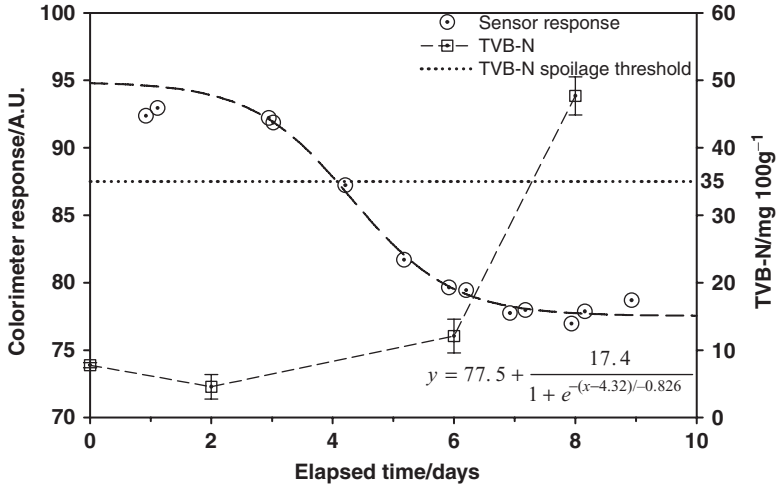


Figure 5.12 Comparison of sensor response to total volatile basic nitrogen measurements for cod fillets.

From Figure 5.11 it appears that the working sensor appears broadly to follow sigmoidal type behaviour. In Figure 5.12, the response of the phenol red sensor is shown with measured TVB-N. In this case a logistic sigmoid has been fitted to the measured data.

$$y = y_0 + \frac{a}{1 + e^{-(x-x_0)/b}} \quad (2)$$

A good correlation can be observed between the curve and colorimetric data. Briefly, the parameters y_0 and a describe the lower and upper thresholds of the curve, respectively while b indicates the *sharpness* or *rapidity* of the change – for spoilage indicator applications the quicker the change the better in order to lessen any ambiguity. x_0 indicates the midpoint of the colour change in the sensor – in this case 4.32 days. The EU TVB-N limit for spoilage is 35 mg per 100 g of flesh and is marked by the dotted line. The TVB-N values for the fillets are seen to cross this line at some stage between the sixth and eighth day, with a sharp increase during this time. From Figure 5.12, it can be seen that this corresponds to the endpoint of the colorimetric sensor. Therefore, the sensor indicates that the packaged fillets have spoiled once the sensor reaches this end state – corresponding to the red colour noted previously. This result has been reproduced in trials involving fish packaged in processors through the supply chain to supermarkets [46]. An example of how the sensors may be accommodated within the packs (showing sensors before and after spoilage) is shown in Figure 5.13. In due course it is anticipated that a full scale roll out of the sensor will be accomplished.

5.7 Overview: TTI versus FQI

A summary of the main points relating to TTIs and FQIs is given in Table 5.5. Due to their increasingly widespread adoption, TTIs are currently leading the charge in terms of smart packaging quality indicators for seafood. As noted, the technology has proved useful for supplier cold-chain management as well as supermarket quality marketing. On the

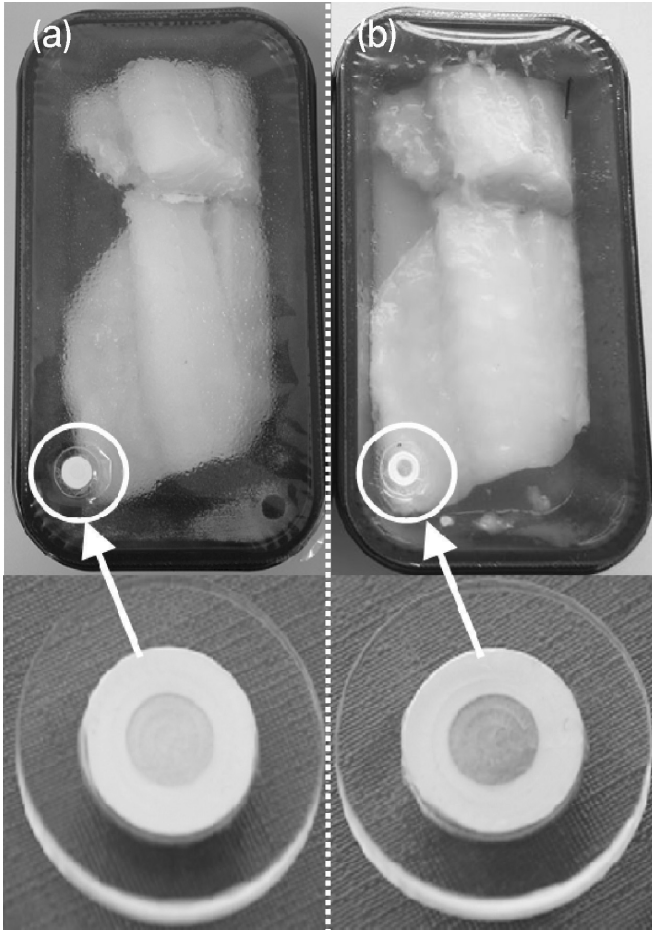


Figure 5.13 An example of one possible implementation of the food quality indicator showing the sensor before (a) and after (b) spoilage.

Table 5.5 Comparisons of the respective advantages and disadvantages of TTIs and FQIs

Time-temperature integrators		Food quality indicators	
Advantages	Disadvantages	Advantages	Disadvantages
Easily read Accepted quality assurance method, commercially available, cheap unit cost science understood – maturing technology	Do not directly indicate actual seafood quality	Easily read Directly indicate quality/spoilage, potentially cheap	Not yet commercially available Affixed inside pack – Restrictions on formulation – Difficult to apply

other hand FQI technology, though embryonic, has also attracted interest from suppliers and supermarkets willing to conduct trials in the new technology, thus demonstrating a potential market for direct indicators of quality. In any event, it would be wrong to think of the two technologies as mutually exclusive and the information provided by each may well be used in a complementary fashion; TTIs to ensure cold-chain compliance and FQIs to ensure quality.

5.8 Modified Atmosphere Packaging (MAP)

MAP solutions are the subject of extensive research and are increasingly used to extend shelf-life of fresh products. Two excellent reviews were written by Sivertsvik *et al.* and Phillips [47, 48]. The achievable extension of shelf life depends on species, fat content, initial microbial population, gas mixture, the ratio of gas volume to product volume and most importantly, storage temperature.

The air surrounding us contains approximately 78 % nitrogen (N₂), 21 % oxygen (O₂) and roughly 1 % of argon (Ar) and other gases [of which about 0.03 % is carbon dioxide (CO₂)]. Atmospheric oxygen, which supports all aerobic respiratory life, leads quite readily to oxidation of molecules and may be coupled to enzymically balanced systems. This process of oxidation continues after death, causing loss of freshness and spoilage [49]. Thus the removal of oxygen extends meat shelf-life efficiently. However anaerobic atmospheres have less effect on fresh fish shelf-life. Not only is the microflora of meat not the same as that of whole, gutted or filleted fish, but many other fish specificities make a direct comparison difficult. For one, the initial load of bacteria present is comparatively larger in fish, consisting of microorganisms capable of growing at low temperature. Some of them are pathogens that may be able to grow before spoilage occurs. Furthermore, the higher pH of the flesh, the redox potential (E_h) of the fish muscle and the structural damage effect of CO₂ on the latter, makes MAP a more complicated science with respect to seafood products [50]. CO₂ is the most important gas used in MAP of fish because of its bacteriostatic and fungistatic properties. It is highly soluble in water and fat and the solubility increases greatly with decreased temperature [47]. Stammen *et al.* [51] showed that even after the packaging has been opened, the CO₂ is slowly released by the product and continues to exert a preservative effect known as 'CO₂s residual effect'. The principal effect of raised carbon dioxide modified-atmosphere packaging is an extension of the 'lag' phase of the growth of the bacteria on the fish, the inhibition of the common spoilage bacteria and the promotion of a predominantly slower growing Gram-positive flora [49, 52]. However it has been reported to increase water loss (drip) and gaping of the muscle by dissolving of muscle cellular structure [53]. The growth of certain yeasts can be stimulated by high levels of CO₂ and thus can be a major cause of spoilage in certain products [48]. On the other hand, adjusting the headspace composition with N₂ reduces the rate of oxidative rancidity in fatty fish. The most widely used gases mixtures in MAP of fish include CO₂, N₂ and O₂ at a 40 %, 30 % and 30 % ratio respectively [54, 55]. N₂ is inert and tasteless, and is mostly used as a filler gas because of its low solubility in water and fat [47] to prevent pack collapse [48]. Cod is without a doubt the preferred species for MAP studies and on average, based on the gas mixture ratio above, shelf-life usually doubles from 6–9 days in air and at chilled temperature to 12–20 days in MAP.

The single most important concern is the potential for outgrowth and toxin production by the psychrotrophic *Clostridium botulinum* type E and non-proteolytic type B and F, which are able to grow at temperatures as low as 3.3 °C, produce toxin and yet remain acceptable with respect to odour and appearance to the customer. The optimum MAP composition packaging method with regard to inhibiting this toxin production was found to be equal parts of O₂ and CO₂ [56]. However, despite these positive results, the use of MAP does not eliminate the necessity nor the need for careful handling at all stages from factory to table [48]. The risk of pathogens or toxin presence is potentially even greater in 'ready to eat' products since they require minimal or no further heating. The use of MAP for any raw product that is subsequently cooked is considered less hazardous as the cooking step would kill all vegetative pathogens.

Packaging materials such as packs and films also play a major role in product quality and shelf life as they can control post-packaging gas exchanges between the atmosphere within and the air outside.

5.9 Conclusion

In the preceding sections, it has been demonstrated how seafood produce is already well-placed to benefit from innovations in smart packaging. Over the past few years, the seafood industry has seen an increase in volume demand despite facing declining stocks and heavy quotas. Moreover, a parallel increased awareness of seafood health benefits has prompted customers to demand the means to make a more informed choice. Smart packaging can provide real time information on the freshness and safety of prepacked seafood while decreasing wastage through more accurate estimation of the best-before dates. Many technologies such as TTI and MAP are compatible and complementary and indeed are already being implemented while others (RFID) show promise but are too costly at present to implement on individual retail-size packs. Food quality indicator technology shows promise but further work is needed to bring it to the market. Current trends are thus driving demand for low-cost sensing technologies situated in intimate contact with packaged food, or its headspace, that can give an accurate visual indication of the food quality and safety. In future, the implementation of wireless sensor networks could allow the real-time remote monitoring of parameters such as temperature or the colour changes of TTI/FQI indicators, eventually allowing a total traceability from 'farm to fork'.

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6

Antimicrobial Active Packaging for Food

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6.1 Background of Antimicrobial Packaging systems for food

In general, the driving force for new technology and product development in food markets is the demand of consumers who are open to new ideas, and the cross over between old world knowledge of food and modern technology. The key question has been “Is this new product worthy?” The interpretation of “worthy” for food applications traditionally meant “healthy” and “safe” and led to the packaging of most foods in the consumer marketplace in films or containers with labels indicating the nutritional facts. Fundamentally, the purpose of packaging products, no matter how fancy, is to provide a means of carrying a presumably safe and wholesome product through warehousing and distribution to the consumer.

Based on these ideas and demands, packaging scientists have developed and introduced a new packaging system known as “Active Packaging” into food applications. Active packaging describes a packaging system which possesses attributes beyond basic barrier properties, which are achieved by adding active ingredients to the packaging system and/or using actively functional polymers (Han, 2002). Such systems interact with the product or the headspace between the package and food to obtain a desired outcome such as the increase of shelf life or enhancement of safety or sensory properties, while maintaining the quality of the product. Antimicrobial food packaging is one of the special applications of active food packaging that controls conditions both inside the food and in the package headspace actively and responsively (Han, 2005; Cooksey, 2005; Lauza and Breene, 1988).

The evidence of global interest and consumer demand for antimicrobial packaging system can be easily found in the number of published international articles as revealed by a

Table 6.1 *The number of articles published in international journals during 1991 to present (May 2007) through Keyword Science citation index.*

Search Topic/Year	The Number of articles in SCI journal		
	"Antimicrobial packaging"	"Active packaging"	Antimicrobial Packaging & Active packaging
1991–2000	38	332	6
2001	9	42	1
2002	17	66	6
2003	21	68	4
2004	22	64	8
2005	30	70	9
2006	34	81	15
2007-Current (May 2007)	11	31	5

Source: ISI Web of Knowledge

keyword search. The interest in antimicrobial packaging as a subset of active packaging has dramatically increased in the past 10 years, as shown in Table 1.

As a specific example of the application of active packaging to food safety, a Japanese company (Beanstalk Snow, 2006) has very recently adapted an antimicrobial packaging system for their food product (baby milk). The company has pioneered a can that keeps baby milk safe from bugs and bacteria. The original milk has been re-launched in the new cans which give added antimicrobial protection. Beanstalk Snow states that this is a world first. It has been developed because of concerns over Severe Acute Respiratory Syndrome(SARS) and Methicillin Resistant Staphylococcus Aureus (MRSA) as well as E. coli and salmonella food poisoning. These products are packed in canisters which have the internal surface coated with US FDA-approved silver ions which have an antimicrobial effect. These antimicrobial canisters have been tested to prove their efficacy. This example shows the relationship between demands of safety and industry need (Eaton and Sadler, 2006).

In keeping with tradition, many food products are still subjected to heat treatment processing, which destroys pathogenic bacteria and reduces microbial populations in order to ensure their safety. However, this process can damage food color, flavor, texture, vitamin and mineral content, and complex fiber and other health-protecting complexes as well. Alternative processes, such as aseptic, vacuum and modified atmosphere packaging, low-dose irradiation or high hydrostatic pressure have also been used in the food market. To replace or reinforce traditional technology, antimicrobial packaging systems have been recently introduced to destroy or retard the growth of microbes. Antimicrobial packaging is one of many applications of active packaging. Currently, various plastic- or biopolymer-based active packaging films and containers have been developed for food and pharmaceutical products.

6.2 Governmental encouragement

In June 2003, the U.S. Department of Agriculture's Food Safety and Inspection Service (FSIS) published a rule to encourage plants to incorporate technologies that can kill the

Table 6.2 Disinfectant & antimicrobial chemical demand (million dollars)

Item	1999	2004	2009	% Annual Growth	
				04/99	09/04
Disinfectants & Antimicrobials	607	730	930	3.8	5.0
Industrial	370	437	554	3.4	4.9
Institutional & Commercial	160	193	240	3.8	4.5
Consumer	77	100	136	5.4	6.3

Source: The Freedonia Group, Inc (www.freedoniagroup.com)
The Demand for Disinfectant & antimicrobial chemicals

bacteria or prevent its growth after cooking and packaging. The measure is designed to drive down the rate of *listeria* in ready-to-eat meat and poultry products. It is focused on helping to generate processor interest in such food-safety elements. The rule requires all establishments producing ready-to-eat goods that are exposed to the environment after cooking to develop written programs to control *listeria* and to verify the effectiveness of those programs through testing. Plants that use steam pasteurization and other processes to kill *listeria* inside a package do not need to test product contact surfaces because the meat and poultry would not be exposed to the environment after cooking, FSIS states. FSIS adds that a recently completed survey of ready-to-eat establishments reveals that they “have responded to the rule appropriately and have strengthened and intensified their programs to control *listeria*.”

6.3 Demand for antimicrobial and disinfectant chemicals in the U.S market

As shown in Table 2, the demand for specialty disinfectant and antimicrobial chemicals in the U.S. is projected to expand 5.0% annually, to \$930 million, by 2009 according to a new report by industrial market research firm The Freedonia Group (Birks, 2005). The use of antimicrobials and disinfectant by consumers is double the use of the past 10 years. The report projects that the market will grow due to increased demand for products that reduce the risk of food-borne illnesses, are effective against antibiotic-resistant organisms and are compatible with other cleaning and sanitizing formulations.

6.4 History of antimicrobial packaging in industry

In 1945, Gooding/Best Foods obtained a patent for incorporating sorbic acid into foods and food wrappers to inhibit mold growth. Sorbic acid and potassium salts are incorporated into food packaging materials for reducing microbial spoilage. They were mixed into a wax layer of natural cheese (Melnick and Luckmann, 1954a & b; Melnick et al., 1954; Smith and Rollin, 1954a & b), wet wax-coating on packaging paper (Ghosh et al., 1973 & 1977), and edible protein coating on intermediate moisture foods (Torres et al., 1985). The results of this research were usefully used in industry in spite of the fact that the release rate and migration profile of antimicrobial agents in these applications were not specifically controlled.

In 1992, Mitsubishi filed a patent which claims the use of zeolite in film using corona surface treatment, where silver is coated onto Zeolite (porous high surface area particle). The silver coating makes Zeomix-containing film much more antimicrobial. The corona treatment etches the film surface to some degree and could expose more silver sites. Currently, silver substituted zeolites are widely used as polymer additives for food applications, especially in Japan. These substituted zeolites are incorporated into polymers like polyethylene, polypropylene, nylon and butadiene styrene at levels of 1-3% (Brody et al., 2001). Silver ions are taken up by microbial cells, disrupting the cells' enzymatic activity. Commercial examples of silver substituted zeolites include Zeomic, Apacider, AgIon, Bactekiller and Novaron.

6.5 Antimicrobial agents in use for commercialization

A chemical preservative can add antimicrobial activity to the packaging material after incorporation into the materials. For example, preservative-releasing films have antimicrobial activity by releasing the preservative at a controlled rate. Oxygen absorbents also reduce headspace oxygen and partially protect food against aerobic spoilage such as mold growth (Smith et al., 1990). Common antimicrobial chemicals for food products are preservatives such as organic acids, their salts, sulfites, nitrites, antibiotics and alcohols (Table 3). As an example, potassium sorbate and sorbic acid have been studied as preservatives for the packaging of cheese products. The antimicrobial mechanism/kinetics and the controlled release profile of potassium sorbate from low density polyethylene (LDPE) film into cheeses were examined and mathematically simulated by Han (1996) to develop preservative-release packaging films.

Another attempt at incorporating chemicals into plastics for antimicrobial packaging films was in antimycotic (fungicide) and antibiotics films. Imazalil was used as the active substance and it was chemically coupled to plastic films to delay the growth of molds. An imazalil in LDPE shrink wrapping film for peppers (Miller et al., 1984) and for cheddar cheese (Weng and Hotchkiss, 1992), and imazalil bound ionomer film (Halek and Garg, 1989) had antifungal properties and controlled the contamination of cheese and peppers. Currently various research has tested the antimicrobial activity of other chemicals, gases, enzymes and natural components as preservatives or sterilizing agents. They include propionic acid, peroxide, ozone, chlorine oxide, eugenol, cinnamaldehyde, allyl isothiocyanate, lysozyme, nisin and others. These antimicrobial agents may be incorporated into packaging materials to develop the antimicrobial packaging system. For example, Franklin et al (2004) and Grower et al (2004) reported that a nisin coating on packaging films successfully inhibited the growth of *Listeria monocytogenes* in hotdogs. Compared to the sterilizing agents (peroxide, ozone and chlorine oxide), other natural agents may have greater advantages for antimicrobial packaging systems as edible components. Biodegradable polymers are currently very actively studied as edible coating or film materials (Krochta and De Mulder-Johnston, 1997). Padgett et al. (1998) demonstrated the antimicrobial activity of lysozyme and nisin in soy protein isolate films and corn zein films. Use of edible films or coatings with incorporation of food preservatives and natural antimicrobial agents may become more popularly utilized in antimicrobial packaging research.

Table 6.3 Applications of antimicrobial food packaging. Reproduced from J. Han, *Food Technology* 54, 3, p. 57. Copyright 2000, the Institute of Food Technologists.

Antimicrobial Agent	Packaging Material	Food	References
Organic Acids			
Potassium sorbate	LDPE	Cheese	Han (1996)
	LDPE	Culture media	Han & Floros (1997)
	MC/palmitic acid		Rico-Pena & Torres (1991)
	MC/HPMC/fatty acid		Vojdani & Torres (1990)
	MC/chitosan	Culture media	Chen et al. (1996)
	Starch/glycerol	Chicken breast	Baron & Sumner (1993)
Calcium sorbate	CMC/paper		Ghosh et al. (1973, 1977)
Propionic acid	Chitosan	Water	Ouattara et al. (1999)
Acetic acid	Chitosan	Water	Ouattara et al. (1999)
Benzoic acid	PE-co-MA	Culture media	Weng et al. (1997)
Sodium benzoate	MC/chitosan	Culture media	Chen et al. (1996)
Sorbic acid anhydride	PE	Culture media	Weng & Chen (1997)
	PE		Weng et al. (1993)
Benzoic acid anhydride	PE	Fish fillet	Huang et al. (1997)
Fungicide/Bacteriocin			
Benomyl	Ionomer	Culture media	Halek & Garg (1989)
Imazalil	LDPE	Bell pepper	Miller et al. (1984)
	LDPE	Cheese	Weng & Hotchkiss (1992)
Nisin (peptide)	Silicon coating		Daeschel et al. (1992)
	SPI, Corn zein films	Culture media	Padgett et al. (1998)
Peptide/Protein/Enzyme			
Lysozyme	PVOH, Nylon, Cellulose acetate	Culture media	Appendini & Hotchkiss (1996)
	SPI film, Corn zein films	Culture media	Padgett et al. (1998)
Nisin	Corola treated PE films	Hot dog	Franklin & Cooksey (2004)
Glucose oxidase		Fish	Field et al. (1986)
Alcohol oxidase			Scott & Hammer (1961)
			Brody & Budny (1995)*
Alcohol/Thiol			
Ethanol	Silicagel sachet	Culture media	Shapero et al. (1978)
	Silicon oxide sachet (Ethicap TM)	Bakery	Smith et al. (1987)
Hinokithiol	Cyclodextrin/plastic (Seiwa TM)		Gontard (1997)*
Oxygen Absorber/Antioxidant			
Reduced iron complex	Sachet (Ageless TM)	Bread	Smith et al. (1986)
BHT	HDPE	Breakfast cereal	Hoojjatte et al. (1987)
Gas			
CO ₂	Calcium hydroxide sachet	Coffee	Labuza (1990)*
		Fruit/Vegetable	Sacharow (1988)*
ClO ₂	Chlorine dioxide sachets	Chicken breast	Ellis & Cooksey (2006)
SO ₂	Sodium metabisulfite	Grape	Gontard (1997)*
Others			
UV irradiation	Nylons	Culture media	Paik & Kelley (1995)
	Nylons	Culture media	Hagelstein et al. (1995)
	Silver zeolite	LDPE	Ishitani (1995)
Grapefruit-seed extract	LDPE	Lettuce	Lee et al. (1998)
	LDPE	Soybean sprouts	Lee et al. (1998)

*From review articles without experimental data. LDPE = low density polyethylene; MC = methyl cellulose; HPMC = hydroxypropyl MC; CMC = carboxyl MC; PE = polyethylene; MA = methacrylic acid; SPI = soy protein isolate; PVOH = polyvinyl alcohol; BHT = butylated hydroxy toluene; HDPE = high density PE

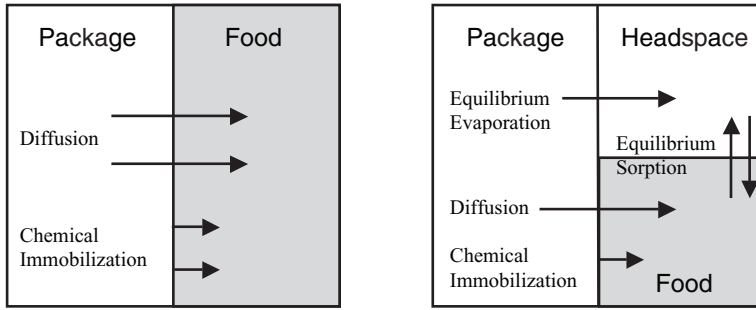


Figure 6.1 *Food Packaging Systems and Migration Phenomena. Reproduced from J. Han, Food Technology 54, 3, p. 58. Copyright 2000, the Institute of Food Technologists.*

6.6 Mechanism of antimicrobial packaging systems

6.6.1 Incorporation of antimicrobial agent into the polymer matrix

As shown in Figure 1, the antimicrobial agents used in polymer applications (both flexible films and rigid plastics) are sub-micron-sized cell wall penetrants designed to disrupt the metabolic function of thin walled microorganisms such as bacteria, yeasts and fungi. This mechanism was well reviewed by Han et al (2002). These built-in agents work best with vacuum packaging because the vacuum packaging material is in intimate contact with the surface of the food. The agent has to reach adequate concentration in the food surface to inhibit microbial growth. Also, the plastic film incorporating the agent must have good heat stability.

Potential uses include both foodservice and manufacturing operations. Described as practical and affordable, these additives—when introduced into the molecular structure of a polymer—attack unwanted organisms, interrupting their ability to function, grow and reproduce. They provide continuous control of a broad range of Gram positive bacteria (for example, *Staph aureus*) and Gram negative bacteria (for examples, *E. Coli*). The antimicrobial additives are introduced into the interstitial (empty) spaces of the polymer matrix by means of a proprietary process and do not affect the physical properties of the plastic (Figure 1). The empty spaces act as reservoirs for the additives, which rise to the surface as needed to police for contaminants. Key to their functionality is the agents' ability to attack only thin-walled cells. Thick-walled cells, like those in humans and animals, are unaffected by the additives. The agents, proven safe for contact with human skin, are registered with EPA, and for specific end-use applications with FDA. The technology can be used in cast, coextruded, injection-molded, roto-molded or blow-molded products. The additives could prove highly effective in polyethylene foodservice wrapping films and polyethylene or polypropylene cutting boards, countertops, garbage cans and shipping crates. Although more research must be conducted specifically for food and food service packaging, industries have successfully employed its proprietary technology in polyethylene and polypropylene blown and cast films, as well as other polymers.

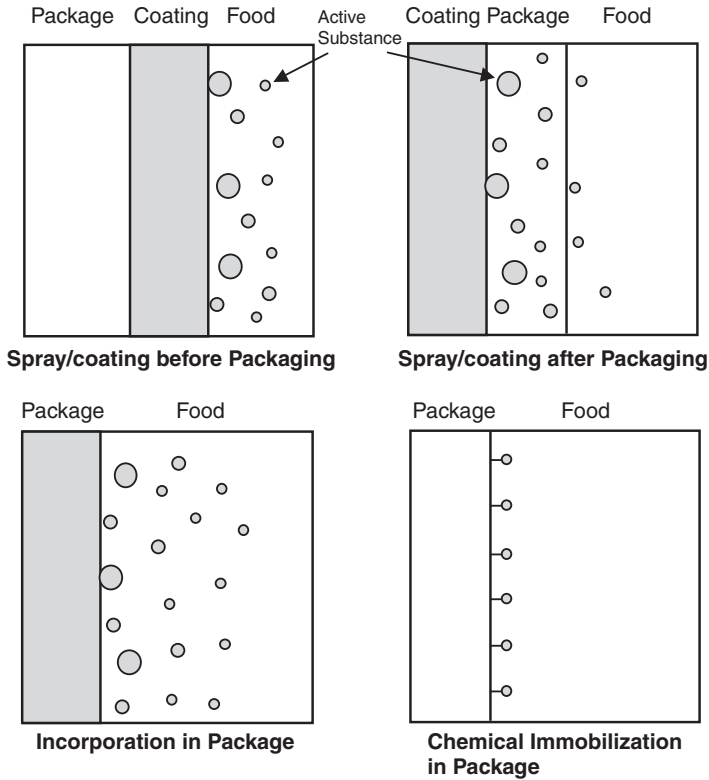


Figure 6.2 Migration of Active Substances. Reproduced from J. Han, *Food Technology* 54, 3, p. 59. Copyright 2000, the Institute of Food Technologists.

6.6.2 Surface modification of packages with antimicrobials

Surface modification includes not only the direct coating/casting of antimicrobial layer but also the implementation of an immobilized layer of antimicrobials on the package surface. This method brings the antimicrobials into direct contact with the food to inhibit the bacterial growth. The mechanism is schematically indicated in Figure 2. Some antimicrobial packaging uses covalently immobilized antibiotics or fungicides. In this case surface suppression of microbial growth by immobilization of the non-food grade antimicrobial substance occurs without diffusional mass transfer. The antimicrobial activity of an immobilized layer requires the presence of functional groups on both the antimicrobial and the polymer. Examples of antimicrobials with functional groups are peptides, enzymes, polyamines and organic acids. Figure 2 also shows how the immobilization method differs in its mass transfer aspects from other mechanisms of antimicrobial activity.

6.6.3 Antimicrobial packaging using gas-based systems

Gas-based antimicrobial systems fall into two groups, one using sachet/pad and the other relying on emitting/flushing a selected gas to inhibit microorganism growth. These systems

have been the most widely used and most successful antimicrobial packaging systems to date. Sachets/pads modify the gas composition inside of the package. They may contain oxygen scavengers, moisture absorbers, ethanol vapor generators, organic acids and surfactants. These systems have been used in bakery, pasta, vegetables and meat product packaging to inhibit oxidation and moisture condensation in the package. They may induce the decrease of A_w and O_2 thus decreasing bacteria growth inside of the package. Ellis et al reported (2006) that chlorine dioxide sachets were very effective in controlling the quality of fresh chicken breasts when combined with modified atmosphere technology. Additional benefits are the minimization of negative consumer responses and the potential economic advantage of increased outputs. Gas-flush systems eliminate the risk of accidental rupture of sachets and inadvertent consumption of their contents. An example of a gas-flush antimicrobial packaging system, is the use of a specific gas composition to control mold in the storage of berries and grapes in produce boxes, which are palletized and stretch-wrapped, then sulfite-flushed to prevent fungal spoilage. It is easy to use these types of bulk gas flushing and controlled/modified atmosphere technologies.

6.6.4 Inherently antimicrobial polymers

Some polymers are inherently antimicrobial and have been used in films and coatings. Some of these polymers enhance barrier properties, as well. It was reported that the chitosans having different molecular weight distributions showed different antimicrobial activity as well as different antioxidant activity (Kim, KW and et al, 2004 and 2005). Other cationic polymers such as poly-L-lysine promote cell adhesion (Goldberg, Doyle & Rosenberg, 1990) since charged amines interact with negative charges on the cell membrane, causing leakage of intracellular constituents.

6.7 Design of antimicrobial packaging systems

Antimicrobial food packaging systems can offer the containment and protection function simultaneously. Before manufacturing a package incorporating an antimicrobial packaging system, several factors should be considered. First of all, the characteristics of not only the food but also the antimicrobial agent which will affect the bacteria should be understood. The physicochemical composition of the food (such as lipid, carbohydrate or protein content ratio) can directly affect the activity of an antimicrobial agent in terms of diffusion rate or miscibility and the growth rate of specific bacteria. Second, the migration kinetics of antimicrobial agents into foods may be important to quantify in order to control the antimicrobial food packaging system and predict, for example, food and package shelf life. Also, the organoleptic properties of the antimicrobial agents might be important in the food application. During commercialization of an antimicrobial food packaging system, the entire packaging dynamics from processing to distribution to consumer should be considered as well to assess feasibility for mass production, cost and safety. Toxicity and regulatory issues will be another factor for designing a successful antimicrobial packaging system.

6.8 Prognosis for commercialization

In many food products, the driving force for commercialization has focused on the convenience and health issues. To ensure the food safety, these technologies used in active packaging systems should meet the convenience criterion for both consumer and manufacturer. Based on market research done by Business Insights Ltd (Eaton and Sadler, 2005), of all the convenient products launched between January 2002 and January 2005, 50.5% were classed innovative. Among the innovative products, 77.3% were innovative in formulation and 20.4% were innovative because of convenience packaging. There are several trends in convenience packaging innovation such as active packaging, antimicrobial packaging or smart packaging. These technologies contribute to the fulfillment of such demands as food safety, product freshness sustainability and elements of food service entering the home. Simultaneously they support convenience trends such as the evolution of sports caps closures and the evolution of the can. Active packaging technology is therefore a very hot topic in all over the world both in the current and future food marketplaces.

On the other hand, some active packaging technologies are looked upon negatively when considering the difficulty of commercialization, in spite of the growing commercial success for such alternatives as sachets/pads and controlled atmosphere packaging. A major technical difficulty with the introduction of active packaging agents into films and moldings is the process temperatures that have to be sustained for these package forming technologies. In addition, equivalent functionality to antimicrobial packages might be easily achieved by incorporating an agent into the food or by coating the food surface with the agent. Another challenge is posed by the global growth of sustainability targets and awareness, since many active packaging systems may not be compatible with sustainability objectives.

6.9 The future of antimicrobial packaging systems

Packaging technology innovation is well-positioned to respond to consumer demands for higher performance food. Innovation should address concepts such as food safety from potentially fatal bacteria and environmentally toxic hormones, nutritional quality and freshness, the package convenience and recyclability or sustainability. Antimicrobial packaging systems can change the condition of packaged food to extend shelf life or improve the safety and sensory properties. These systems are attracting the interest of researchers and industry due to their potential to provide quality and safety benefits. Antimicrobial packaging technologies have been successfully used in many commercial food products especially in the US and Japanese markets. Moreover, they may be combined with other active packaging technologies such as modified atmosphere packaging (MAP), radio frequency identification (RFID) systems, fresh indicator packaging or tamper resistance systems in order to increase the degree of success in verifying, preserving and enhancing food product quality in the eyes consumers. The combination of various active packaging technologies with antimicrobial packaging has not been fully used in industry yet. Nevertheless, the development of such combination systems in response to consumers' increasing demands can be foreseen in the not-to-distant future. In addition, the increasing attention on renewable sources of energy and more sustainable forms of packaging will also drive higher commitments of

industry and government to support R&D and commercialization of antimicrobial packaging systems based on natural products.

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7

Freshness Indicators for Food Packaging

Maria Smolander

7.1 Introduction

The idea of freshness indicators is that they monitor the quality of the packed food by reacting in one way or another to changes taking place in the fresh food product as a result of microbiological growth and metabolism. Contrary to concepts reflecting the requirements of the product quality, like package integrity and time–temperature history of the product, the freshness indicators indicate directly the quality of the product. The indication of microbiological quality is, for example, based on a reaction between the indicator and the metabolites produced during growth of microorganisms in the product. The general idea of a freshness indicator is not new, since as early as in the 1940s Clark (1949) filed a patent application describing an indicator for food product that ‘exhibits an irreversible change in visual appearance upon an appreciable multiplication of bacteria in the indicator’. A direct determination of a volatile metabolite, namely CO₂ from the microbiologically spoiling product itself with pH-dye based indicator was proposed by Lawdermilt (1962). Recent publications reviewing freshness indicators have been compiled by Smolander (2003) and Kerry *et al.* (2006).

A crucial prerequisite in the successful development of freshness indicators is knowledge about the quality-indicating metabolites. Evidently, the developed indicator concept has to be able to react to the presence of these compounds with the required sensitivity. Moreover, the indicator system should comply with legislation since the indicator needs to be brought into contact either directly with the food product or with the package headspace. Hence the indicator generally needs to be placed inside the food package unless the packaging

material is a breathable or gas-permeable wrap like that described by Williams *et al.* (2006). It is also essential to avoid false negatives, which are likely to dissuade producers from adopting indicators in real use (Kerry *et al.*, 2006).

7.2 Freshness Indicators for Quality Indicating Metabolites

Quality indicating metabolites have been widely studied since they offer the possibility of replacing the time-consuming sensory and microbiological analyses traditionally used in the quality evaluation of food products (Dainty, 1996). There are several potential quality indicating metabolites that could be utilised as target molecules of the freshness indicators. However, it should be kept in mind that the formation of the different metabolites depends on the nature of the packaged food product, spoilage flora and the type of packaging, and the indicating capacity of a particular metabolite should always be verified case by case. It is also beneficial from the point of freshness indicator development to trace a compound with non-existent or low initial concentrations. A wide variety of freshness indicators reacting to the presence of quality indicating metabolites has been presented in the scientific literature (Table 7.1). Most of these concepts are based on a colour change of the indicator tag due to the presence of microbial metabolites produced during spoilage (e.g. Williams *et al.*, 2006; Smolander *et al.*, 2002, 2004b; Miller *et al.*, 1999; Wallach and Novikov, 1998; Kahn, 1996; Namiki, 1996). Concepts based on optical or electronic measurement have also been presented (e.g. Pacquit *et al.*, 2006, 2007; VanVeen, 2004; Smolander *et al.*, 2003; Byrne *et al.*, 2002; Payne and Persaud, 1995; Wolfbeis and List, 1995; Honeybourne, 1993) and existing technologies like biosensors and electronic nose are likely to serve as the technological basis for the development of new, even more advanced, freshness indicator concepts in the future. The utilisation of biomolecules as the metabolite recognising elements can be expected to expand. The different types of biomolecule as well as examples of their potential utilisation for functional purposes, e.g. in diagnostics and packaging, were recently reviewed by Aikio *et al.* (2006).

7.2.1 Metabolites Related to Glucose Fermentation

Ethanol, in addition to lactic and acetic acids, is a major end product of fermentative metabolism of lactic acid bacteria and it has been proposed that an increase in ethanol concentration in meat and fish indicates an increase of total viable count of the product. Concentration of ethanol has been found to increase as a function of storage time, e.g. in studies by Rehbein (1993) who studied the formation of ethanol in iced fish and smoked vacuum-packed salmon, and by Randell *et al.* (1995) who studied modified-atmosphere packaged, marinated salmon trout slices and chicken pieces. In our unpublished studies analogous to Randell *et al.* (1995) we have also seen an effect of storage temperature on the ethanol concentration.

Accumulation of ethanol from fresh produce due to low oxygen concentration and elevated carbon dioxide concentration is generally considered to be a measure of anaerobic metabolism and a remarkable cause for quality deterioration (Gonzalez-Aguilar *et al.*, 2004). Some trials to utilise ethanol for quality indication of packaged products have been

Table 7.1 Summary of the freshness indicating metabolites and indicator concepts available for their detection

Quality indicating metabolite	Corresponding food types	Potential indicator and sensor principles	Commercial freshness indicating products
Ethanol	Seafood (Rehbein, 1993; Randell <i>et al.</i> , 1995) Fresh produce (Gonzalez-Aguilar <i>et al.</i> , 2004)	Enzymatic determination for package head-space (Smyth <i>et al.</i> , 1999 ; Cameron and Talasila, 1995)	
Organic acids	Fresh fish (Kakouri <i>et al.</i> , 1997; Drosinos and Nychas, 1997) Meat (Nychas <i>et al.</i> , 1998) Poultry (Smolander, unpublished) Meat (Dainty, 1996)	Published methods applicable as package integrated concepts not available	
Glucose		DTN by knife-type probe (inside the product) (Kress-Rogers <i>et al.</i> , 1993)	
Volatile nitrogen compounds (e.g. ammonia, dimethylamine, trimethylamine)	Seafood (depending on species and season) (e.g. Dainty, 1996)	DTN of volatile sulfur compounds from the package head-space, reaction based on pH sensitive dyes as a visual colour change (e.g. Williams <i>et al.</i> , 2005, 2006; Miller <i>et al.</i> , 1999) or with optical sensor (e.g. Oberg <i>et al.</i> , 2006; Pacquit <i>et al.</i> , 2006; Byrne <i>et al.</i> , 2002)	FreshTag (Cox Recorders, USA) (previously available) freshQ (Food Quality Sensor International, Inc., USA)
Biogenic amines (e.g. tyramine, cadaverine, putrescine, histamine)	Poultry (Rokka <i>et al.</i> , 2004; Schmitt and Schmidt-Lorenz, 1992) Beef (Smith <i>et al.</i> , 1993; Edwards <i>et al.</i> , 1987; Yano <i>et al.</i> , 1995b) Pork (Ordonez <i>et al.</i> , 1991)	Electrochemical biosensors or spectrophotometric assay based on enzymatic determination, direct contact with food required (e.g. Yano <i>et al.</i> , 1995b; Okuma <i>et al.</i> , 2000; Niculescu <i>et al.</i> , 2000; Frebort <i>et al.</i> , 2000; Punakivi <i>et al.</i> , 2006)	

(Continued)

Table 7.1 (Continued)

Quality indicating metabolite	Corresponding food types	Potential indicator and sensor principles	Commercial freshness indicating products
Carbon dioxide	Indication of microbial growth in several food types (Fu <i>et al.</i> , 1992; Mattila <i>et al.</i> , 1990) Indication of product ripeness (Korean kimchi) (Hong & Park, 2000)	DTN of CO ₂ from package head-space, reaction based on pH sensitive dyes (e.g. Morris, 2006; Horan, 2000; Hong & Park, 2000)	For appropriate level of CO ₂ in MA-packages (Sealed Air, USA) Previously available)
ATP degradation products	Meat, especially seafood (Hattula <i>et al.</i> , 1997)	Test strips and electrochemical biosensors based on enzymatic determination, direct contact with food required (e.g. Yano <i>et al.</i> , 1995a; Mulchandani <i>et al.</i> , 1990)	Transia GmbH (Germany) test strips
Sulfuric compounds	Poultry meat (e.g. Lea <i>et al.</i> , 1969; Rajamäki <i>et al.</i> , 2006) Seafood (Olafsdottir and Florence, 1997)	DTN of volatile sulfur compounds from the package head-space, reaction based on colour change of myoglobin (Smolander <i>et al.</i> , 2002), colour change of nano-scale silver layer (Smolander <i>et al.</i> , 2004b) or conductivity change of package intergrated, RF readable silver layer based tag (Smolander <i>et al.</i> , 2003)	Freshness Guard Indicator (UPM Raflatac, Finland)
Undefined volatiles	Meat (deli, cooked, raw)	DTN of volatile compounds from the head-space of a storage bag or container, reaction based on visual colour change of a dye	It's Fresh™ (It's Fresh! Inc.) (concept for consumers own use)
Microbial enzymes	Not specifically defined, several	DTN of substrate conversion due to the enzymatic activity, reaction requiring a direct contact with the food (Van Veen, 2004)	
Pathogenic bacteria	Not specifically defined, several	Immunochemical DTN requiring a direct contact with the food product (Bodenhamer, 2000; Goldsmith, 1994; Woodaman, 2002)	Toxin Guard™ (Toxin Alert Inc., Canada) Food Sentinel System™ (Sira Technologies, USA)

published. Cameron and Talasila (1995) explored the potential of detecting the unacceptability of packaged, respiring products by measuring ethanol in the package headspace with the aid of alcohol oxidase, peroxidase and a chromogenic substrate. Smyth *et al.* (1999) reported that enzyme-based test strips for ethanol could be used to measure ethanol in the gas phase and were suitable for detecting low-oxygen injury in modified atmosphere (MA) packages containing lightly processed vegetables.

In addition to ethanol, organic acids like lactic acid and acetic acid are the major compounds with a role in glucose fermentation by lactic acid bacteria. Acetate concentrations have been reported to increase during storage of fresh fish (Kakouri *et al.*, 1997). In our unpublished studies with modified-atmosphere packaged poultry meat we have also found that the concentration of acetic acid in the tissue fluid and homogenised meat increased as a function of storage time and temperature. The amount of L-lactic acid has generally been reported to decrease during storage of fish and meat (Kakouri *et al.*, 1997; Drosinos and Nychas, 1997; Nychas *et al.* 1998) whereas the concentration of D-lactate has been reported to increase during storage of meat. Hence D-lactate seems to be a more promising freshness indicator (Shu *et al.*, 1993).

Glucose as an initial substrate for many spoilage bacteria in air, vacuum packages and modified atmosphere packages is consumed from the meat surface as the microbial growth takes place (Dainty, 1996). It has been proposed by Kress-Rogers *et al.* (1993) that the measurement of the glucose gradient measured with a knife-type freshness probe could be utilised to predict the remaining shelf-life of meat.

7.3 Volatile Nitrogen Compounds

Volatile amines such as trimethylamine (TMA), ammonia (NH₃) and dimethylamine (DMA) comprise total volatile basic nitrogen compounds (TVB-N), the levels of which have been recognised as useful indicators of seafood spoilage under EU Directive 95/149/EEC. The European Commission has specified that TVB-N levels be used if sensory methods raise doubts about the freshness of seafood species. Many studies have concentrated on fish freshness determination by means of detecting trimethylamine, dimethylamine and/or ammonia using either headspace-gas chromatography (Elias and Krzymien, 1990), semi-conductor gas sensors (Ohashi *et al.*, 1991) or ammonia ion-selective electrodes (Pivarnik *et al.*, 2001). Trimethylamine, formed by microbial action in the fish muscle, is generally considered as a major metabolite responsible for the spoilage odours of seafood. A drawback of using trimethylamine as a quality indicator for seafood is the variation in the concentration of its precursor trimethylamine *N*-oxide according to the species and season (Dainty, 1996; Rodríguez *et al.*, 1999).

Numerous freshness indicator concepts targeted to volatile amines have been presented. A concept of an indicator compound provided on a substrate and reacting to volatile amines with a colour change hence indicating freshness of packaged food has been patented by Miller *et al.* (1999). This concept has been marketed by COX Recorders (USA) with trade name FreshTag[®]. Naturally occurring betalain or flavonoid based molecules have been used as pH-sensitive dyes for detecting amines from packaged foodstuff (Williams and Myers, 2005; Williams *et al.*, 2006). They describe a colour changing indicator, the sensitivity of which can be adjusted by tuning the original pH of the indicator. By pH tuning, the indicator

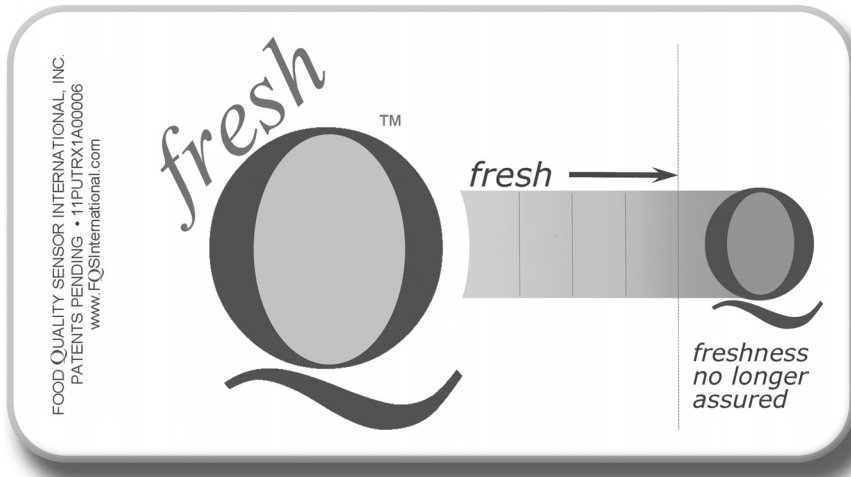


Figure 7.1 *freshQTM indicator. (Reproduced with permission from Food Quality Sensor International, Inc.).*

can also be used to observe production of acidic compounds during microbial spoilage. The concept by Williams *et al.* is currently being marketed as *freshQTM* (Figure 7.1).

Khalil *et al.* (2003) have presented a device for ammonia or volatile amines detection that is based on the colour change of pH-dyes on PTFE-carrier solid phase indicator film. Morris *et al.* (2004) have described a device detecting the presence of bacteria in a perishable food product based on a pH indicator, the colour change of which is caused by the presence of the spoilage metabolite (e.g. ammonia, CO₂). The invention of Wallach (2002, 2003) is also based on pH-sensitive dyes being used for detecting volatile amines, but also carbon dioxide or volatile carboxylic acids from food packages.

Loughran and Diamond (2000) propose a simple method for the determination of volatile nitrogen compounds (NH₃, DMA, TMA) with the aid of chromogenic dye calix[4]arene impregnated on a paper disk. Byrne *et al.* (2002) determined headspace-TVB-N from fish samples using pH indicator dye (cresol red) films as sensors. It was suggested that in the future, this approach could be used for making an on-package sensor in individual packages, using inexpensive colour measurement equipment, e.g. an LED and photodiode array detector, or using a reference set of colours to reflect the critical TVB-N concentration and spoilage state of the specific fish species.

Oberg *et al.* (2006) describe a simple optical sensor for amine vapours. The sensor is based on silica microspheres dyed with the pH indicator bromocresol green. Bromocresol green is also used by Pacquit *et al.* (2006, 2007), who describe an on-package sensor responding through visible colour change and interrogated with LED-based reflectance colorimeter.

7.4 Biogenic Amines

Biogenic amines, tyramine, histamine, tryptamine, phenylethylamine, serotonin, putrescine, cadaverine, spermine and spermidine, are found in fresh food only in small

concentrations. They could hence serve as useful indicators of quality deterioration, even if they do not themselves contribute to the sensory quality of the product. In addition to the quality indicative nature, biogenic amines can have pharmacological, physiological and toxic effects. Due to the health risks, a tolerance level of 100 mg/kg of fish has been established for histamine by FDA (Kaniou, 2001).

Biogenic amines are produced in the growth of decarboxylase-positive microorganisms under conditions favourable to enzyme activity (Roig, 2002). Many Enterobacteriaceae, *Pseudomonas* spp. and certain lactobacilli, enterococci and staphylococci are active in the formation of biogenic amines. These amine-positive microorganisms may constitute part of the normally associated population of the food product or may appear in the product by contamination before, during or after processing.

For instance the accumulation of tyramine at bacterial numbers above $10^6/g$ has been reported in many studies of different types of stored meat, and tyramine has been proposed as a quality indicator for beef, pork and poultry (Edwards *et al.*, 1987; Schmitt and Schmidt-Lorenz, 1992; Ordonez *et al.*, 1991; Smith *et al.*, 1993; Yano *et al.*, 1995b).

The effect of storage temperature in various constant and variable temperature schemes on the formation of biogenic amines of modified atmosphere (MA)-packed broiler chicken cuts, as well as the applicability of biogenic amines as quality indicating metabolites of MA-packaged broiler chicken cuts, has been studied in collaboration between the former National Veterinary and Food Research Institute of Finland EELA (presently Finnish Food Safety Authority, Evira) and VTT (Rokka *et al.*, 2004). In this study broiler chicken cuts, which were stored in modified atmosphere packages in constant and variable temperatures, were analysed for their content of biogenic amines. It was found out that the storage temperature significantly affected the formation rate of tyramine (Figure 7.2). The levels

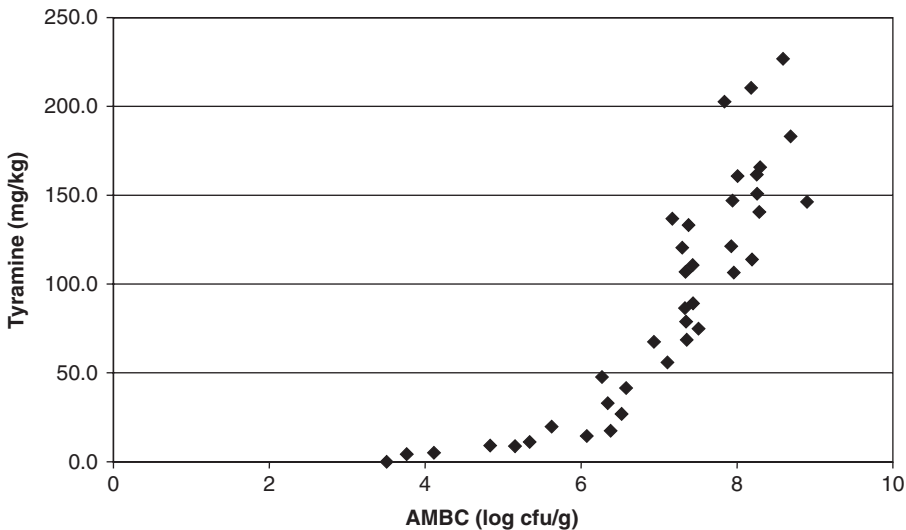


Figure 7.2 Correlation between tyramine and aerobic mesophilic bacterial counts during the storage of broiler chicken cuts. (Reproduced from Rokka *et al.*, Food Control 15, 8, pp. 601–607. Copyright (2004) with permission from Elsevier).

of tyramine had increased after 5 days of storage if the storage temperature was above 6 °C, which is the highest statutory storage temperature in Finland. The levels of putrescine increased after 7 days and the levels of cadaverine increased after 9 days, respectively. The formation of tyramine seemed to be highly consistent with the increase in the aerobic mesophilic viable count. Putrescine and cadaverine were not formed below 6 °C. In these conditions without putrescine and cadaverine formation the growth of Enterobacteriaceae, proteolytic bacteria, hydrogen sulphide producing bacteria and clostridia was also clearly retarded. Thus the three amines tyramine, cadaverine and putrescine seemed to be promising indicators for both storage time and temperature as well as for the microbiological quality of MA packed broiler chicken cuts. In the future the results could be exploited in the development of new methods for the quality control of packaged poultry products.

According to our knowledge, there are no specific freshness indicator concepts for biogenic amines, but several types of enzymatic biosensors have been developed for the detection of biogenic amines from, for instance, poultry (Okuma *et al.*, 2000), fish (Niculescu *et al.*, 2000; Frébort *et al.*, 2000) and beef (Yano *et al.*, 1995b). An enzymatic determination of the total amount of biogenic amines with transglutaminase was suggested by Punakivi *et al.* (2006).

7.5 Carbon Dioxide

Carbon dioxide (CO₂) is produced during microbial growth. Due to its bacteriostatic effects it is also typically added as protecting gas to modified atmosphere packages, together with inert nitrogen (typically 20–80 %). Due to microbial growth the CO₂ concentration can further increase during storage (Fu *et al.*, 1992). However, it is difficult to indicate the microbial growth by CO₂ in these modified atmosphere packages that already contain a high concentration of CO₂, but it is possible to use the increase in CO₂ concentration as a means of determining microbial contamination in other types of products. For instance Mattila *et al.* (1990) found a correlation between CO₂ concentration and the growth of microbes in aseptically packed soup, either in air or in a mixture of oxygen and nitrogen.

Several freshness indicator concepts based on pH dyes, using CO₂ as the main target metabolite have been proposed. The use of the pH dye bromothymol blue as an indicator for the formation of CO₂ by microbial growth has been suggested (e.g. Holte, 1993; Mattila *et al.*, 1990). A combination of bromothymol blue and methyl red solution packaged in gas permeable film was recently suggested by Morris (2006). In addition to the detection of spoilage, pH-dyes reacting to the presence of CO₂ have also been used to construct intelligent packaging concepts indicating the ripeness of traditional fermented vegetable foods in Korea (*kimchi*) (Hong and Park, 2000). In addition to the most frequently used pH dye, bromothymol blue, many other reagents, e.g. xylenol blue, bromocresol purple, bromocresol green, cresol red, phenol red, methyl red and alizarin, among others, have been proposed for the same purpose (Horan, 2000). Besides CO₂, also other metabolites like SO₂, NH₄, volatile amines and organic acids have been proposed as suitable target molecules for these pH-sensitive indicators (Mattila and Auvinen, 1990a, b; Horan, 2000).

7.5.1 ATP Degradation Products

K-Value is defined as the ratio of the sum of hypoxanthine and inosine and the total concentration of ATP-related compounds (Henehan *et al.*, 1997). This value indicating the extent of ATP-degradation correlates with the sensory quality of fish and also other types of meat and has been used as a freshness indicating parameter (Watanabe *et al.*, 1989; Yano *et al.*, 1995a). For fresh meat the value is low since the concentration of ATP-degradation products is low as compared with the concentration of all ATP-related compounds. The correlation between ATP-degradation products and fish quality has been extensively studied, e.g. by Hattula (1997). *K*-value can also be replaced by K_1 -value, which excludes ATP, ADP and AMP determination (Özogul and Özogul, 2000).

Package integrated freshness-indicating concepts reacting to ATP degradation products have not been presented to our knowledge. However ATP degradation products indicating the quality deterioration of fish can be analysed by enzymatic test strips manufactured by Transia. ATP degradation products have also been frequently measured with biosensors. For instance, Yano *et al.* (1995a) and Mulchandani *et al.* (1990) developed an enzyme based electrochemical sensor for the quality control of beef. Recently, a non-destructive colorimetric test for the evaluation of remaining shelf-life of Japanese raw fish dish, *sashimi* was presented by Watanabe *et al.* (2005). The idea is that a test solution containing hypoxanthine, thiazole blue redox dye and xanthine oxidase is kept with a fish product and reacts analogously with it to the storage time and conditions.

7.5.2 Sulfuric Compounds

Sulfuric compounds have a remarkable effect on the sensory quality of meat products due to their typical odour and low odour threshold. Hydrogen sulfide (H_2S) is produced from cysteine and triggered by glucose limitation (Borch *et al.*, 1996). H_2S forms a green pigment, sulfmyoglobin, when it is bound to myoglobin (Paine and Paine, 1992; Egan *et al.*, 1989).

H_2S and other sulfur compounds have been found to be produced during the spoilage of poultry by *Pseudomonas*, *Alteromonas* sp. and psychrotrophic anaerobic clostridia (Freeman *et al.*, 1976; Lea *et al.*, 1969; Russell *et al.*, 1997; Viessweg *et al.*, 1989; Arnaut-Rollier *et al.*, 1999; Kalinowski and Tompkin, 1999). According to Dainty (1996), production of H_2S can be used as an indication of Enterobacteriaceae and hence also of hygienic problems in aerobically stored meat. H_2S production by *Alteromonas putrefaciens*, *Enterobacter liquefaciens* and *pseudomonas* was discovered in high ultimate pH beef from stressed animals (Gill and Newton, 1979; Nicol *et al.*, 1970). It has also been found out that in vacuum packed meat H_2S indicates the growth of particular strains of lactic acid bacteria (Egan *et al.*, 1989). Additionally, volatile sulfur compounds have been suggested as the main cause of putrid spoilage aromas in fish (Olafsdottir and Fleurence, 1997). In our studies we report that modified-atmosphere packaged broiler chicken cuts shows a clear effect of the storage time and temperature on the accumulation of hydrogen sulfide and dimethyl sulfide (Rajamäki *et al.*, 2006) and on the sulfurous odour of the product (Smolander *et al.*, 2004a) (Figure 7.3).

In our work aiming at the development of freshness indicators for poultry products, we have utilized a reaction between hydrogen sulfide and myoglobin in a freshness indicator for the quality control of modified-atmosphere-packed poultry meat (Ahvenainen *et al.*,

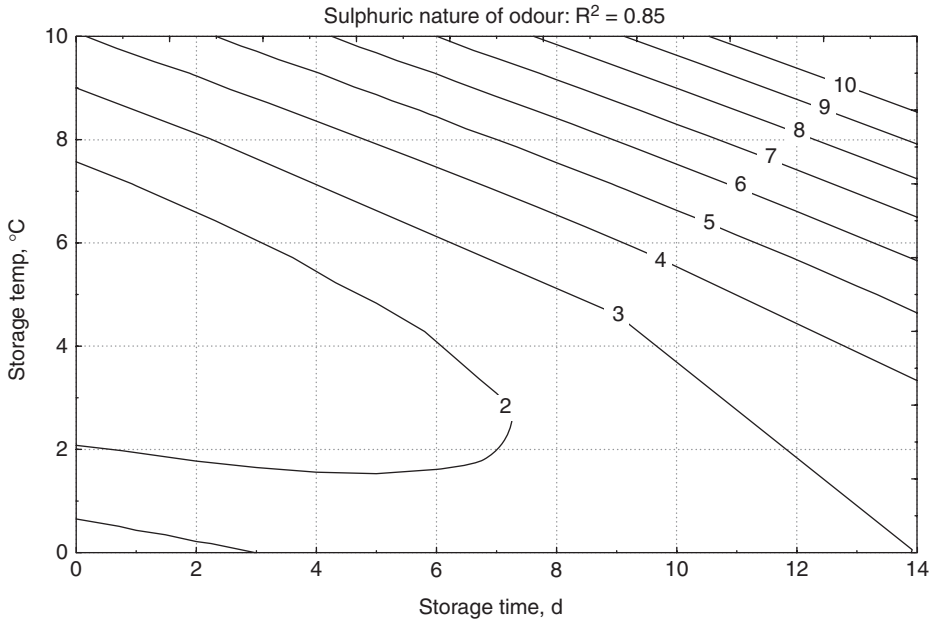


Figure 7.3 The effect of storage time and temperature on the sulfurous nature of the odour in the package head-space of modified-atmosphere packaged broiler chicken cuts. (Reproduced from Smolander *et al.*, *Food Control*, **15**, 3, pp. 217–229. Copyright (2004) with permission from Elsevier).

1997; Smolander *et al.*, 2002). Freshness indication is based on the colour change of myoglobin by hydrogen sulfide (H_2S) and the indicators were tested in the quality control of MA-packaged fresh, unmarinated broiler cuts. It was found that the colour change of the myoglobin-based indicators corresponded with the deterioration of the product quality, hence it could be concluded that the myoglobin-based indicators seem to be promising for the quality control of packaged poultry products.

The capability of sulfur compounds to indicate the quality of packaged poultry meat has been exploited in the recently launched ‘Freshness Guard’ by UPM Raflatac, one of the world’s leading suppliers of paper-based and filmic pressure sensitive labelstock. The indicator specifically designed for use with fresh poultry is based on a reaction between hydrogen sulfide and nano-scale layer of silver (Smolander *et al.*, 2004b). Originally the colour of the thin silver layer is opaque light brown, but as silver sulfide is formed the colour of the layer is converted to transparent (Figure 7.4). The label can be used to evaluate product quality throughout the distribution chain and can be considered particularly beneficial at seasons like Christmas and Easter that require the maintenance of large stocks of poultry.

Another concept relying on the utilisation of silver layer in RF readable, package integrated sensors has also been presented by Smolander *et al.* (2003). The idea of this concept is to measure the change in conductivity of a silver layer taking place due to the reaction between silver and hydrogen sulfide.



Figure 7.4 Freshness Guard. (Reproduced with permission from UPM-Kymmene).

7.6 Other Quality Indicators for Microbial Spoilage and Contamination

In addition to the indicators reacting to the volatiles produced by normal spoilage of food products as described above, other systems for the detection of microbial contamination in the food product have also been presented.

A food freshness indicator for consumers' own use is offered by It'sFresh! Inc. The indicator is suitable for many types of meat-containing food products like salads as well as cooked and deli meats (seafood, poultry, beef and pork). The idea of the concept is that the consumer places the indicator inside a storage bag or container, which is then placed in the refrigerator for 8 hours. If the colour of the indicator is changed from pink to yellow the quality of the product is likely to be deteriorated (Figure 7.5).

Van Veen (2004) described a method for non-invasive detection of contamination by a microorganism in a closed, sterile container, which is based on detecting an extracellular



Figure 7.5 It's Fresh containers with indicators. (Used with permission from Packaging Materials and Technologies Ltd).

enzyme or its activity in the microorganism. A substrate is provided in either the contents of the container or alternatively in a coating of the inner side of a package, and the conversion of this substrate by the enzyme is detected either visually or by means of an optical measuring device.

Under development for both commercial and military applications, is Toxin Guard™ by Toxin Alert, Inc. (Ontario, Canada), which is a polyethylene-based packaging film that can detect the presence of specific pathogenic bacteria (*Salmonella*, *Campylobacter*, *Escherichia coli* O157 and *Listeria*) with the aid of immobilized antibodies. As the analyte (toxin, microorganism) is in contact with the material it will be bound first to a specific, labelled antibody and then to a capturing antibody printed as a certain pattern (Bodenhamer, 2000). The method could also be applied to the detection of pesticide residues or proteins resulting from genetic modifications.

Specific indicator material for the detection of *Escherichia coli* O157 enterotoxin has been developed at Lawrence Berkeley National Laboratory (Kahn, 1996; Quan and Stevens, 1998). This sensor material, which can be incorporated in the packaging material, is composed of cross-polymerised polydiacetylene molecules and has a deep blue colour. The molecules specifically binding the toxin are trapped in this polydiacetylene matrix and as the toxin is bound to the film, the colour of the film changes from blue to red.

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8

An Active Moisture-Management Packaging System for Food and Other Products: A Case Study

Robert Esse and Albert Saari

8.1 Introduction

Many manufactured food products are adversely affected by moisture changes that directly impact their shelf life and quality when they are consumed. These foods will lose desirable texture characteristics if allowed to lose or gain too much moisture. Brown sugar becomes hard and lumpy; raisins become hard. Ready-to-eat cereals lose their favored crisp textures if they gain moisture. Jerky becomes tough and dry. Fruit filled cookies become either hard and crumbly or soft and sticky.

In addition, numerous other changes are affected by changes in moisture level. Some dry grain based products can become rancid more rapidly through free radical oxidation at low humidities and thus become unacceptable. Labile nutrients such as vitamins and natural colors such as chlorophyll are oxidized more rapidly if stored at low moisture levels. On the other hand, if the moisture level is elevated, enzyme mediated hydrolysis rates are increased significantly and the rate of Maillard type non-enzymatic browning is enhanced.

Even small variations in storage temperatures will lead to localized high moisture conditions in an intermediate moisture food. These areas can be prime locations for microbial spoilage such as loci for molds or bacteria causing food infections or toxins of various types. Active moisture management systems should include humidity regulation.

Packaging materials are used to control the ingress or egress of moisture vapor. Even if the packaging film has excellent moisture barrier properties, it can not preserve

the product in its optimal condition. The product, as produced, may be slightly different from the optimum moisture to achieve the longest shelf-life because of variability in the ingredients or the processing/manufacturing system. A package may have minute leaks because of flex cracking of the material or flaws in the heat seal. The body of the package itself will have some measurable permeability to moisture vapor. These factors affect the changing moisture level of a food significantly, impacting the shelf-life and quality of a food product.

The optimal approach is to have an active moisture regulation system that can react to and manage the changing conditions that take place over the life of a product.

This chapter will help the reader to understand such principles as water activity, moisture isotherm and moisture management/regulation systems using two-way humidity control. Understanding these principles is vital for development and distribution of products intended to be distributed nationally requiring shelf-life of 6 months or more. They may be helpful also in preparation of 'fresh' products that are distributed and consumed within a week or two.

8.2 Principles of Moisture Management and Water Activity

The historical and popular measure of water in food and other natural products is expressed as a percentage or portion of water in the product. This 'absolute humidity' is a poor predictor of reactions during storage of such products. The quantity of moisture to participate in degradation processes is highly dependent on the affinity for water by components of the product. Hence another measure must be employed.

To understand and apply a moisture management system, we must first have a basic understanding of water activity. This term, abbreviated to a_w , is a measurable value for all food products. It is a ratio and is expressed as a decimal fraction of 1.00 to two or three significant figures. Water activity (a_w), is a very useful parameter. It is defined as: $a_w = p_s/P_w^\dagger$ where p_s is the vapor pressure of a product or solution and P_w is the vapor pressure of pure water. While this value is not precisely according to Raoult's Law, it is an adequate estimate for almost all situations. Further, since it is empirically measured, it reliably serves the purpose and is satisfactory for food product applications.

a_w values will range from 0.00 (absolutely dry) to 1.00 (pure water). Thus one obtains values such as 0.33 or 0.62 for water activities of specific products, a ready-to-eat cereal or dried fruit, respectively. This is a well understood measurement by practitioners of food research. Instruments to measure directly a_w are readily available. Among the most reliable, moderately priced, instruments are the dew-point measuring meters, which yield a numerical readout of the a_w within a few minutes for a sample. A careful experimenter can attain a repeatability of 0.002.

[†] This is a simplified derivative of Raoult's Law, which describes the effect of changes in number of ions (molal) in true solution on the vapor pressure, boiling point and freezing point of the solvent. Raoult's Law ($P_A = X_A P_S$, where P_A is partial pressure of solvent, P_S is the vapor pressure of pure solvent at the same environmental temperature and pressure and X_A is the mole fraction of the solute) applies to ideal solutions.

When reporting results to a non-scientist, it may be conceptually preferable to convert the a_w number to relative humidity. We know the term relative humidity from weather reports and from being exposed to environments that can be expected to be comfortable, or uncomfortable:

$$\text{By definition : relative humidity (RH) = } a_w \times 100$$

Thus in the examples above, the food products can be said to have a 33 % or 62 % relative humidity, respectively, in the headspace of closed containers of the products.

When the water vapor pressure of the food and the air surrounding it are equal, they are in equilibrium. This is not a static system, but a dynamic system where the loss of water molecules from the product equals the gain of water molecules from the environment. Many cereal products such as crackers and ready-to-eat cereals store well with little change in quality at a relative humidity of 33 %.

When this cereal food product is exposed to an environment above or below this ideal relative humidity, the protective package and its moisture barrier properties will determine how much the food will be impacted. The second factor is the quality of the package reclosure. In drier climates the product may lose moisture and in more humid areas, it will gain. If by chance it is exposed to a 33 % relative humidity, no net moisture change will take place because the interior of the package is in equilibrium with its environment. It is obvious that the quality of the product can be maintained with proper moisture management systems.

Formulated or natural food products each have a unique a_w at which their texture is optimal. Changing the formulation can also change the a_w value, particularly if there is a change in a solute. For example, adding sucrose as a sweetener will reduce the a_w of a product. If a monosaccharide such as glucose or fructose is added in place of some of the sucrose, the a_w reduction will be almost double since a unit weight of glucose will add approximately 1.9 times as many molecules in solution as the same unit weight of sucrose[†]. Unfortunately, reducing sugars such as glucose and fructose take part in detrimental chemical reactions.

If two or more products with different a_w s are placed in a package, they will converge to an intermediate a_w value. Consequently, none of the components will be at their optimal moisture content. If it is necessary to combine such components in a single package such as a cookie with a fruit preserve filling, all of the components need to be reformulated to a common a_w . Otherwise the cookie portion will seem 'soggy', lacking crispness and/or the filling will be firm and hard to chew.

It is a great challenge to produce a succulent fruit filling and a crisp cookie at an intermediate a_w . By selecting a mixture of sugars, flours, fats, emulsifiers, etc., a reasonably acceptable product with a long shelf stability (6 – 12 months) can be produced. However, such a product has a relatively narrow tolerance to changes in moisture or a_w .

Natural products such as fruits, vegetables and cereal grains move through an a_w range as they grow from small green specimens to a fully ripened edible product. Ripening often involves conversion of biopolymers such as starch to glucose or fructose as part

[†] It is obvious that a food product high in mono- or disaccharides will have a much lower a_w at a particular value for total moisture content than a product low in soluble compounds of low molecular weight. Disaccharides have about half as much effect on a_w .

of the process, thus reducing the a_w . Most fruits and berries develop reduced a_w during ripening at a given total moisture content because polysaccharides are converted to mono- and disaccharides. During storage, most fruits, including apples, will consume some of the glucose to provide energy to sustain life. In time, the apples will become wrinkled and much less crisp as they lose moisture. Lettuce and other leafy vegetables wilt, losing turgidity and thereby their desirable crisp bite. This moisture loss can be slowed markedly by placing the food item in a higher humidity environment where it will achieve its longest shelf-life. It will retain acceptable flavor and texture. In some products this can be days, in others it may be months.

However there is a downside to high humidity environments. Relatively small fluctuations in temperature may lead to condensation of water on the package or the product. This localized a_w of essentially 1.0 will encourage all microorganisms to grow. Cycling of temperature may tend to draw moisture out of a product. The rate of moisture loss is usually more rapid than take up, so a product subjected to frequent temperature cycles will have a net loss of moisture. And since such environments are usually at a much lower humidity, the products tend to have a net loss with each temperature cycle.

It should also be noted that, contrary to perception, refrigerated spaces have a relatively low relative humidity, generally in the 30 to 40 % range. The dew point of the air in a refrigerator is a function of the temperature of the cooling refrigeration coils in the chamber, be it a home refrigerator or a cold storage facility. Newer refrigeration systems operate with higher cooling coil temperatures, thus may be at a somewhat higher relative humidity.

All food products have an optimal a_w . In some cases, a slight change in the moisture content can make the product unacceptable. Examples might be freeze-dried mushrooms or powdered tomato base, which each become unacceptable with only a slight increase in moisture. Beef jerky can have a noticeable change in texture between an a_w of 0.74 and 0.76, a tolerance of less than ± 0.01 . When this tolerance is very tight, it may mean that the product will need to be protected from the exposed environment with a more expensive, high moisture barrier package.

Other products have a high tolerance to fluctuation in their moisture/ a_w values. In fruit/berry preserves, a range of $a_w \pm 0.1$ is hardly noticeable. Pasta products can be exposed to widely fluctuating moisture levels and not be significantly harmed other than an immaterial change in the rate of water uptake during cooking. We thus see pastas available in super markets in non-barrier bags or even in unlined paperboard cartons.

8.3 Moisture Sorption Isotherm

A moisture sorption isotherm is a useful piece of information for a formulator who is seeking an ideal a_w value for his product. It gives the formulator an idea of the a_w value that is least sensitive to absolute moisture changes. A moisture sorption isotherm is the result of a plot of the a_w vs moisture content of the product equilibrated against a broad range of a_w conditions. Typically, seven to nine values of a_w are employed from about 0.05 up to 0.85 in tightly sealed containers conditioned with saturated aqueous salt solutions chosen to produce a_w values in this range. When a sample reaches a constant weight (equilibrium), its moisture is determined by a rigorous method such as vacuum oven or Karl Fischer titration. If the absolute humidity (moisture content) of the sample is known accurately, the changes

can be monitored by weighing and equilibration to a constant weight for each a_w . A new instrument is being developed to determine the moisture sorption isotherm in 24 to 36 hours.

Typically, the equilibrium moisture is plotted on the x -axis against the relative humidity or a_w on the y -axis over the full range from 0% to close to 100%. In practice, the product that is exposed to these various humidity levels is also examined for changes that have been triggered by the increase or decrease in initial moisture level. This will then suggest how much moisture the product can gain or lose before it can impact its quality (see Figure 8.1).

The interpretation of the moisture sorption isotherm curve is the source of basic information for the product and packaging development people to determine how much moisture barrier is required in a package for a particular product. Comparison of the isotherms for cellulose (paper) and a ready-to-eat wheat cereal shows that products are unique and very different. The moisture content of the cellulose changes little between an $a_w = 0.2$ and 0.6. The difference in properties will probably be relatively minor at any a_w between those points. However, above $a_w 0.7$, a small change in a_w results in a large change in moisture content leading to progressively weaker paper as the a_w increases. This tells us that the strength of paper is compromised as its a_w increases above 0.7. So, if paper were, employed for packages for use in a tropical, humid climate, the packaging material for an overwrap of the package should have significant moisture barrier properties.

The cereal has a minimal change in a_w until the proportion of water reaches about 7%. Above 10% water, the a_w of the cereal changes rapidly with small increases in moisture. This indicates that there are considerable changes in its structure after the a_w reaches about 0.3. Observations on the cereal show that it exhibits much less crispness, becoming rather tough and gummy at an a_w above 0.5. Because the ready-to-eat wheat cereal has a narrow tolerance

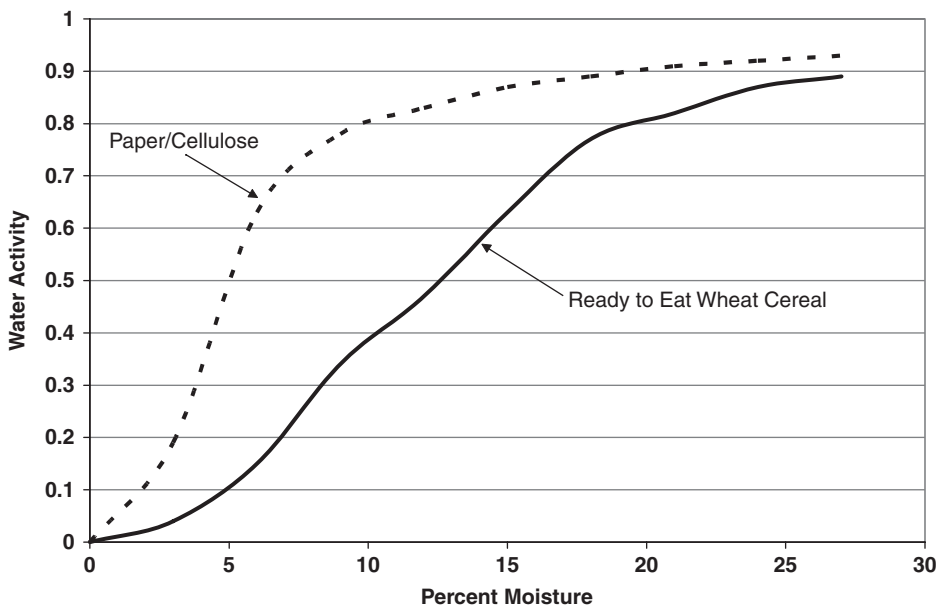


Figure 8.1 Moisture sorption isotherms for paper and wheat ready-to-eat cereal.

to moisture loss or gain, it must be protected in a package with a material that is a very good barrier to moisture vapor. After opening the package, unless the customer is diligent about reclosing the package, the contents will take up moisture from the home environment and become tough and/or soggy. Modern homes in much of North America have relative humidities over 50 % most of the time. There may be an opportunity to preserve the texture of RTE cereals, crackers, cookies, and other susceptible products sold in such climates.

However, the choice of formula or package is not always simple. During storage, changes in the product such as crystallization of sugars, will release water and cause an increase in a_w of the product while its moisture content remains constant. For example, the baked product, chocolate brownies, prepared with sucrose can have an a_w of 0.65 when fresh, but after a few months in a high barrier package, the product can have a humidity of up to 80 % and be moldy as well as very crumbly. A significant portion of the sucrose has crystallized so a formulator must add a 'doctor', a substance that inhibits crystallization of sucrose. Monosaccharides such as glucose or in its crude form, corn syrup, will serve this purpose well.

8.3.1 Moisture Effects on Storage Stability of Food

There are at least three important categories of the food sold in grocery stores:

- Manufactured products developed for convenient at-home preparation. These include bakery mixes (high-ratio cakes, angel food cakes, cookies, brownies, icings, muffins, biscuits), skillet dinners, beverages, sliced and shredded cheeses, sausages, among others.
- Manufactured products sold in grocery stores include ready to eat products such as cookies, yogurt, butter/margarine, cereals, snack foods, fruit leather, nuts, etc.
- Food products include fresh fruits and vegetables and ingredients for home prepared meals.

A large number of food products, called intermediate moisture foods (IMF) are best at or near those water activities at which microorganisms grow. Because of the threat of food borne illness, the relationship between moisture content and microbiological spoilage of food is of utmost importance. Food infections by *Shigella* sp., *Klebsiella* sp., *Escherichia* sp., *Vibrio* sp., *Salmonella* sp., among others, bring about much human misery through gastrointestinal distress. Food intoxications brought about by secretions of organisms such as *Clostridium botulinum*, *Staphylococcus* sp., and *Bacillus cereus* are serious matters, even fatal to the victims. Many molds produce very toxic substances with insidious effects such as carcinogenicity, mutagenicity, neurotoxicity, estrogenic and allergic consequences.

As noted in Table 8.1, the a_w of the environment of the organism is a crucial factor in reproduction of these organisms in food and food products. Some of the toxin-producing organisms are affected by the a_w of the product. The product development team must be aware of these detrimental effects and take appropriate action in moisture management, processing and packaging. From the table, it is obvious that microbiological problems do not occur during storage at an a_w below 0.6.

Under both home and commercial storage/distribution, products are subjected to changes in temperature. The air in a package can hold considerably more moisture at elevated temperatures (42 g/m³ at 100 °F/37.8 °C) than at refrigerated temperatures (6 g/m³ at 40 °F/4.4 °C). Thus, at the higher temperature, the a_w (% relative humidity) of the air is

Table 8.1 Examples of the effect of water activity (a_w) on the growth of microorganisms

a_w (water activity)	Typical food items	Genus of microorganism
0.95–1.0	Fresh foods and meats, breads, Approx 40 % sucrose and 8 % NaCl	<i>Pseudomonas</i> , <i>Escherichia</i> , <i>Proteus</i> , <i>Bacillus</i> , <i>Clostridium</i> , <i>Shigella</i> , <i>Klebsiella</i>
0.91–0.95	Medium cheeses, cured meat (ham), retail fruit juice concentrate, 55 % sucrose and 7 % NaCl	<i>Salmonella</i> , <i>Vibrio</i> , <i>Serratia</i> , <i>Lactobacillus</i> , Yeast– <i>Rhodotorula</i>
0.87–0.91	Fermented hard sausage, dry cheese, margarine, 65 % sucrose and 15 % NaCl	Most yeasts – <i>Candida</i> , <i>Torulopsis</i> , <i>Hansenula</i> , <i>Micrococcus</i>
0.80–0.87	Commercial fruit juice concentrate, chocolate syrup, maple and fruit syrup, flour, fruit cake, fondants, high-ratio cake	<i>Saccharomyces</i> , <i>Staphylococcus aureus</i> , <i>Saccharomyces</i> , mycotoxigenic penicillia
0.75–0.80	Fruit and berry preserves, marmalade, marshmallows, meat jerky	Halophilic bacteria, mycotoxigenic <i>Aspergillus</i> sp.
0.65–0.75	Rolled oats, fudge, marshmallow, raisins, fruit preserves, molasses, nuts, soft prunes	Xerophilic molds (<i>Aspergillus candidus</i> , <i>A. chevalieri</i>)
0.60–0.65	Dried fruit (<20 % water), toffee, caramels, honey	Osmophilic yeasts, molds – <i>Aspergillus echinulatus</i> , <i>Monascus bisporus</i>
0.50–0.60	Pasta (12 % water), spices	No microbial growth
0.40–0.50	Whole egg powder at 5 % water	No microbial growth
0.30–0.40	Cookies, crackers, bread crusts (5 % water)	No microbial growth
0.20–0.30	Whole milk powder, dried vegetables, ready-to-eat cereals, hard cookies	No microbial growth

reduced substantially, while at the lower temperature, the a_w (% relative humidity) of the air is increased. As the temperature increases, the contents of a package will give off moisture in attempting to restore a_w equilibrium between the air and the contents in the package.

Conversely, on cooling, the air will transfer some moisture back into the product, but more likely, form some condensate on the inside wall of the container or package. The product is likely to establish a gradient of a_w from very high on the surface to the original a_w of the bulk product because in most cases the diffusion process is comparatively slow in intermediate moisture foods. This thin layer of high a_w is a fertile layer for microbial growth, be it bacteria, yeast or mold. A complete moisture management system will help to control this potential microbial problem.

Some products such as meat jerky are significantly above the minimum a_w for mold growth. Since molds are obligate aerobic organisms (require oxygen), the products are normally packaged in a substantially oxygen free environment prepared by flushing with nitrogen or other inert gas. Usually, an oxygen scavenging system is included in the package to react with and remove oxygen that diffuses from the air through the package, thus assuring that anaerobic conditions are maintained.

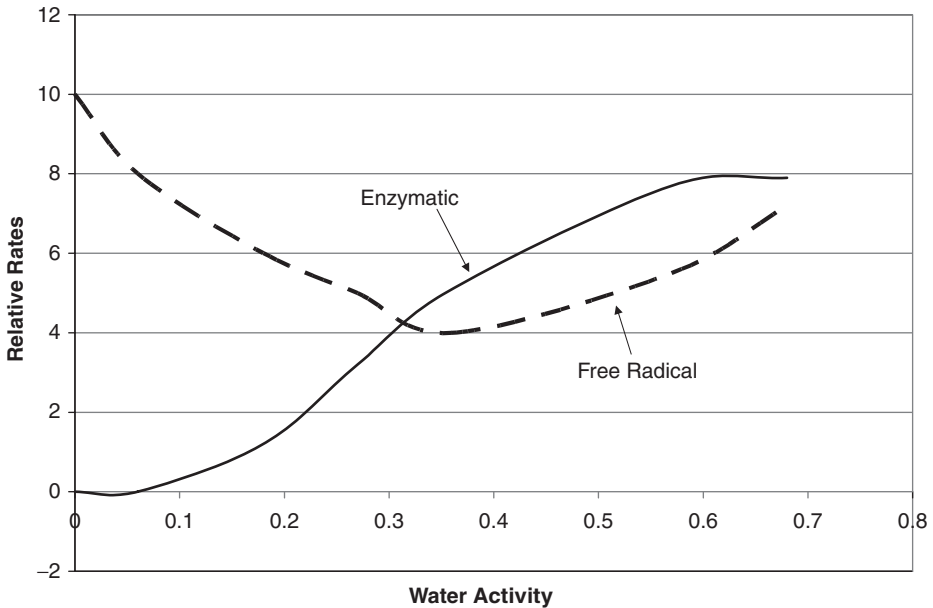


Figure 8.2 The effect of a_w on oxidation of unsaturated oil, enzymatic and free radical auto-oxidation.

Several other detrimental effects that are inhibited by an optimal a_w of a food are pointed out in Figures 8.2 and 8.3. These curves are generic, but illustrative of the reactions covered. Detailed discussion is beyond the scope of this paper.

Figure 8.2, demonstrates that lipoxidases begin to catalyze oxidation of unsaturated fats at a significant rate above an a_w of about 0.3. The rate of oxidation increases rapidly as the a_w increases. On the other hand, the rate of non-enzymatic, free radical oxidation of unsaturated lipids decreases from $a_w = 0.0$ to about $a_w = 0.35$ upon which the rate gradually increases with a_w . This is explained by the observation that in most dry cereal products, an a_w of 0.35 corresponds to a moisture level of 8 to 10 %, which is the amount of water necessary to form a protective monolayer over the surfaces of polysaccharides and proteins that are associated with unsaturated lipids. This monolayer acts as a barrier to free radical oxygen attack on the carbon-to-carbon double bond system.

Figure 8.3, shows the relationship between four other modes of deterioration of a food and the a_w of the product.

Hydrolytic rancidity is the enzymatic hydrolysis of fatty acids from glycerol. Normally this is of little consequence except when the fatty acids are of largely short or intermediate chain-length from butyric to lauric acid. Butyric and the 'goat acids', capric, caproic and caprylic, are volatile enough to be recognized as off flavors at very low concentrations except, of course, in cheeses, Myristic and lauric acids impart an undesirable 'soapy' taste to a product in which they develop.

The maillard browning reaction is undesirable because of the color change in a product and production of bitter components in a food product. This complex series of reactions,

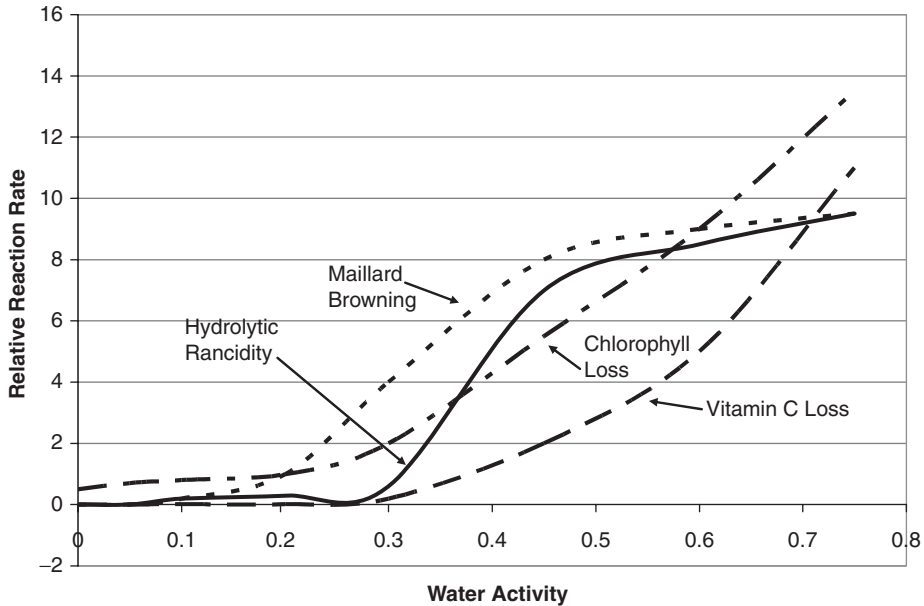


Figure 8.3 The effect of changes in a_w on various rate of deterioration of food products by various mechanisms during storage.

beginning with an amine (protein or amino acid) combining with a carbonyl moiety (reducing sugar), progresses through a broad range of compounds leading to dark colored polymers. The rate accelerates as the a_w increases above 0.25–0.3.

Color losses occur as the a_w increases. This process is illustrated by the curve for chlorophyll, which begins to deteriorate above $a_w = 0.35$. Similar curves can be drawn for carotenoids, anthocyanins, and others.

Vitamins such as ascorbic acid are susceptible to oxidative processes but are less reactive at very low a_w conditions. Others, such as Vitamin A, are subject to free radical autoxidation processes as mentioned in Figure 8.1.

8.4 An Active Moisture-Management System

In many cases, the food product has the best, moist, tender texture at an a_w near that at which microorganisms grow. A system that controls the a_w in a narrow range near this optimal point will enable the manufacturer to formulate and assure the best product possible with such a system with assurance of microbiological safety.

There are a number of factors apart from moisture that impact the shelf-life of a food product. They can include oxygen, ultraviolet light, heat, freezing conditions, as well as others that may be unique to certain products. There are commercially available means to control these factors that accelerate a product's deterioration with the exception of moisture.

Chemists, and even alchemists, have understood for years that addition of a solute to water or other solvent will raise the boiling point and reduce the freezing point of the solvent.

Later it was observed that a saturated salt solution will create a headspace environment of a specific relative humidity as a function of the salts employed. These phenomena are collectively known as colligative properties and are all a function of particles in solution in a unit weight of solvent, i.e., molality (Raoult's law).

Food chemists have employed this technique to help develop stable intermediate moisture food products such as fruit leather, confections, sweet baked goods. Known constant humidity environments have been generated in small chambers such as desiccators with saturated salt solutions. Experimental products are equilibrated against these known environments, establishing optimized formulae for such products.

These saturated salt solutions are not practical in a food package subjected to the typical distribution system because of the potential for spillage. Electronic control systems are not economically feasible for individual packages. Desiccants such as silica gel, molecular sieves or hydration devices employing a wick from a reservoir of water are acceptable only if the objective is to keep the product very dry or very moist respectively. These systems cannot maintain a narrow range of water activity in the package.

Colligative properties, constant humidity of aqueous solutions, have been harnessed to maintain constant relative humidities in chambers including guitar cases, woodwind reeds, tobacco products, and pharmaceuticals, among other applications.

An inexpensive, safe, effective moisture management system described in this chapter has not been available previously. This two-way moisture management technology that has been patented by Humidipak, Inc.[†] It basically consists of a saturated salt solution with excess crystalline solute thickened with a gum system. The thickening, to a viscosity of about 5000 or more centipoises (cps), serves three important functions:

- excess solute is suspended to assure uniform capability to absorb moisture from unit to unit;
- loss of the contents of the pack is minimized if the pack is punctured, suffers stress cracks or a compromised seal;
- permits use of more permeable films.

As discussed above, moisture management means that the product optimal water activity is maintained over time as the product and package are exposed to varying environmental conditions. It will provide moisture to the product when required or remove it by absorbing it when conditions demand it so that the a_w remains constant in the package. Both scenarios are available at any time during the life of the moisture management system and are designed to keep the product at the optimum a_w .

This filling is packaged in a material that is highly permeable to water vapor (high MVTR). This technology delivers the desired relative humidity in a range of less than $a_w = 0.02$ within a closed environment over an extended period of time under normal commercial distribution temperatures. Four patents have been issued and at the time of writing, two more are pending.

This two-way moisture management system is currently available as packets, tubes and tubs (shallow plastic cups or trays). Food compatible water activities available include: 0.95, 0.84, 0.80, 0.78, 0.75, 0.73, 0.70, 0.65, 0.62, 0.32, all made with food grade materials.

[†] Humidipak, Inc., Wayzata, Minnesota, USA.

Other a_w values are available such as 0.69, 0.58, 0.52, 0.45, 0.13, but these are not of food grade materials.

8.4.1 Application to Beef Jerky

Some products, such as jerky, are best in a very narrow range of a_w that is very close to a legally defined standard of identity. In these cases, the moisture management packet can be employed to 'finish' the drying step in the retail package.

Meat jerky has been a fast growing product in the food industry. Jerky is marinated beef, or turkey, or game or mixtures that has been dried to a USDA standard of identity level of moisture. The maximum moisture allowed is on the order of 30 % with a water activity on the order of 0.8. According to an expert taste panel, at a_w of 0.78 to 0.8, 'natural style' jerky is subjectively relatively easy to bite and has a moist mouth feel. This loss of moistness becomes more apparent as the a_w is reduced from 0.75. The texture of jerky becomes less succulent and tough as the water activity decreases from 0.75 and becomes decidedly less palatable as the value drops below 0.73 to a hard, tough product giving a noticeably dry mouth feel.

Jerky is best at an a_w at which molds grow. Therefore, jerky is usually packaged with an oxygen free atmosphere and oxygen scavenger packets. The oxygen absorbing iron powder has been successfully employed in maintaining a very low oxygen level in jerky packages.

Analysis of numerous samples of jerky from numerous manufacturers obtained by diverse sellers such as groceries, convenience stores, sports stores, and warehouse markets, showed a wide variety in the a_w of product available to the consumer. Some of these are summarized in Figure 8.4.

Table 8.2 shows that a Humidipak moisture regulator maintains the a_w of jerky at room temperature and reasonably well at a storage temperature of 100 °F (37.8 °C) for 90 days, a condition that predicts the storage deterioration equivalent to about 1 year at room temperature (21 °C).

In the experiments summarized above, according to a panel, the jerky without a Humidipak regulator was definitely inferior to the jerky with humidity regulators at an a_w of 0.78.

8.4.2 Humidity Restoration in Beef Jerky

Since the regulator is two-way, it can restore a product that has been dehydrated. However, the process is slow in jerky, hence it is far more important to maintain the proper moisture/water activity of jerky during storage and distribution.

Figure 8.5 shows how a package of jerky manufactured at a_w of about 0.78 lost enough moisture after 11 months in distribution to fall to a very poor quality $a_w = 0.67$. When a Humidipak regulator at $a_w = 0.75$ was placed into the jerky package, the a_w of the jerky increased to 0.73 in 3 months. This rehydrated jerky had an acceptable texture. Had a higher humidity Humidipak been added, the jerky would probably have attained a value of over 0.75. However, mold could probably have developed since nitrogen flush equipment was unavailable for this experiment.

It is difficult for a manufacturing process to hold the a_w of a product to ± 0.02 . By introducing a two-way regulator into the package, the initial product will be adjusted to the

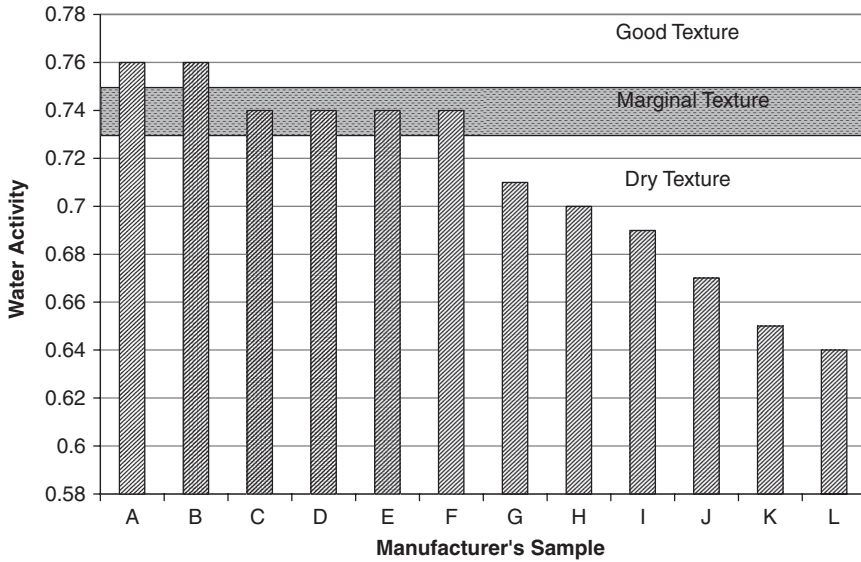


Figure 8.4 Water activities of samples of 4-oz bags of jerky by five manufacturers purchased from various retail outlets ages 6 to 11 months. The shaded area between 0.73 and 0.75 is an area of marginal moistness and tenderness.

target specification by either absorbing or giving off water to the product. This is especially important for food items that are near the a_w where microbial growth can occur. A superior, yet safe, product can be provided for the consumer.

While restoration of moisture to a dehydrated product is possible by many methods, it does not return most products to the same organoleptic condition as the original. Therefore it is very important to maintain a constant humidity in the package so that the water activity of the contents remains the same.

Table 8.2 Accelerated storage test of beef jerky with or without Humidipak pouches that had an oxygen scavenger. The storage condition was 100 °F (37.8 °C) at 25 % relative humidity, which corresponds to 12 months of storage at ambient room conditions of 70 °F (21 °C)

Time	a_w with Humidipak		a_w without Humidipak	
	RT	100 °F	RT	100 °F
0	0.79–0.80	0.79–0.80	0.79–0.80	0.79–0.80
90 days	0.78–0.79	0.75–0.77	0.76–0.74	0.73–0.74

Time	% Oxygen		% Oxygen	
	RT	100 °F	RT	100 °F
90 days	0.0–0.0	0.0–0.09	0.0–0.02	0.0–0.12

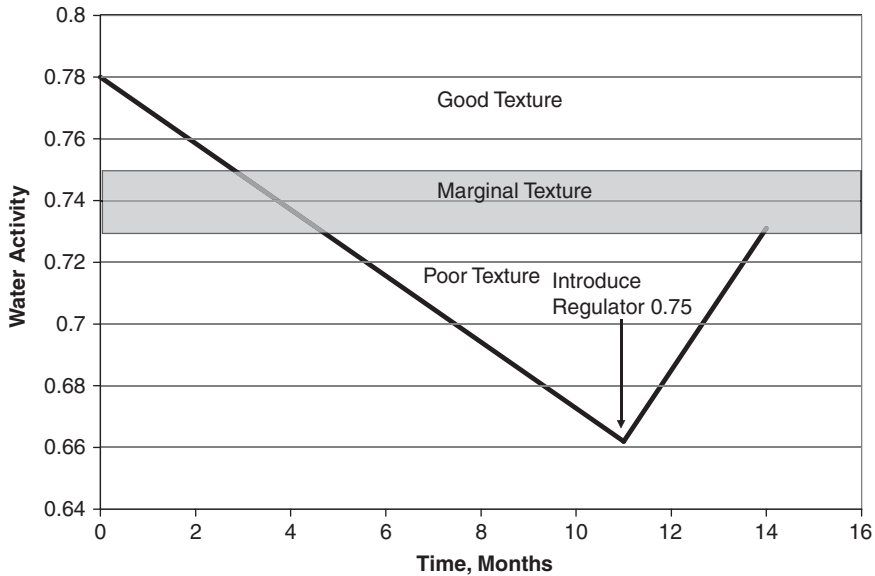


Figure 8.5 Loss of moisture in jerky during 11 months of distribution storage (sample from a convenience store) and rehydration with a Humidipak, $a_w = 0.75$.

8.5 Mold Inhibition

An oxygen scavenger system can be added to many of these two-way humidity regulators. While these scavengers do not have as rapid a reaction rate as do the dry, commercially available, oxygen scavenger packets, the combined regulator/scavenger system has sufficient reaction rate to be practical in nitrogen flushed applications such as meat jerky. Jerky stored for at least 18 months at room temperature has retained a headspace oxygen level of less than 0.1 % oxygen. In the test, the commercially available scavenger packets had a slightly higher average but fully satisfactory oxygen level of about 0.15 %.

It has also been found that mold growth can be further reduced by adding a mold inhibitor to the regulator packet, or applying some inhibitor onto the surface of the pouch.

Standard practice in the jerky industry employs commercially available oxygen scavenger packets to maintain a low level of oxygen in the headspace. Such an oxygen scavenging system has been incorporated into the humidity regulator. Table 8.2 shows that the Humidipak with scavenger packet is just as effective as commercially available oxygen scavenger packets. These values are a composite of field tests conducted with two manufacturers and represent some 30 samples of each test scheme.

The control consisted of the product as manufactured with nitrogen flushing of the filled jerky pouch with a commercial 50-ml oxygen scavenger packet. The other two test samples had Humidipak humidity regulators at 78 % relative humidity. The data from the regulator with scavenger system is reported in the middle column, the data with plain regulator and the same oxygen scavenger packet as the control is given in the right-hand column.

These samples were stored for 90 days at 100 °F and 25 % relative humidity, conditions that generally predict storage deterioration of 1 year at 70 °F. Samples held for 90 days at 70 °F had values approximately 25 % of the results of the 100 °C samples. This was also true of the weight loss of the whole package with jerky as well as the jerky itself, thus corroborating the validity of this accelerated storage test.

8.6 Printing Potassium Sorbate

Standard mold inhibitors such as sodium propionate, calcium propionate and potassium sorbate are only partially effective, if incorporated into the filling of the humidity regulator. The rate of diffusion of the anion is inhibited by the nature of the semipermeable film used in these trials. A more effective method is to 'print' a pattern of concentrated solution at the same time that graphics are printed on the film. In any case, because of the low volatility of sorbic acid, the regulator must be slightly acidic and be in very close proximity to the product. It will add 14 to 21 days to the life of a properly hydrated jerky after opening a nitrogen flushed, resealable package.

Flavors can be added to the filling. When about 0.4 % of a smoke flavor was incorporated into the packets, the product had a fresher, somewhat more 'smoky' flavor than jerky in a package without the moisture management system.

8.7 Packaging Executions

The salt solution required for a specific application can vary from 1 gram to 60 grams or more as a function of what the requirements are. It is often packaged in a pouch or other container and sealed shut to prevent leakage. This pouch or container is then placed, along with the food product being protected, in an outer package that has a moisture barrier to the outside environmental conditions.

Examples that have been commercialized or thoroughly lab tested are as follows (partial list):

- Printing/35# Kraft Paper/1.5 mil extruded Hytrel* film;
- Thermoformed polypropylene cup/heat seal coating/Tyvek* membrane;
- Printing/35# Kraft Paper/1.1 K-Resin from Phillips;
- Nylon film 1 mil thick formed into a chub package.

It is very critical that the package and weight of salt solution be determined and designed properly for each food application. There are many variables and we have found that if the detailed laboratory analysis and studies are completed at the start of an investigation, the actual results of the recommendations will be found to be acceptable and comparable to the laboratory testing.

The rate at which of water vapor enters and exits the container holding the salt solution is a variable that can be matched with the desired function. If the moisture management system is to preserve the food product over an extended period of time, the permeability of this system can be slower. If it is to manage moisture levels while a package is being

opened and reclosed numerous times, the moisture permeability rate needs to be faster so that the desired levels can be reached within a few hours.

Once the product has been selected for a study and the a_w has been determined, the salt solution will be formulated such that it will keep the product being protected in its optimum state. In order to determine and define the specifications for the package size and material, we need answers to a number of pertinent questions:

- (i) What is the water activity (a_w) of the product being managed? Has a moisture sorption isotherm been made?
- (ii) What is the product weight?
- (iii) How much water, in weight, is present in this quantity of product?
- (iv) What tolerance does the product have to moisture gain and loss?
- (v) How long is the desired shelf-life before opening?
- (vi) Are there conditions of reclosure that must be managed?
- (vii) In what geographic area and environmental conditions is this product being distributed or held?
- (viii) What is the package profile and general construction?
- (ix) What is the surface area of the exterior package holding the product?
- (x) What is the water vapor transmission rate of this outer package?
- (xi) Any other product characteristics that might be unique?

With these answers, we can then select the pouch or container material to be used in this application, calculate the weight of salt solution required and conduct laboratory trials to observe the moisture management system's impact on shelf-life and product quality over time.

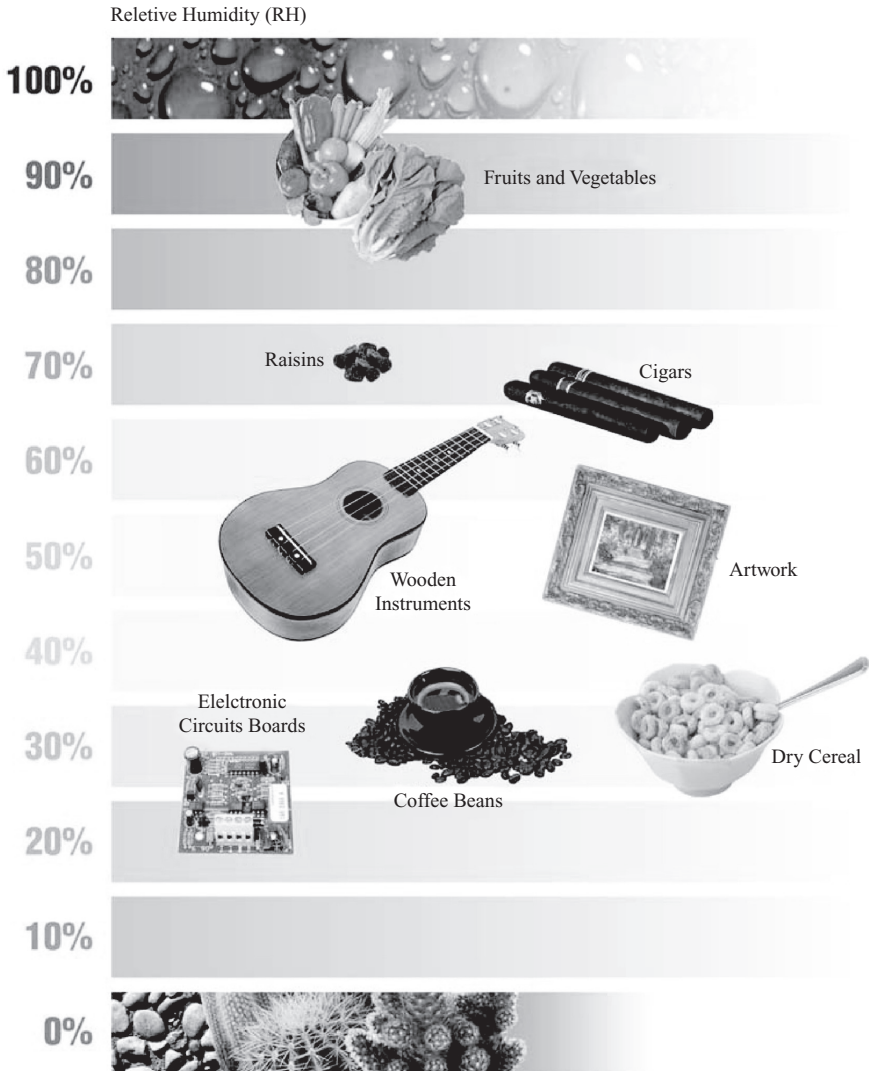
There is significant flexibility in designing the pouch or container to hold the salt solution. It must be designed to be cost effective for the application while delivering on the performance required.

8.8 Marketplace Executions and Testing

The current commercial uses of moisture management systems are in the tobacco market, which is very similar to food products in deterioration modes and the potential impact of moisture on shelf-life of these products.

The primary initial use of a moisture management system has been in the cigar area. Here it is used to keep high quality cigars that were purchased from a retailer with a walk in humidor in a pristine state until consumed by the user. These cigars may sell for anywhere from \$ 5 to \$ 35 each. It is also being used commercially for such items as the 25 count boxes of cigars that are packaged in very humid Central American countries and protects the products as they travel via various carriers and through unknown environments to the end point.

A further application is in the retail package of expensive cigars being merchandized in gasoline stations or convenience stores. Cigars of high quality that would normally only be sold from a walk-in humidor at a tobacco shop, can now be packaged and fully protected over their shelf-life under ambient conditions in any geographic location. For cigars, this means keeping them exposed to the optimum level of 70 % relative humidity that the moisture management system is fully capable of doing.



Ideal Relative Humidity Chart courtesy of  Humidipak.

Figure 8.6 Ideal relative humidity chart.

Laboratory testing is underway for a wide variety of applications, only a few of which are itemized below. For security and confidential disclosure agreements that are in place, other products under test cannot be revealed at this time. See Figure 8.6 for generic product targets.

8.8.1 Beef Jerky

Beef jerky is a product that can become very tough and chewy when moisture levels drop and are not at their optimum levels. If the moisture is too high, the product can become

moldy or fail to meet the legal definition of jerky. The moisture management system can target about 0.02 below this optimum point and provide a high quality performance of the product over its 12 to 18 month shelf-life.

8.8.2 Dry Spices

The unique flavor nodes and free flowing characteristics of many spices are significantly harmed when moisture levels are too high or too low. The consumer expects these products to last indefinitely but it is apparent to the gourmet using them that the standard packaging used is often inadequate for protecting a spice for more than a very few months. This is especially true if the reclosable container is opened repeatedly under dry conditions.

8.8.3 Dried Fruit

These products can be a delicacy when available in the proper state. But again this is a critical and relatively narrow moisture range where the product is in its pristine and delectable state. A moisture management has proven to yield long term stability and can even be used to salvage dried out products, restoring them to nearly their original condition.

8.8.4 Musical Instruments Made of Wood

When a stringed instrument such as a violin or guitar is exposed to a low or high humidity, the wood will lose or gain moisture. This will result in the wood shrinking or expanding, thus bringing about warping that changes the sound characteristics of the instrument. Worse, cracks may appear and even cause the adhesive joints to break apart. The appearance of cracks will reduce the value of the instrument by as much as one half of its value which can be several hundred thousand dollars, or priceless in the case of a Stradivarius violin.

Owners of these instruments will readily relate to the issues in keeping guitars, violins, etc. under widely varying conditions that change with the seasons. It is almost farcical to explain methods being used today to provide moisture protection. Ideally, these instruments should be stored between 40 and 60 % RH \pm 3 % according to moisture sorption isotherms prepared from the woods used in manufacture. Wet sponges are the most common element in many of the systems used today and naturally they try to reach 100 % RH, but because of leakage in the packaging, may average out at something in the middle of the range. They also require daily monitoring and most likely the addition of distilled water to protect the instrument properly. A suitably designed moisture management system has been introduced to deliver several months of optimum conditions for an instrument without any required daily effort. See one such application in Figure 8.7.

8.8.5 Works of Art

Museums around the world expend considerable time and effort to maintain the optimum temperature and humidity conditions for a wide variety of historical and extremely valuable works. This may include timeframes for the artworks while on display, in warehouses, or while being transported short and long distances. Today, one of the systems in use requires the conditioning and monitoring of silica gel, which if not properly handled, can cause



Figure 8.7 *Guitar preservation system.*

significant harm. A moisture management system as described herein using salt solutions can provide an ongoing and specifically targeted relative humidity atmosphere for each application over an extended period of time.

Another significant use for moisture regulators is to calibrate the humidity sensors in displays and galleries in museums. Calibration bags are available periodically to calibrate hygrometers. Dial type hygrometers can often be 15 percentage points to high or low. Digital type hygrometers are more accurate, but they too should be checked periodically as they tend to drift over time.

8.8.6 Nylon Parts

Nylon connectors have an optimal humidity when they do not crack when compressed or blister when heat is applied. Wood veneers can be formed over small radii only over a narrow range of moisture content. Powdered materials such as laser printer cartridges will tend to produce fuzzy images if too dry where static charges develop, or form lumps if too moist.

8.8.7 Clothing Storage in Humid Environments

Natural fabrics should be stored at a relative humidity of less than 50% to minimize the development of 'mustiness' that necessitates lengthy 'airing' or cleaning before use. This is especially important in the Southern Atlantic coast, the Gulf coast, and Pacific Northwest states. The summer months in the Mississippi/Missouri valley also experience high ambient relative humidities from May into September. Even new homes in these states experience relative humidities exceeding 60%. Pouches have been prepared and tested to hold the relative humidity in storage bins and garment bags made of films with low MVTR.

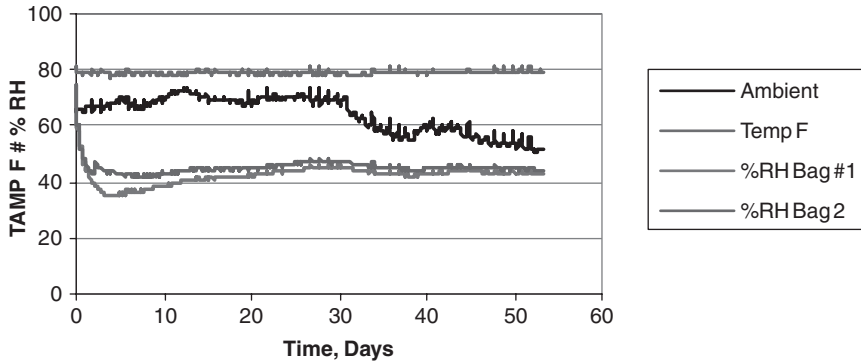


Figure 8.8 Hunting Clothing Storage, Florida Home June July.

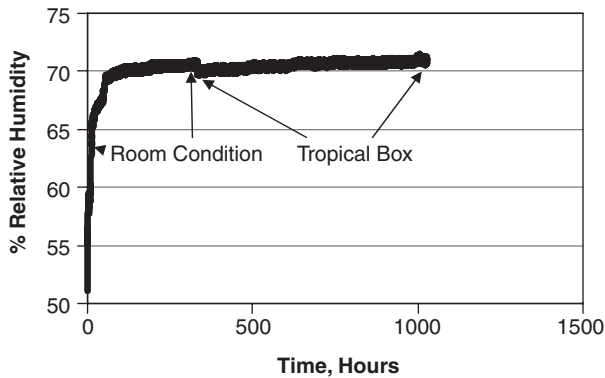


Figure 8.9 A two-way moisture regulator maintains a constant relative humidity of 70% at room conditions as well as in a tropical chamber with an 84% atmosphere.

Figure 8.8 shows the relative humidity in two garment bags containing winter hunting jackets stored in a bedroom closet in a new Southern Florida home.

8.9 Competitive Technology

Moisture management has been limited to formulation, processing and packaging. These have employed expensive, high barrier films, or resorted to glass or metal containers.

Active systems to control moisture have been limited to desiccants such as silica gels, molecular sieves, certain clays, selected salts. Desiccants tend to reduce the a_w of the products to near zero, and thus have limited application. Other active systems include a wide variety of devices to add moisture to the environment, such as wicks, sponges, and semipermeable films. These hydration devices tend to increase the a_w to high levels, especially in humid environments. For this reason, such devices require a certain rate of loss of moisture from the container.

Conditioned silica gels and some clays have the property of absorbing and desorbing moisture over a relatively narrow range of humidities. While effective, they suffer from a very limited capacity, often only 5 to 10 % of their weight, and their precision is fair at best.

Electronic devices to maintain a constant humidity in chambers, even buildings, are available. However, they are rather expensive and not practical for portable use. Also, they require significant, regular maintenance to be reliable.

8.10 Future Trends

A number of food products can be greatly aided in their shelf-life if a moisture management system is designed to work in conjunction with temperature and in some instances headspace gas control. Some examples where this technology will be commercialized within the next 5 years will potentially include:

- (i) International shipping of fresh fruits and vegetables. Moisture and humidity control has never been readily available to help prevent dehydration during ocean shipments and thus has forced some products into air freight. A moisture management system could offer cost savings while ensuring a superior product being delivered.
- (ii) The fresh produce sector has grown dramatically within the past 5 years with the many iterations of cut lettuce in various consumer pack varieties. Current systems do an excellent job of controlling the headspace gases but cannot impact the moisture and humidity within the package. As a result, packages moving from temperature controlled environments through the normal handling and consumer use systems will experience changes that can result in product deterioration and unacceptable products before the shelf-life limit has been reached. A moisture management system is a tool that could greatly aid this delivery system.
- (iii) With improving economic status and having all adults in a household employed, the demand for ready-to-eat prepared vegetables and cut fruits or vegetables is increasing rapidly. The maintenance of constant humidity in the package is critical to preserving quality of appearance, flavor and texture.
- (iv) Products in the home that are stored for future use could be better preserved if stored in a food protection system that included moisture management. Examples would be dried fruit, raisins, fresh fruits, etc.
- (v) Moisture management is an important component in controlling the growth of microorganisms. With increasing public awareness of food-borne infections and microbial toxins, providing constant humidity in a package will contribute to delivery of safe foods.

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9

Smart Packaging Technologies for Fruits and Vegetables

M.F.F. Poças, T.F. Delgado and F.A.R. Oliveira

9.1 Introduction

Traditional packaging has contributed greatly to the early development of food distribution systems. However, it is no longer sufficient because today's society became increasingly complex. Innovative packaging with enhanced functions is constantly being sought in response to the consumer demands for minimally processed foods with fewer preservatives, increased regulatory requirements, market globalization, concern for food safety and the recent threat of food bioterrorism [1]. Active packaging (AP) and intelligent (smart) packaging (IP) are becoming increasingly popular among researchers and industry.

Apparently there is no common, clear and unequivocal definition of these two types of system. The legislation [2] presents the following definitions: 'Active food contact materials and articles means materials and articles that are intended to extend the shelf-life or to maintain or improve the condition of packaged food; they are designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food'. 'Intelligent food contact materials and articles means materials and articles which monitor the condition of packaged food or the environment surrounding the food'. Active packaging is associated with the preservation and protection function and it refers to systems that are able to change the conditions the product is exposed to. Examples include oxygen absorbers, materials with permeability depending on temperature, antimicrobial materials, etc.

Smart or intelligent packaging is associated with communication: a system capable of detecting, sensing, recording, tracing, communicating, and applying science logic, to facilitate

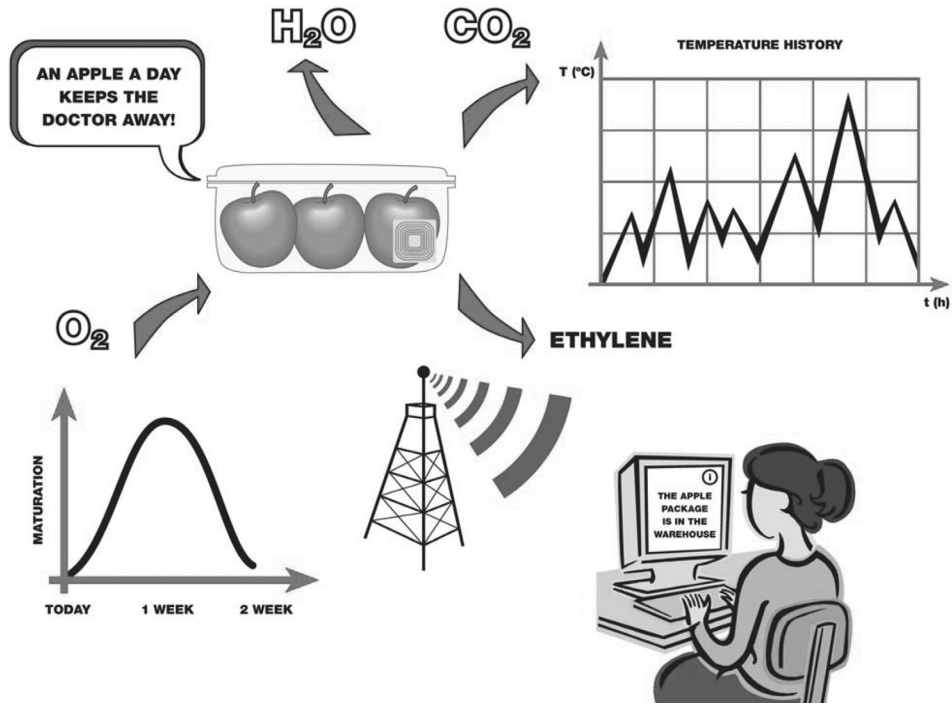


Figure 9.1 *Smart packaging for fruits and vegetables.*

decision making, to extend shelf-life, enhance safety, improve quality, provide information, and warn about possible problems [1]. Examples of technologies associated with smart packaging systems are time–temperature indicators (TTIs), gas indicators, biosensors and radio frequency (RFID) tags for identification and/or for monitoring product properties or the ambient conditions the product is exposed to (Figure 9.1). Smart and intelligent packaging may also include physical shock indicators and smart labels. Although in its infancy, smart labels may consist of systems that detect a diabetic consumer and alert him/her to the sugar content of the product, and systems that alert the patient on the schedule for taking prescribed medicines. Thermochromic inks already have a few applications that show when an optimal or dangerous temperature has been reached, for example the temperature of the beer bottle (refrigerated) or the right cooking temperature of pre-prepared soups.

Nanotechnology is expected to have an important influence in active and intelligent packaging, as in most areas of science and technology [3,4]. It may be used to improve polymer barrier properties (e.g. nanoparticles of clay dispersed throughout plastic are able to block oxygen, carbon dioxide and moisture); to create functional coatings (e.g. antimicrobial and preservative released ‘on command’), sensors (of pathogens for example) and smart inks; and to produce printed devices and systems. An example would be electronic consumption dates that automatically adjust according to time and temperature history of the product.

Active and smart packaging usage in the food sector is more advanced in markets like Japan and USA than in Europe. Furthermore, there is more experience in the application of

smart packaging in very expensive products and in products highly sensitive to damage by distribution handling conditions, like medical and medicinal products, electronics devices, etc. The fruits and vegetables sector is, as compared with other products and food products, a low margin sector, in which periods for investment return are longer and decisions on implementation of technical solutions that have an impact on structural issues of the organisation and its supply chain are slower. Legislation and costs are also factors that may have some contribution on a relative unbalance between the real commercial applications of smart packaging and the interest recorded at research and development initiatives and trials.

This chapter includes a section focusing on the packaging requirements for fruits and vegetables. The smart systems, which application is potentially more relevant to the fruits and vegetables sector, are also focused on (i) time–temperature indicators (since the temperature control during the distribution chain is of major importance in the product deterioration rate); (ii) control of gas composition and gas indicators, and (iii) radio frequency tags, for product identification and traceability. Since these topics are covered at depth in other chapters, the specific application to fruits and vegetables, its benefits and limitations are covered here.

9.2 Packaging Requirements for Fruits and Vegetables

Fresh fruits and vegetables are, in general, highly perishable products that require controlled handling conditions all over the distribution chain, from production to consumer, in order to maintain quality and safety and to increase the shelf-life. These products are living products that keep respiring, consuming oxygen and producing carbon dioxide after harvesting. The post-harvesting deterioration process is influenced by intrinsic factors of the product, such as the cultivar, the maturation stage, etc., by its handling conditions and by ambient factors.

Temperature is, without a doubt, the most important single factor that can be used to retard the deterioration process of fruits and vegetables since it strongly affects the respiration, ethylene production and transpiration rates. As a general rule, the rate of respiration increases two to three times for each increase of 10 °C and this variation may normally be described by an equation of the Arrhenius law type. The energy of activation ranges from 40 to 105 kJ/mol and depends on the composition of the atmosphere surrounding the product. However, some products, like banana, lemon and mango for example, are susceptible to physiological damage at low temperatures. Most products suffer irreversible damage at temperatures lower than –1 °C. Therefore, temperature control and monitoring during all stages of distribution and storage are of prime importance for these products.

Handling conditions are also important since mechanical damage caused by impact, compression or vibration accelerates the senescence process. Tomato fruit quality, for example, is substantially reduced by bruise (i.e. impact) damage. Bruising is considered to be a two-step process, in which mechanical damage occurs first and then enzymatic degradation of the affected tissue, including cell walls, takes place. This could result in a rapid enzymatic breakdown of the cell wall polysaccharides, observed as soft spots or bruises on the fruit [5]. The mechanical damage during transportation is the principal cause of lost quality of tomato. The frequencies around 8 Hz and acceleration of 1 g are conditions of damage during the transport of tomatoes and these should be avoided in the transport system when the fruit is packed in cardboard boxes with plastic trays [6].

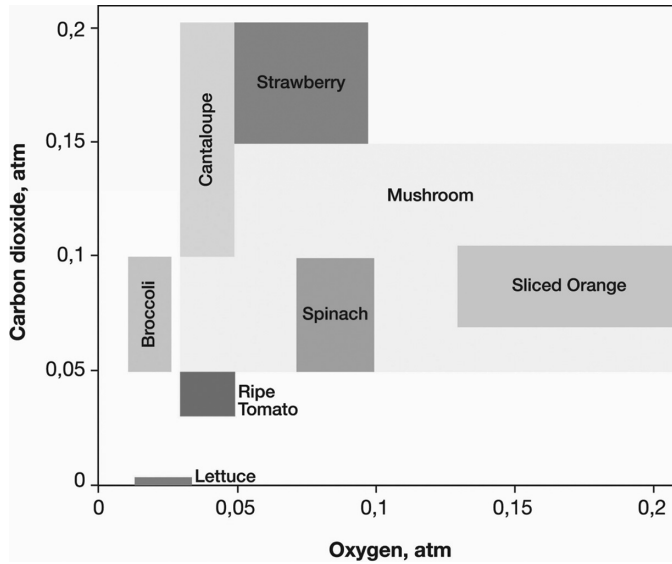


Figure 9.2 Optimum recommended gas composition for different fruits and vegetables.

The concentration of gases in the product surroundings also plays a very important role in the rate of respiration, and the quality and shelf-life of the product can largely benefit from the use of a modified atmosphere packaging system. The respiration rate decreases with the decrease in oxygen concentration. The carbon dioxide has, usually, an opposite effect, although depending on the type of product, degree of maturation, concentrations range and time of exposure. For example, high levels of carbon dioxide may cause tissue damage and thus induce an increase in the respiration rate. Figure 9.2 represents the range of optimum concentrations of oxygen and carbon dioxide to extend the shelf-life of different common fruits and vegetables. Every product needs a different and sometimes very specific gas concentration ratio to maximise shelf-life. This specific ratio depends on cultivar, temperature and duration of storage. Even if modified atmosphere packaging delivers those ratios to produce at the point of packing, these ratios immediately begin to change with time due to respiratory processes and, particularly if there are temperature fluctuations, compromising the product's shelf-life. The concentration of gases inside the package depends on the equilibrium between the product respiration and the gas transfer through the package. These processes have, in most cases, different sensibility to temperature. Variations in temperature cause a perturbation in the equilibrium and consequently a drift away from the optimum ratio of gas concentration. Packaging materials with gas permeability responding to temperature variations are an important example of smart packaging for compensation of the temperature oscillations occurring during transport.

Minimally processed fruits and vegetables are a relatively recent but drastically expanding market, due to the consumer demand for convenience. These products, however, are very perishable. The processing operations (peeling, cutting, etc.), although minimal, break the cell walls, bringing enzymes and substrates into contact, promoting contact with microorganisms, and creating 'stress' conditions. As a consequence, there is an increase

in the respiration and ethylene production rates, in oxidation, water loss and degradation of lipidic membranes. These changes increase the susceptibility of the product to degradation and simultaneously yield the accumulation of metabolites such as ethanol, lactic acid and ethyl acetate. These products are more demanding in packaging requirements, and modified atmosphere packaging is most often required. Barrier properties, in particular the permeability to oxygen and to carbon dioxide and its variation with temperature, are parameters that should be carefully selected. Active and smart packaging may find in this type of product an interesting application market, to increase their shelf-life and to monitor their quality and safety.

The packaging specific requirements for fresh fruits and vegetables are essentially related to maintaining, controlling and/or monitoring:

- temperature,
- gas composition and humidity,
- mechanical damage.

Besides these technical functions of preservation and protection, packaging functions also include communication with the consumer, which is a well proven marketing tool, and convenience of use.

9.3 Time–Temperature Indicators

TTIs are typically small self adhesives attached to, or small devices incorporated in, the package providing a visual indication, most commonly by changing colour or moving colour front, as a response to temperature history during distribution and storage. These indicators may be placed in the shipping container or in the individual consumer package [1].

There are three basic types of TTIs: full history (those that start integration immediately once activated), partial history (those that start integration when a certain temperature threshold has been achieved), and critical temperature or abuse indicators (that show a change if a certain temperature was achieved and whose response does not depend on the time the product has been packaged).

Regardless the mechanism of the indicator, the rate of change of the visual indication must be temperature dependent, increasing at higher temperatures similarly to most physicochemical reactions. The major mechanisms on which the TTIs are based include enzymatic reaction, polymerisation, melting point and diffusion of a substance. More recently, TTIs based on microbial growth and based on reactions in crystal phase have been made available. In the first case, once the indicator is activated, an enzymatic reaction takes place causing a pH change and a consequent colour change. Indicators that work based on polymerisation have a polymer coating that gets darker at a rate that depends on the temperature. The colour of the polymer is compared to a colour reference surface printed on the indicator. These indicators are usually self-activated, thus requiring deep low temperature storage before use. In the case of the new crystal indicators, the colour gets lighter and, more importantly, the reaction can be initiated by activation of the indicator by UV light when necessary. Some indicators are based on melting point of a certain substance. When the substance melts, a different colour appears on the indicator window. This is matched with a product critical temperature. Such indicators are abuse indicators, since they indicate

that the critical temperature was achieved but the colour change shown does not indicate anything about the time the product was exposed to that temperature. This type of indicator may be combined with a mechanism of progression over a base material of the coloured substance after melting. The rate of progression depends on the temperature and thus the indicator can be designed to match a certain food degradation process. The more recent mechanisms applied to an indicator are based on a pH change due to the microbial growth.

The indicators must:

- be easily activated,
- exhibit an easily measurable change dependent of temperature/time,
- be irreversible and with low time of response,
- correlate well with the food deterioration mechanism.

This latter requirement depends on how close the value of activation energy of the indicator reaction is from the value of activation energy of the food's deterioration reaction.

The product deterioration can be monitored by measuring, over time, a specific characteristic Q critical to the shelf-life, like colour in mushrooms, firmness in strawberries or the microbial count in salad (Figure 9.3). If the reaction of Q loss follows a first order kinetics, it may be represented as:

$$-\frac{dQ}{dt} = kQ \quad (1)$$

where t represents the time and k represents the reaction rate constant. This depends on temperature according to Arrhenius law:

$$k = k_o \exp \left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right] \quad (2)$$

where E_a is the activation energy of the characteristic loss rate, representing product degradation. In chemical reactions, E_a is usually in the range of 41–126 kJ/mol. Table 9.1 presents values of E_a for respiration rate of some fruits and vegetables or E_a of product characteristics measured during storage to monitor product quality loss.

The same mathematical modelling can be made for the visible response X of the TTI: colour change can be measured by reflectance; colour front movement can be measured by

Table 9.1 Values of activation energy (E_a) for different processes occurring in fruits and vegetables

Product	Q	E_a , (KJ/mol)	Source
Carrots			
Shredded		79	[20]
Sliced	Respiration rate	70	[21]
Whole		55	[21]
Onion	Respiration rate	35	[22]
Mushrooms	Colour change	63	[8]
Lettuce	Colour change	37	[8]
Strawberry	Firmness loss	39	[8]
Fresh apple	Respiration rate	29	[23]

Table 9.2 Characteristics of three commercially available TTIs

TTI	Working principle	E_a (kJ/mol)
MonitorMark [®]	Diffusion	33–50
CheckPoint [®]	Enzymatic reaction	50–113
Fresh-Check [®]	Solid state polymerisation	84–100
OnVu [™]	Solid state reaction	NA
eO [®]	pH change due to microbial growth	NA
TT Sensor [™]	Diffusion reaction	NA

* NA – not available

length, etc. The change of X with time can be represented as [7]:

$$X = f(t) \quad (3)$$

If we define a function F such as:

$$F(X) = k_{TTI}t \quad (4)$$

Where k_{TTI} represents the rate of TTI change, which is also a function of temperature according to Arrhenius Law:

$$\frac{dF(X)}{dt} = k_{TTI} = k_{TTIa} \exp \left[\frac{-E_{TTI}}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right] \quad (5)$$

The selection of a TTI for a particular application must take into consideration the match of these two values of energy of activation. The E_a value is a characteristic of the TTI and it is used to select a suitable indicator for a specific application, knowing the E_a of the degradation of the critical characteristic of the product. Table 9.2 presents the E_a of some commercially available TTIs: MonitorMark[®] (from 3M), CheckPoint[®] (from Vitsab) and Fresh-Check[®] (from TempTime Co.). Other commercial indicators can be mentioned WarmMark[™] (Cold Ice, Inc.), OnVu[™] (Ciba Specialty Chemicals and FreshPoint), eO[®] TTI (Cryolog, SA) and TT Sensor[™] (Avery Dennison Co.).

The major factors that affect the reliability of a TTI are: (i) the variability in the value of response between indicators of the same type at the same conditions; (ii) the uncertainty in the Arrhenius model of the TTI; and (iii) the difference between the activation energies of the food product and the TTI [8]. The performance and reproducibility of the indicators should be assessed by a series of tests under controlled conditions, in particular, the temperature response test, the temperature cycling test including abuse temperatures, and the accuracy of point of activation and of end point determination.

The TTIs in the fruits and vegetables sector have a particularly interesting application in the case of minimally processed products, such as fresh-cut salads, since these products require a very good temperature control: higher than optimal temperature results in an acceleration of decay rate, a slimy texture, and off-odours and off-flavours. Lower than optimal temperatures are also not recommended as the vegetables leaves become translucent and the shelf-life is shortened due to breakdown; temperature fluctuations result in accumulation of free water in the package, which increases decay (Figure 9.3).

TTIs have been used in France since the early 1990s by Monoprix, a retail chain. This retailer wanted to upgrade its image and to differentiate its stores, giving emphasis to

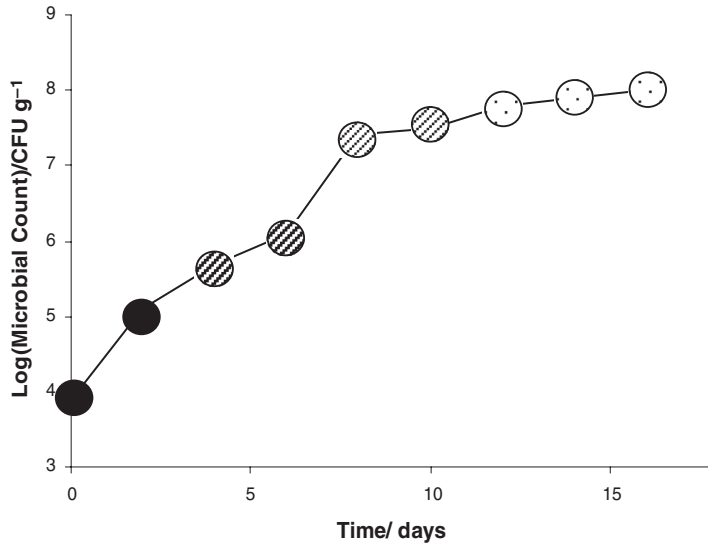


Figure 9.3 *Change in TTI visual indication and the change in quality of minimally processed lettuce salad during refrigerated storage.*

products of premium quality and to superior service. Therefore, it initiated the application of Fresh-Check[®] (from TempTime Co.) to individual packages to provide the consumers an assurance of freshness from the time of packing throughout the grocery and distribution (Figure 9.4). The programme started in 1990 with a limited number of private labels and stores, and since then, it has expanded to 400 perishable store brands and about 250 stores.

Carrefour is also using TTIs on its products. Since November 2005, fresh fruits and vegetables sold online via the web site Ooshop are being delivered with Fresh-Check[®].

Temperature monitoring at home is also very important for food safety. Timestrip[®] is a single-use consumer activated smart-label for monitoring elapsed time on perishable products. It was designed to enable consumers to record time elapsed since activation of the label. This functionality is particularly suitable for packaging or labelling perishable products or products requiring regular maintenance or replacement (refrigerated and frozen products). It automatically monitors lapsed time, from 10 minutes to 12 months. The label is automatically activated when the consumer opens the packaging or it can be supplied as an external label that consumers can manually activate when they first use a product.

9.4 Breathable Materials

As previously discussed, each fruit and vegetable has a specific optimum atmosphere which, together with a controlled temperature, improves the preservation of products quality and freshness. If, however, there is a failure in the temperature control, the respiration rate increases and the oxygen consumption may increase beyond the capacity of the package in allowing the oxygen come into the package. As a result, the oxygen concentration will become too low (and conversely the carbon dioxide concentration will become too high)



Figure 9.4 Application of TTI Fresh Check®. Reproduced with permission from Packaging Materials & Technologies Ltd.

and the produce will be spoiled. This situation occurs because respiration rate of produce is more sensitive to temperature when compared with the permeability of most traditional packaging films, for example polyethylene (Table 9.3).

A new concept of packages, with permeability to gases responding to temperature changes to compensate moderate fluctuations occurring through transportation, was developed and is commercialised as BreatheWay™ membrane technology. This is a means of providing different package permeabilities, to create specific optimum oxygen and carbon dioxide levels in the package, and maintain this optimum atmosphere composition within limits even if the temperature changes. The system consists in a highly permeable membrane applied over a hole in the package. The membrane is made by coating a porous substrate with a proprietary side-chain crystallisable (SCC) polymer. SCC polymers are polymers in which the side chain crystallises independently from the main chain. Examples of such polymers are siloxanes and acrylic polymers. The polymer changes from solid or crystalline state to amorphous fluid when heated. This sharp transition temperature

Table 9.3 Change in respiration rate and in permeability of films with an 10 °C increase in temperature [24]

Increase in rate for a temperature change from 0 to 10 °C	
Broccoli (3 % O ₂ atmosphere)	1.86
Permeability of PE film	1.4
Permeability of BreatheWay™	1.8

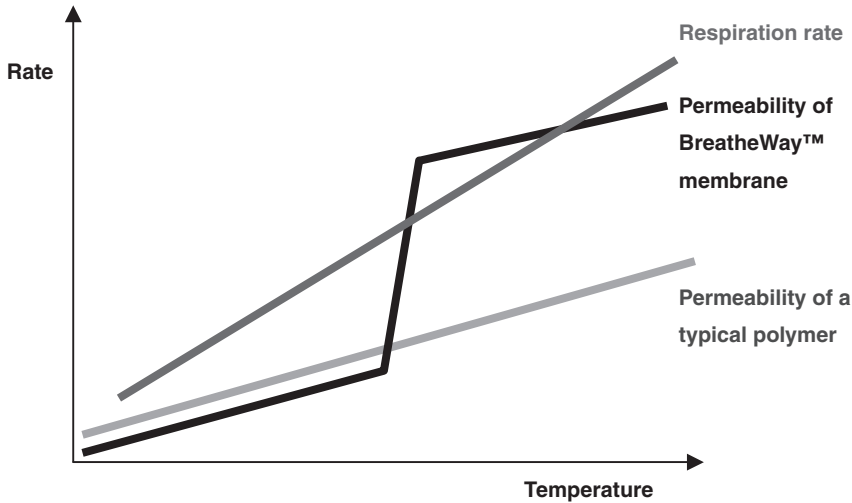


Figure 9.5 Influence of temperature on permeability of packaging films and respiration rate of produce.

works as a switch since the polymer permeability changes, increasing significantly when going from below to above this temperature (Figure 9.5). The temperature switch allows membrane permeability to increase up to 1.8 times when a 10 °C increase in temperature occurs, thereby compensating for the increase in respiration rate of produce, for example broccoli (Table 9.3). The membrane can be supplied for pouches, case liners, pallet bags and some rigid containers. The SCC polymers are intrinsically highly permeable, but the polymer properties may be modified by the inclusion of other monomers and by varying the length of the side chain, in order to change the ratio of O₂ to CO₂ permeabilities, and alter the temperature switch or other physical properties to match the specific produce requirements.

This technology is used for ice-less shipments of cut broccoli (Figure 9.6), reducing the freight costs and minimising problems caused by temporary breaks in the cold chain. Chiquita Brands International, Inc., is using this technology in premium bananas for convenience stores that require ready-to-eat products.

9.5 Gas and Volatiles Indicators

In this class of indicators, we may include indicator of food spoilage and food quality loss or ageing, commonly referred to as freshness indicators, and leakage indicators, based on the detection of oxygen and/or carbon dioxide. Freshness indicators are not developed at a commercial level as an extension of TTIs, in spite the fact that, in patent and research literature, a number of concepts for freshness indicators and detectors has been described [9]. They are based on the detection of volatile metabolites produced during food deterioration, such as carbon dioxide, diacetyl, amines, ammonia, ethanol, and hydrogen sulfide.

The only known commercial application to produce is the ripeSense[®] sensor label – a ripeness indicator, developed in New Zealand by Jenkins Group, in partnership with



Figure 9.6 Products packaged with BreatheWay™ technology. Reproduced with permission from Packaging Materials and Technologies Ltd.

HortResearch. Ripening is the term used to describe physiological changes jointly with the development of textural and sensorial characteristics rendering the fruit good to eat. There is an increase in sweetness (due to organic acids breakdown and conversion of starch to sugars), a decrease in firmness (due to loss of cell turgor, conversion of pectins and breakdown of cell wall components), an increase in flavour (due to production of aromatic volatile compounds), and changes in colour due to production and breakdown of pigments).

In some fruits, changes in colour can be used by consumers to decide when the fruit is ripe and 'good to eat' (e.g. bananas, avocado, tomatoes). However, some fruit doesn't exhibit obvious visual indication of ripening, such as kiwifruit and most varieties of pears. This sensor – ripeSense® – was developed specifically for pears [10]. The package is a four-pear polyethylene terephthalate clamshell that is moulded to fit the shape of the pears. The container design, developed to capture the emitted aroma, protects the fruit from crushing or bruising, allowing retailers to sell ripe, tender and ready-to-eat fruit without excessive shrinkage (Figure 9.7). The package also incorporates interlocking feet for easy stacking and display at a 35° angle, and ventilation holes that enable excess CO₂ and moisture to escape [11]. The sensor changes colour by detecting the naturally occurring aroma compounds given off by the fruit as it ripens. The sensor is initially red and graduates to orange and finally yellow. By matching the colour of the sensor with their eating preferences, customers can accurately choose fruit as ripe as they like it.



Figure 9.7 Pears clamshell package with ripeSense[®] sensor. Image used with permission of RIPESENSE Limited (ripesense.com).

9.6 RFID in the Fresh and Minimally Processed Fruits and Vegetables

RFID is probably the topic that has generated most discussion recently in the produce sector. RFID stands for radio frequency identification and is a generic term for technologies that use radio waves automatically to identify individual items. Traceability is one of the most important applications but incorporating a RFID tag, into a package or on its label, associated with the proper sensors, may provide a mobile database moving with the product and carrying potentially all the details needed about the product and its history [12].

Merit-Trax Technologies, Inc. (Canada) developed an application based on RFID designed to record and report quality inspections and environmental conditions of fresh fruits and vegetables from harvest to retail. The development is the product of a partnership with Canadian companies: Sensor Wireless, Inc. providing the sensor technology, Syscan International, Inc. supplying the RFID, and Merit-Trax contributing with its Trax-IT Fructus software application. The solution Trax-IT Fructus provides traceability, quality and inspection management [13].

RFID systems are used to collect, process and analyse data concerning the distribution of packaged salad by Fresh Express, a division of Chiquita Brands International [14]. The system (TR3 Solutions) reads data from RFID tags (RFID Gen 2 UHF) at retailers and distribution centres, collects information on how long products take to move through the

supply chain, and where bottlenecks may be in keeping goods from reaching store shelves before their expiration dates. Fresh Express also can use data provided by the service to expedite recalls. The tags are applied in cartons and pallets of salad mix. Each carton's unique EPC (electronic product code) number links it to data, including the type of product, destination, shipping date and expiration date. The tags are first read as they leave the Fresh Express plant through the loading dock onto trucks. After that, they are read again as they enter and leave distribution centres, at the back rooms of the retailers and on the way to store shelves [15].

Traceability with RFID technology may definitely be a major contribution to food safety, for example, in outbreaks of infection. Recently in USA, an outbreak of *E.coli* in bags of fresh spinach highlighted the need for better traceability in the food chain, namely in tracing the source of food-borne illnesses and enabling authorities to locate the source of an outbreak in hours rather than weeks [16].

The RFID tag has the advantage of potentially performing more functions than just product identification. The technology can also be used with TTIs and with virtually any other device built to monitor the status or condition of an item, such as pressure, humidity, gas leakage and tampering. Currently there are active tags which can monitor real time temperature, shock, and location. Therefore, this technology may have a tremendous impact on the cold chain.

An example of combination of RFID and temperature monitoring of fresh produce in transit is the system called X_Tract™ Cold Chain Monitoring Service created by GL&I (Victoria, Australia) in partnership with Exago Ltd [17]. The system has been released for commercial use. X_Tract™ is a web-based performance evaluation and data management service, comprising three core elements: a semi-active RFID enabled 'smart label (TempSens® made by KSW Microtec AG (Dresden, Germany)); a RFID reader, which uploads this data via a secure web portal; and customised software that enables the customer to view the data from anywhere and at anytime [17]. Encased in protective plastic skin and about the size of a credit card, the tag can be attached to the surface of a shipping crate or box, or can be inserted into a shipment or pallet load of perishable goods as it leaves the farm, wharf or warehouse. The tag continuously monitors and stores temperature of fruits and vegetables and time data throughout the supply chain. The data is then checked at various predetermined points. If the goods are found to have spoiled, the information on the tag will determine who was responsible by providing temperature and time data. The data is uploaded – either by means of an Internet connection or via a GPRS cell phone network – to an online database that is part of the X_Tract Web site managed by Exago. The desktop reader is connected to a PC and therefore to the Internet via a serial connection. The handheld model can be plugged into a PDA that uses a standard GPRS wireless connection to upload and download data. A customer uses a password to access its data on the X_Tract Web site, which system also generates e-alerts. The customer can configure and operate the X_Tract Web site through his or her Internet connection, allowing remote access to temperature and travel time information. In addition, the X_Tract Web site can be established to e-mail the customer and other companies in the supply chain to alert them whenever data is available for viewing at the company's database or if there has been a temperature violation [17].

Apart from being able to perform functions other than identification and traceability, RFID has many inherent benefits. For example, unlike bar-codes that are dependent of

line-of-sight technology, RFID can be read at any angle as well as through packaging and most other materials. In addition, hundreds of tags can be read simultaneously. However, implementation will be gradual as the technology matures and becomes less costly. Bar codes will remain a viable technology, co-existing with the gradual adoption of RFID for some years to come [18].

Particularly for the fresh produce sector, which is typically an industry with high volume and low margin, some limitations are still present: fresh produce companies that are currently participating in RFID initiatives are finding that the technology is expensive and problematic. It is expected, however, that as the demand for RFID technology increases, costs will drop accordingly. There are multiple standards, internal computer systems are often not RFID capable, and many procedures have yet to be resolved [18]. There is a major need for data synchronisation between trading partners and for standardisation. There are well-developed standards for low- and high-frequency RFID systems, but standards for UHF weren't established until recently [19].

Presently, trials and pilot applications have been made mainly at the pallet and case levels, and little testing has been done on clamshells or on flexible packaging for fresh produce [18]. A potential problem of the RFID tags is the fragility of the antennas if they are not on a flat and stable surface of rigid cases, as mechanical damage makes the tag unusable. Table 9.4 lists the major issues that are to be addressed in the implementation of RFID in the produce industry.

Application of RFID in the food supply chain has raised a lot of interest and a great effort has been put on developments towards technical aspects of the technology application, the mechanics and workability of tags and readers. However, organisational issues should be addressed by the produce supply chain, such as building up a data infrastructure around RFID deployments that supports compliance in the short-term but can scale to meet long-term needs.

Table 9.4 *Specific challenges of RFID in the fruits and vegetables sector*

Specifics	Description
Location of packing and tag application	Application of tag in the field or in the warehouse, to track each case or each pallet
Product water content	It may affect the selection of frequency of tag operation
Handling conditions	It influences the durability of tags: handling heavy duty produce that hit the tag may lead to damage of tags depending on the weight/density and shape of product
Post-harvest treatment	The tags must stand the high values of humidity in cooling chambers and treatments like, for example, the sulfur dioxide treatment
Pallet density	Relation with readability of the tags
Tags orientation	
Type of packaging	Reusable plastic container (returnable) or corrugated (single trip)
Tags application	Tags may be embedded in the container itself or applied via a label; flexible packages present more difficulties

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10

The Influence of Product and Packaging Characteristics on Passive RFID Readability

Robb Clarke

10.1 Introduction

Many people assume that once you purchase and set up an RFID system, all you have to do is turn it on to get information that will help you save money. Of course, nothing is further from the truth, not only because an RFID reader system is somewhat more complex than simply plug-and-play, but also because the articles you are trying to read may actually be interfering with data collection. More often than not, they are, and if you are not aware of this, you are doomed to wasted time, energy and resources in pursuit of useable information.

To get something of use from this chapter, you must realize why the focus on packaging and materials is important. First of all, everything that is made and/or transported is packaged in some manner. All industries and companies use packaging, so there is no one that can skip the lessons to be learned herein.

Various product or package materials can hinder reads, though in some instances, they might be of help. What is important is being able to capture the reads you want so that you can act upon the results generated. It must also be recognized that RFID reads are a condition of the product composition as well as the packaging and handling materials being used. You must not fall into the trap of being conditioned to believe axioms such as 'RFID will not work around metals or water', though in many cases this is true. Still, there are many instances where this is really not a concern, depending on how the read system is configured. Further, flatly stating that RFID can easily read through certain materials,

like paper, is equally incorrect in many cases. Hence, knowing how materials play a role in RFID readability will help you get the information to determine accurately the benefits or detriments of a given product/package system.

10.2 What is Packaging?

Packaging is a unique field in that hardly anyone considers a package system unless it doesn't perform its intended job. Every day, billions of packages are handled, used, resealed, stored and recycled with nary a consideration. However, let that one package leak or not open properly and people curse aloud while impugning the heritage of those that designed it. While some of us declare, with tongue-in-cheek, that packaging is the center of the universe, consider the difficulty in advancing beyond basic hunting and gathering without proper means of handling food or storing goods to last a drought or winter.

Packaging has been defined as the enclosure for products, items, or other packages, such as a wrap, pouch, bag, box, cup, tray, can, tube, bottle, or other container form, to perform *one or more* of the following major functions [1]:

- containment,
- protection and/or preservation,
- communication and/or identification,
- utility.

Containment, the original function of packaging, refers to handling, transportation and use. This basic requirement enables product movement. Imagine the handling and transportation of drinking water or free flowing powders and grains without a container and you can see how this requirement serves a critical function.

Protection is an interesting function in that it is a two-way consideration. Most people, rightfully so, consider the need to protect the product from damage due to outside influences, such as drops and shock, harsh vibration, excessive moisture, gases, light, *et cetera*, and a slew of other conditions. However, protective packaging must also be considered in the movement, handling and storage of hazardous materials such as nuclear waste, oils, certain biologics and the like, where exposure of the product can cause damage to the environment. These protections must be viable for the expected life span of the product, regardless of the external environment.

Communication and identification commonly refer to package contents, directions for use, product manufacturer, labeling or decoration, or other means by which people can tell which product the package contains. An international example of this visual communication is the classic package shape of a bottle of Coca-Cola. People worldwide recognize and identify the contents through the shape of the package. Of course, this entire book relates to one of the newer technologies for communication and identification, RFID.

Utility refers to the function of a package that facilitates dispensing and use of products, such as ease of opening and resealing, apportionment, application and dispensing features, safety and stability, secondary or post-use packaging applications, etc.

When a device or container performs one or more of these major functions, it is considered to be a package [1].

The field of packaging can further be examined from several perspectives. For example, packaging can look at the differing requirements for industrial, consumer or military packaging. Each, obviously, needs different components to do their respective jobs, whether that is crating and labeling, eye-catching decoration, or protection from heat and cold over a 20-year period. Similarly, different requirements are expected from packaging that has specific functions. Consider the packaging that contains and stores a sensitive product. Regardless of whether that product is sensitive to light, oxygen, moisture, etc., the first, or primary level of packaging has requirements that are different than the package that holds multiple units of the primary package (in essence, a secondary package).

10.3 Discussion of Specific Packaging Materials

There are five main categories of packaging materials. These are wood, paper, plastic, glass and metal. There are similarities to be found between wood and paper, and this should come as no surprise. There are also similarities between plastic and glass, though this is less commonly understood. Metal is generally considered to be a bad material for use with RFID systems though this, too, needs to be understood so a rational decision can be made for many package systems. Composite materials can also be utilized for packaging, though the individual layers making up the composite, i.e., the aluminum and polyethylene layers of metalized plastic will act according to the dictates of each respective individual material.

The following discussion is meant as a basic background for these five categories. Note, however, that the field of packaging is much too expansive to give a full discourse in this limited space, so you would be advised to peruse the reference section as a starting point to a more thorough packaging education.

10.3.1 Wood

Wood [2] is a solid material derived from woody plants, notably trees but also shrubs. Wood is a heterogeneous, hygroscopic, cellular and anisotropic material. Wood is composed of fibers of cellulose (40 %–50 %) and hemi-cellulose (15 %–25 %) held together by lignin (15 %–30 %). [3]

Although wood has been used as fuel for the life of mankind, it is also used as for furniture, weapons, tools, as a construction material, and, of course, boxes, crating and pallets.

There is a strong relationship between the properties of wood and the properties of the particular tree that yielded it. For every tree species there is a range of density for the wood it yields. There is a rough correlation between density of a wood and its strength (mechanical properties) [2].

Wood is commonly classified as either softwood or hardwood. The wood from conifers (e.g. pine) is called softwood, and the wood from broad-leaved trees (e.g. oak) is called hardwood. These names are a bit misleading, as hardwoods are not necessarily hard, and softwoods are not necessarily soft. The well-known balsa (a hardwood) is actually softer than any commercial softwood. Conversely, some softwoods (e.g. yew) are harder than most hardwoods [2].

Water Content. Water occurs in living wood in three conditions, namely: (i) in the cell walls, (ii) in the protoplasmic contents of the cells, and (iii) as free water in the cell cavities and spaces. In heartwood it occurs only in the first and last forms. Wood that is thoroughly air dried retains from 8–16 % of water in the cell walls, and none, or practically none, in the other forms. Even oven-dried wood retains a small percentage of moisture, but for all except chemical purposes, may be considered absolutely dry [2].

Wood packages include baskets (dating back over 12 000 years), barrels (casks), wooden boxes, crates, pallets, and more [4]. In the United States, wooden boxes had a relatively short life cycle, running from the mid 1800s to the 1920s, when they were displaced by the newly invented corrugated and solid fiberboard shipping containers [4].

Wood unsuitable for construction in its native form may be broken down mechanically (into fibers or chips) or chemically (into cellulose) and used as a raw material for other building materials such as chipboard, engineered wood, hardboard, medium-density fiberboard (MDF), oriented strand board (OSB). Such wood derivatives are widely used: wood fibers are an important component of most paper, and cellulose is used as a component of some synthetic materials, for example vinyl windows [2].

10.3.2 Paper

Paper represents the largest proportion of materials used in packaging; representing 34 % by volume and 37 % by weight [5].

The ‘modern’ process of making paper was developed by the Chinese over 2 000 years ago. Prior to that, the Egyptians sandwiched plant material together to form papyrus, a crude but useable form of paper [5].

Paper was hand made until the early 1800s when the Fourdrinier brothers built the first papermaking machine. The fourdrinier machine allows paper to be made in a continuous process, and allows most modern conversion processes to take place, especially those that are web-fed, like printing, bag-making, and corrugating [4]. While an exhaustive discourse on paper making is germane to RFID due to the interest in embedding chips and/or inlays in the paper and box making process, I will leave it to the reader to peruse Twede and Selke if there is sufficient interest.

What is of interest in paper making is the process of paper coating and surface treatments. Pigmented coatings are ‘... used to provide a glossy, white, smooth surface for printing, and are usually applied in line with the papermaking machine.’ Functional coatings ‘... provide a barrier of lacquer, varnish, or plastic and are usually applied in a separate process from papermaking [4]’. These are important issues in that coating and treatments can affect RFID readability and may have to be taken into account during package design or testing.

10.3.3 Plastic

The generic term ‘plastic’ is one of those great descriptors in that it can define almost any material thing to anyone in any situation. There is no single item that immediately defines plastic, and few items that immediately raise the concept of plastic packaging without adding that term into the description. Plastic bag, plastic can, plastic box, etc. As to the role of plastics in packaging, one description notes that ‘the term plastics is used instead of polymer to indicate a specific category of high molecular weight materials that can be

shaped using a combination of heat, pressure, and time. All plastics are polymers, but not all polymers are plastics [6].

The use of plastics in packaging began in earnest around the 1950s. Early uses were plastic bags to replace waxed paper, and plastic used as an adhesive for sealing of paperboard packages [6]. The major benefit of plastics is that its final composition can be uniquely defined dependent on the intended application. Thus, a plastic can be specifically tailored to assist with the functions of packaging. This is generally considered to be a good thing, but bear in mind that this also brings the use of multiple materials into play and can affect RF wave propagation if care is not taken in the material selection.

Because of their adaptability, plastics can readily be used with other non-plastic materials to create combination material laminates. Flexible pouches made of paper, metal and plastic are examples of this. Also, note the adhesive layer that binds metal foils to paper is typically a plastic coating because of its ability to bond to multiple materials where there is no natural affinity to do so.

It is the ability to create specific material combinations that can cause difficulties with RFID. As materials are added to create a package material, the likelihood grows that one of the materials will not be radiolucent. Radiolucency is the property of a material to allow RF wave transmission through the material without deterioration. The more radiolucent a material is, the less impact it will have on a radio signal.

10.3.4 Glass

Soroka defines glass as 'An inorganic compound fused at high temperatures and cooled quickly so that it solidifies to a vitreous or noncrystalline condition. While glass can be made from many inorganic elements, the majority of container glass used for packaging is soda-lime glass, made by fusing silica sand (silicon oxide), limestone (calcium carbonate), and soda ash (sodium carbonate), along with a number of other minerals that help in processing, improve clarity, and provide color [7]'. A typical bottle grade of glass may include calcium oxide (10–12 %), sodium oxide (12–15 %), magnesium oxide (0.5–3.0 %), alumina (1.5–2.0 %), and trace amounts of iron oxide and sulfur trioxide [5].

In designing glass containers, the following benefits are noted: It is rigid, inert, impermeable, and odorless, can be transparent, and come in a variety of shapes, sizes and colors to provide utility and customer appeal [8].

Of import is the use of additional materials and minerals that are added to get the physical and chemical properties desired for the container. Similarly to putting additives in plastics, glass can be radiolucent, or completely block RF energy. Hence, one cannot make the claim that glass, like plastic, is RF friendly, even though this is true for much of the glass market. Users of these materials are advised to define the level of additives when discussing RFID applicability.

10.3.5 Metal

Metal is used in packaging for cans, bottles, closures, trays, pails, drums, bulk containers, racking, strapping, and lamination with papers and films. The most commonly used packaging metals are steel, tin and aluminum. Metal containers have the benefit of being

reasonably inexpensive, thermally stable, rigid, easy to process on high-speed packaging lines, and readily recyclable. Like glass, metal offers a 100 % gas barrier, but unlike most glass, it also offers a complete light barrier [7].

Like glass, metal packaging has come under assault from developments in the plastics industry, though its continued use will be assured due to its having the highest absolute performance in heat tolerance, physical strength and durability, barrier, absence of flavor or odor, stiffness and deadfold [5]. Their use in bulk transport without breakage, and the ability to be completely recycled support their use for many package systems.

10.3.6 Summary of Materials

Each of the discussed materials can have an effect on the tag readability in RFID systems. While each material *can* be read with RFID, this does not mean that all materials can or will be read successfully. For example, dry paper packaging will easily let RF energy waves pass through, though the same material, being hygroscopic (readily absorbs moisture), will increase its barrier properties in a humid atmosphere. Metal packaging easily reflects RF waves, but can be successfully read provided a small offset from the material surface is designed into a tag (3–5 mm), or the frequency of use is altered (moved from 915 MHz to 2.45 GHz).

There is a number of factors that come into play, and the following section will discuss these more fully.

10.4 The Influence of Product and Packaging Materials on RFID

10.4.1 Introduction

Product materials and package materials both play a major role in whether or not RFID can be read. The readability or lack thereof, is the result of complex situations including physics, frequency, localized environment, and product and package material interactions. Physics plays the key role, since interactions are largely a result of physical properties and laws. This section will explain some of these in depth and relate them to how they impact successful RF reads.

10.4.2 How Materials Impact RFID

There are several issues with respect to materials that will affect RFID readability. Chief among these are the following:

- translucency,
- reflection,
- absorption,
- interference, and
- detuning [9].

Translucency refers to the ability of RF waves to pass easily through a material. The easier they pass through a material, the more translucent the material is. Low moisture

materials like paper or plastic having no interfering properties or additives are the most translucent, while these same materials can drastically cut down on wave transmission through increased moisture content (paper) or metalized lamination (plastic).

Reflection of RF waves is akin to shining a laser light onto a mirror. The mirror ‘reflects’ the energy beam away, thereby keeping said energy from reaching and activating the intended transponder. If reflection does take place, the reflected energy could pick up extraneous transponders resulting in phantom tag reads. This phenomenon is well known to users in tag-intensive environments, making shielding, and verification of the intended tag read, a critical requirement or accurate data management.

Absorption of RF signals occurs when the signal strength is weakened through contact with a material or medium. Water is the best known example of this, though other materials also absorb signals, notably graphite or salty foods [9]. The weakening of a transmitted RF signal means that either there is not enough energy to activate the transponder (especially a passive tag), or the transponder response signal is too weak for the receiver to process it. The greater the absorption of RF signals (due to a material), the less translucent that material will be.

Interference is caused by disruption of the RF signal transmissions due to regularly occurring or transient electromagnetic (EM) emanations. Such interfering emanations come from nearby electronic sources, examples of which are high energy electrical wiring or electronic motors. In some cases, the term ‘nearby’ may mean a fair distance away, dependent on the source of the EM. Power stations and large satellite dishes have been known to impact RFID systems, even when not readily visible from a ‘nearby’ supply chain warehouse. The seemingly sporadic nature of the interference can greatly complicate trial pilots or successful RFID implementation. This is the reason that facilities need a full energy audit before an RFID system can be installed and used. Here, a word to the wise is in order: the audit should not be a snapshot, but rather, a lengthened analysis that will note and record transient energy interference.

Detuning most often occurs when multiple transponders are placed in densely packed arrangements. The capacitive coupling from one transponder to another detunes the transponder antennae and renders the tags useless.

10.4.3 Classification of Materials

Packaging materials (and all substrates) should be considered as a resistive medium rather than a translucent energy gate. The material resistance should be recognized as a source of power loss and ‘noise’ generation [10]. In this manner, the impact of materials is more easily understood and compensated for.

The *permittivity* of a medium is an intensive physical quantity that describes how an electric field affects and is affected by the medium. In electromagnetism one can define an electric displacement field D , which represents how an applied electric field E will influence the organization of electrical charges in the medium, including charge migration and electric dipole reorientation.

Materials can be classified according to their permittivity and conductivity. Materials with a large amount of loss inhibit the propagation of electromagnetic waves. In this case, the material would be considered to be a good conductor. Materials with a permittivity that

has a negative real part are considered to be metals, in which no propagating electromagnetic waves exist. Those with a positive real part are dielectrics [11]. Dielectrics are associated with lossless or low-loss materials. A perfect dielectric is a material that has no conductivity, thus exhibiting only a displacement current. Therefore it stores and returns electrical energy as if it were an ideal capacitor [12].

The dielectric constant is defined to reflect the amount of reduction of effective electric field [13]. There are three variables that must be equated in order to characterize the effective field: σ , which is the charge per unit area, dielectric constant ϵ , which is the permittivity of space, and k the increase of capacitance. These variables are related in an equation such as:

$$E_{\text{effective}} = E - E_{\text{polarization}} = \frac{\sigma}{k\epsilon_0} \quad (1)$$

The effect of the dielectric constant reduces the force produced between two electric charges. The velocity of the wave is reduced as it travels through a dielectric, and behaves as if it were a shorter wavelength. Electrically the dielectric constant is a measure of the extent to which a substance concentrates the electrostatic lines of flux. More specifically, it is the ratio of the amount of electrical energy stored in an insulator, when an electrical field is imposed across it, relative to a vacuum [14].

The constant k is used to designate specific materials, each of which has its own constant assigned to it much like that of metals in a periodic table (Table 10.1).

Though robust RFID systems work very well in various environments and conditions, the low-power and short-range RFID signals are easily interfered with, absorbed, and/or reflected by surrounding electronic devices, dielectric materials, large amounts of metallic content, and even by the human body. Thereafter, system performance and stability may be impacted. In a real environment, the RFID interrogator (reader) through an antenna transmits RFID signals that penetrate multiple media, such as wood (pallet), paperboard (box), and various kinds of packaging material and product content. Further, the RFID transponder (tag) backscatters the modulated RF signal to the interrogator along the same path.

Table 10.1 *Dielectric constants for common materials*

Packaging material	Dielectric constant
Corning glass	6.3–6.7
Pyrex glass	4–6
PE	3
PET (Mylar)	2.5
PP	2.6
Nylon	2.4
Paper	3–4
Teflon	2.1
Wood	1.2–5
Vacuum	1 (by definition)
Air	1.0005

With water content from 0 % to 100 % and water ingredients such as salt, the different materials show variable dielectric properties when electromagnetic fields are applied. To differentiate the influence of the amount of water content in any product, tests should be conducted. By measuring the RFID power dissipation and dispersion in the path of the RF signal along with the water concentration, the influence of water in the product with respect to RFID performance and stability may be learned. The influence of dielectric properties on RFID performance and stability may be also profiled through measurement of the dielectric properties of the same samples [15].

10.4.4 RFID Principles that Affect Reads

RFID systems generally operate in several frequency ranges from low frequency (125 kHz) to super high frequency (5.8 GHz). Different frequencies have various advantages and disadvantages for RFID operation. High frequencies have longer read range while low frequencies have less interference from water content and the human body, shorter read ranges and slower data transfer rates. The radio frequency allocations are regulated by the government of a given country and managed by some international organizations, such as Federal Communications Commission (FCC) and International Frequency Registration Board of International Telecommunication Union (IFRB/ITU), respectively. The specific frequency within a range such as UHF may run at different frequencies for different regions, due to frequency availability and regulation. RFID systems operating in UHF (860~960 MHz) are more popular and preferable due to the read range they exhibit (see Table 10.2). The general RFID frequency allocation within each field is as follows:

- LF 125~134 kHz
- HF 13.56 MHz
- UHF 400~960 MHz
- UHF 2.45 GHz (S band)
- SHF 5.8 GHz (C band)

Near Field and Far Field. In LF and HF, the RFID system is mainly based on mutual inductance coupling in which the magnetic field produced by the loop antenna coils rapidly drops off with distance ($1/r^3$) in free space (see Figure 10.1). R is the distance for the path of the signal. The attenuation of a magnetic field limits the read range for all passive RFID devices [16].

Table 10.2 Near field and far field regions

Name	Frequency range	Near field region	Far field region
LF	30 K–300 K	<120 m	>12 km
HF	3 M–30 M	<1 m	>110 m
UHF	300 M–3 G	<1.65 cm	>1.65 m
SHF	3 G–30 G	<0.25 cm	>0.25 cm



Figure 10.1 Attenuation of magnetic strength versus distance in near-field region.

At UHF, the RFID transponder and interrogator communicate in both the near field and far field, which allows broader read ranges and a faster data transfer rate [17]. Near field refers to a region generally in close proximity to the radiation source where the electric and magnetic fields do not indicate a completely plane wave characteristic, but alternate considerably from point to point [18]. The near field is further split into the reactive near-field region, which is the nearest to the radiation source and accommodates most or nearly all of the stored energy, and the radiating near-field region where the radiation predominates over the reactive field but lacks substantial plane-wave character [18]. In the near field, both the electric field (E) and the magnetic field (H) are relatively static, without propagation. Maxwell had proved that beyond the quasistatic near field, both the electric field and the magnetic field, at a certain distance, detached themselves from the conductor and propagated into free space as a combined wave at light speed with a constant ratio of $E/H = 120 \pi = 377 \Omega$ [18].

The critical point at which separation happens is called the far field. This field has a predominantly plane-wave characteristic. Electric field strength and magnetic field strength are represented in transverse planes normal relative to the path of propagation and are separated distributions. In far field, the transmission power of the propagation RF signal attenuates as the inverse square of distance,

$$S = \frac{P_t}{4\pi r^2} \quad (2)$$

where S is signal strength at a distance r from the source and P_t is transmission power. The farther the RFID transponder is from the interrogator, the less RF power can be received from the interrogator. If the distance is less than 1/20th of a wavelength, it is in the near field; if the distance is longer than 5 wavelengths, it is generally in the far field (see Table 10.2). Therefore, at UHF, transponders operate both the far field and transition field (between the far field and near field) [17, 19].

Read Range and Power Assumption. Read range is the maximum distance at which the RFID interrogator and transponder can communicate with each other. Read range is an important specification and characteristic of an RFID system. Active RFID transponders

have longer read ranges compared with those of passive RFID transponders that are completely powered by the received RF energy. The actual read range depends on the frequency, antenna designs and the effective isotropically radiated power (EIRP) [16, 20].

Within this read range, the RFID transponders receive enough RF energy and power up the integrated circuit to backscatter the modulated signal to the reader [21]. LF and HF RFID systems are based on inductive coupling, such as the TI-RFID running at 13.56 MHz. The read range of this kind of RFID system is no more than a few inches. Read ranges of ultra-high frequency RFID systems, for instance 915 MHz, are more than several feet, which is based on electromagnetic backscatter coupling. This system is also called a long range system versus the forward short range system [17].

There are two ways to increase the read range. One is to increase the transmission power and the other is to decrease the minimal threshold operating power required by the transponder or increasing the power conversion efficiency [21]. Read range can be calculated using the Friis free-space formula (notice it is assumed that the read range is in free space):

$$r_{\max} = \frac{\lambda}{4\pi} \sqrt{\frac{P_t G_t G_r (1 - |S|^2)}{P_{\text{th}}}} \quad (3)$$

where λ is the wavelength, P_t is the power transmitted by reader, G_t is the transmitting antenna gain, G_r is the tag antenna gain, P_{th} is the minimum threshold power to power up the tag, and $|s|^2$ is the power reflection coefficient at the tag resonant frequency. $P_t G_t$ is the EIRP [22]. Power or current gain can be expressed as a decibel (dB) value. The dB value is calculated by taking the log of the ratio of the measured power with respect to a reference power multiplied by 10.

$$\left(\text{dB} = 10 \log_{10} \frac{P_{\text{out}}}{P_{\text{in}}}, \quad \text{dBm} = 10 \log \frac{P_{\text{out}}}{1 \text{ mW}} \right). \quad (4)$$

In passive RFID systems, power reflected from the tags is negligible in comparison with the power radiated from the reader. Consequently, the reader might not be able to pick up the coupled response from the tags. A low frequency subcarrier modulated within the RFID system can avoid this occurring. For an RFID system with a carrier frequency of 13.56 MHz, the subcarrier frequency could adopt 847 KHz (1/16), 424 KHz (1/32) or 212 KHz (1/64). This depends on the data transfer rate required in the application, and standards for the system [17].

Electromagnetic Properties

Dielectric Permittivity. Permittivity (ϵ) of a dielectric substance describes quantitative characteristics of any electric field affected by the dielectric substance, which presents the polarized ability of the substance to an applied electric field. In comparison with electrical conductivity (σ), it relates to charge in isolation rather than current. When a voltage is applied to dielectric substance, if there are no free charge carriers, such as electrons and ions, the substance tends to pass current; the voltage source provides the energy to move charge. The charge displaced is restricted by the polarity of molecules in the substance.

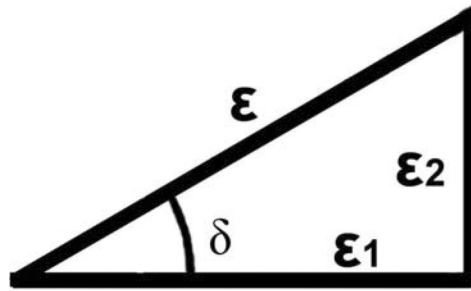


Figure 10.2 Complex permittivity and loss tangent ($\tan \delta = \varepsilon_2/\varepsilon_1$).

Permittivity is a complex, frequency-dependant quantity with the real part and imaginary part, expressed as

$$\varepsilon = \varepsilon_1 \pm j\varepsilon_2 \quad (5)$$

the real part, $\text{Re}(\varepsilon)$ presents the propagation characteristics of the energy. The imaginary part, $\text{Im}(\varepsilon)$ referred to as loss factor represents energy loss in the substance due to polarization of molecules [18]. The sign of the imaginary part is dependant on the numeric sign conversion. The dielectric permittivity of free space ε_0 is 8.85×10^{-12} F/m. Permittivity is usually given as the ratio of that of free space, known as relative permittivity or dielectric constant (ε_r), which is frequency dependent in parts of frequency range, and dimensionless (Figure 10.2). Relative permittivity of free space is defined as 1, relative permittivity of air is about 1.0005 and relative permittivity of water is approximately 80. Higher permittivity of substances stores greater charges with the same applied electric field. As a result, the substance has higher capacitance. For most materials, dielectric constant depends on temperature, frequency, atomic structure, and salinity of the material [23].

Dielectric Absorption. Dielectric absorption indicates the conversion of electromagnetic energy into heat energy. Dielectric absorption has a few mechanisms: relaxation effects associated with permanent and induced molecular dipoles, and resonance effects occurring in the rotations or vibrations of atoms, ions, or electrons [24]. Dielectric relaxation occurs in insulating materials with negligible or low electrical conductivity. Polarization relaxation occurs in high dielectric constant substances. Absorption of the field's energy leads to energy dissipation. The mechanism of dipoles relaxing is called dielectric relaxation and, for ideal dipoles without damping, is described by the classic Debye relaxation [24]. Polarity of a molecular structure and ionized molecules solicits energy dissipation to change the moments of polar molecules in applied electromagnetic fields. The traits of RF absorption in a dielectric substance represent the electromagnetic properties. Dielectric permittivity and loss factor generally represent a material's electromagnetic properties. Radio frequency waves propagate in a straight line in free space. They may be reflected, transmitted or absorbed by dielectric substances in the path. Products, such as foods or drugs with water content, absorb RF energy and transform it into heat. A typical example that describes this process is a microwave oven in the kitchen.

Water Content in Foods

Water Activity. Foodstuffs and medication materials contain water. As a polar molecule, water can be partly aligned by an applied electric field; however, there are forces in water preventing its molecules from moving freely. Thus, the energy counteracting this resistance is transferred to the ions and then to neighboring atoms or molecules. Food products or any material containing such charged ions are able to interact with any electric fields. Water absorbs radio frequency energy and turns it into heat [25].

Water content is a very important factor in determining food quality, shelf stability and textural properties. Natural moisture content in produce offers freshness and quality. The crisp, fragile biscuit or one in a limp state is determined by the water content and its distribution within the biscuit. To maintain the special textures and flavors in a food product, the food ingredients strictly limit the water content and distribution within the food product. Controlling the water activity and reactivity with unbound water content in food product will really help to attain food stability. In spite of the microstructure, local viscosity and associated molecular mobility are very important to food stability. Nevertheless, moisture content is one of the key factors in determining these parameters of a food matrix [26]. To extend the shelf life, adjusting the water content is a common approach. Sublimation or evaporation is often used to remove liquid water to enhance the product stability [27].

Water Forms. The water molecules in foods appear in different forms depending on surrounding molecular environments, generally in forms that have different physicochemical properties as follows:

- (i) Free water. Water in this form is enveloped by other water molecules only. The physicochemical properties are the same as these of pure water.
- (ii) Capillary water or trapped water. Water in this form is enveloped by a physical barrier or retained by tiny channels. The physicochemical properties are the same as those of free water due to normal water–water bonding in this form.
- (iii) Bound water. Water in this form is partly enclosed by other food components in molecular contact, which leads to a significant difference in physicochemical properties as compared with free water.

Due to different bonding existing in foods, they are considered as heterogeneous mixtures from the standpoint of chemistry, though the macrostructure of the food material may be homogeneous [28, 29].

Dielectric Properties. The state of water in a food substance lies in the degree of interaction between water molecules and the glassy solid pertaining to hydrogen bonding. Lechuga-Ballesteros *et al.*, [30] found that the proportion of high mobility water molecules at 1 GHz increased for hydration levels above the hydration limit [31]. Thus, more water molecules are relatively free to respond to applied electric fields and show a dipole moment near to gaseous water molecules due to hydration-induced conformational changes. The dielectric parameter increase is proportional to the increasing of water concentration in the foods [31].

The amount of water content in a material greatly affects its electromagnetic properties [32]. Water has a high dielectric constant at room temperature (see Table 10.3). Dry materials have low dielectric constants often less than 10. Therefore the percentage of water

Table 10.3 Dielectric properties of foodstuffs and other packaging materials at 2.45 GHz and 68 °F (Source: Sacharow and Schiffman: *Microwave Packaging* [31])

Substance	Dielectric constant	Loss factor	Loss tangent
Water	80	12.5	0.16
Mashed potato	65	22.1	0.34
Cooked ham	45	25.2	0.56
Peas	63	15.8	0.25
Most plastics	2~4.5	0.002~0.09	0.001~0.02
Woods	1.2~5	0.01~0.5	0.01~0.1
Papers	3~4	0.15~0.4	0.05~0.1

content in the substance is indicative of the dielectric properties. A high water percentage usually shows proportional increases of the loss factor of the substance and a high dielectric constant. The dielectric constant of a mixed substance commonly is based on its components and stands between the medial of its components. Dielectric loss has a complicated transaction mechanism. For example, it may increase 20~30 % with raising the water content percentage of the substance, and then decrease rapidly [32].

Material Combinations. Typically, combinations of materials depict the worst scenario. While the material structure may represent the best possible physical structure for a given product/package system, it offers the worst RFID-friendly aspect of each individual material/layer within the structure.

10.5 The Influence of Packaging System Characteristics on RFID

10.5.1 RF Interference Issues

It is critical to consider radio frequency interference issues when implementing RFID systems, and to recognize that interference can be caused by a number of packaging materials.

The maximum concern comes from the properties of waves, which seem to undergo very strong alterations when exposed to metals. When using RFID technology, the metal of certain packages significantly impacts the readability rate of the antenna from the transponder. A corrugated tray that holds aluminum cans, for example, can have little to no readability when it is passed through a portal of antennas. Granted, frequency, tag antenna design and careful site selection can greatly improve readability (from zero), but this is not common with low cost, Gen 2, tags.

Wave interference is the phenomenon that occurs when two waves meet while traveling along the same medium. The interference of waves causes the medium to take on a shape that results from the net effect of the two individual waves upon the particles of the medium [33, 34].

Wave interference can occur in two forms: constructive interference and destructive interference (Figure 10.3). Constructive interference takes place when two waves meet in the same medium, and end up overlapping and taking the same form. This type of response

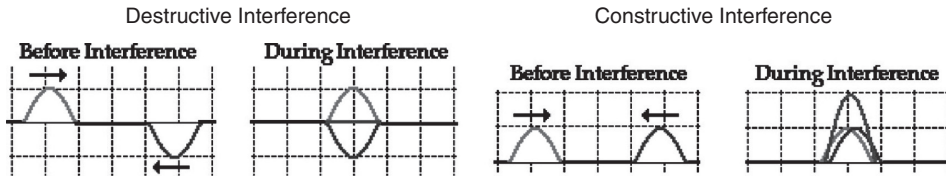


Figure 10.3 Constructive and destructive interference charts [32].

produces a complementary system of transmitting frequency in a clear and readable form. Destructive interference is a type of interference that occurs at any location along the medium where the two interfering waves have a displacement in the opposite direction [35]. When a frequency is traveling from the antenna to the transponder, the response is cancelled or changed in a manner to produce little to no readability. Metal creates destructive interference by doing just that, canceling or changing frequency via the material makeup of the metal. The antenna, in the case of RF, after not receiving the frequency in which it has transmitted, searches for another method to verify the drastically changed waveform to another bandwidth, but fails, thus resulting in no reads.

It is widely accepted that metal and water have a detrimental affect on the operation and use of radio waves. Metal reflects radio waves while water absorbs radio waves, making these two materials very difficult to use around and with RFID systems [35]. Many products falling under RFID mandates contain metal and water, and solutions to make RFID systems work in their presence are not commercially available at an economic price. Products with high water content included in this category are shampoo, soft drinks, juices, fruits and vegetables to name a few. Products containing high metal content or metal within their packages may cause problems with RFID systems. Products and packages in this category include: steel and aluminum cans, some powdered detergents, foil laminated bags and pouches, metal bins and totes [36].

RFID testing that has been conducted on these types of product includes testing conducted by Hewlett-Packard, Gillette and BP Castrol. Hewlett-Packard has been able to overcome the problems associated with water and metal in their ink cartridges by changing the orientation in which they were packed [37]. Gillette has run RFID pilots, at the case and item level, with their razorblades for the Metro Group with mixed success [38]. RFID testing has been done by BP Castrol on its GTX 5-quart container of motor oil with results depending on location of the tags relation to the lubricant in the bottles [39]. A graduate student at Michigan State University's School of Packaging conducted research on the RFID transponders ability to read through refrigerated and frozen beef loin muscle. The research found that the tags performed successfully when reading through frozen beef and were unsuccessful when reading through refrigerated beef, thus showing liquid water is a problem area [40].

There are many other factors that can cause interference and are not addressed by known research. The effect of packaging and packaging materials on RFID systems is not widely known or publicized. Everything from packaging materials to packaging additives may have an effect on the readability of RFID tags. However, since the discipline of packaging enjoys limited understanding, little research has been done specifically on it. RFID tracking of reusable plastic containers, totes and pallets is being conducted by CHEP; Trenstar is tracking kegs of beer and AIS is tracking metal carts for flowers all using RFID [41]. The

technology is being used with a variety of packaging materials; however, little information is available about the efficiency of the RFID systems being used. Rick Fox, president and CEO of Fox IV Technologies, notes the following: ‘The functionality of the RFID tag will change based on the position of the tag on the container, the type of product in the container, the pallet packaging configuration and the power of the tag reader’ [42]. Until further researched, the effect these variables have on RFID systems will remain the proprietary knowledge of the leading companies implementing RFID, which will not help the technology, on the whole, to grow and succeed [36].

Interference with RFID systems goes beyond packaging materials and product properties. Operating systems and other wireless communication devices in a facility can create RF noise and interrupt the ability of RFID tags and readers to communicate properly. These systems may include wireless communication on handheld scanners, cell phones, robots and/or computers. Operating equipment such as conveyors, fork trucks, filling and sealing equipment can also have negative effects on the operation of an RFID system. In hospitals, different electromagnetic interference becomes a major issue, with the inability for certain systems to work coherently alongside each other.

The effect of static discharge on tags is not widely known and could lead to an inability of tags to read. RFID tags are also affected by the speed at which they pass through the read field, though successive generations of tags mitigate this issue to some degree. The faster a tag travels through the field the less likely it is going to be read. Multiple RFID readers, antennae and tags in an area can have an adverse affect on the systems operating correctly; this phenomenon is known as collision and proper shielding becomes a primary concern.

The results of one early experiment shows that tag orientation and package content have a considerable effect on the readability of RFID transponders when viewed as a pallet load of product (Figure 10.4). The physical characteristics of the product in the package coupled with the orientation of the tag lead to a significant amount of no-reads in certain instances. On the other hand, 100 % of the tags were read in the nine experiments using empty cases, foam-in-place filled cases, and empty bottle filled cases coupled with outward, forward and upward tag orientations [36].

The following few sections will help in understanding Figure 10.4 and how it can be of use in evaluating product/package systems with respect to RFID readability. With respect to Figure 10.4, note that the red rows demonstrate statistically significant variation as a result of product content, the yellow columns demonstrate statistically significant variation as a result of tag orientation, and the combination (orange) cells represent the worst condition from both effects.

While technological change has progressed since this research was completed, this should not diminish the findings that product content, tag orientation and case location all contribute to the difficulties in RFID reading.

Product Contents. The effect of package content on the RFID tag’s ability to read was not evident for certain products. Empty cases, cases filled with foam-in-place and cases filled with empty polyethylene terephthalate (PET) bottles showed no major statistical difference between total read rates for any orientation. However, rice and filled water bottle cases show major statistical differences between each other and the three products discussed above when evaluated, based on total reads. In this work, it was found that filled water bottle cases and rice filled cases have the greatest effect on the readability of RFID tags. Note that dry rice does not have any noticeable water content and would not normally come

		TAG ORIENTATION				
		OUTWARD	INWARD	FORWARD	UPWARD	DOWNWARD
PRODUCT	Total Tag Read % (Standard Error %)					
	EMPTY	100% (0%)	97.1% (0.8%)	100% (0%)	100% (0%)	97.8% (0.4%)
	FOAM	100% (0%)	98.6% (0.4%)	100% (0%)	100% (0%)	98.0% (0.4%)
	EMPTY BOTTLES	100% (0%)	97.0% (0.5%)	100% (0%)	100% (0%)	99.3% (0.2%)
	RICE	99.7% (0.4%)	60.5% (0.9%)	82.6% (0.6%)	82.3% (0.9%)	78.3% (1.3%)
WATER BOTTLES	67.0% (0.2%)	0.8% (0.3%)	32.3% (0.6%)	25.0% (0%)	0% (0%)	

Notes:
 Data in each cell represent percentage of 1200 tag reads (25 trials of 48 cases on a pallet). For example, when the cases contained rice and the tags faced inward (to the center of the pallet rather than out), 60.5% or 726 out of 1200 total tags read correctly. A total of 25 runs (i.e. tags oriented OUT with EMPTY cases) of 25 samples (with each sample comprising a pallet of 48 cases) were made.

Significant Findings:
 RED = Product Specific Yellow = Orientation Specific Orange = Both

Figure 10.4 Results of Tazelaar experiment on product/package influence on RFID readability.

to mind as far as causing interference. Its interference, like that of dry dish washing powder, is more a result of the product metal content (iron) than it is of water content.

Tag Orientation. When evaluating the data from rice and filled water bottle cases, tag orientation on readability became evident. Rice and water were the only products tested that showed significant statistical differences between total tag reads for the designated tag orientations. A major difference due to tag orientation was noticed in the number of trials having 100 % reads, although orientation did not have an effect on the overall number of reads for empty cases, foam-in-place filled cases or empty-bottle filled cases. Because tag orientation had no effect on the overall number of reads for these three products, they will not be used in evaluating the effect tag orientation has on the readability of RFID transponders.

Water plays a significant role in the readability of RFID tags; therefore, the orientation of the tag on a case of liquid product also has consequences in the readability of the tags. Water absorbs ultra-high frequency (UHF) radio frequency waves and, therefore, any cases with tags not in the direct line-of-sight for the RFID system antennae have extreme difficulty in reading, causing the system to be ineffective. This phenomenon is also found in reading pallet loads of aluminum and steel beverage cans in corrugated trays, fiberboard cartons, and corrugated cases, respectively.

When looking at the total number of reads, tags facing inward and downward had the greatest effect on the readability of RFID tags. Tags facing outward were impacted the least by products. Tags facing forward, upward and outward read 100 % of the time for

empty, foam and empty-bottle filled cases. However, tag and reader advances mean that these specific orientations cannot be cited as a given result for any product/package system. Rather, it is specific to this experiment and, as such, individual results should be established for any and all systems.

Orientation played a large role in the readability of tags when evaluating the number of trials with 100 % case reads. This is not evident for water-bottle filled and rice-filled cases, in that they had no 100 % reads in any single trial except for the rice filled cases with tags facing outward, which had four. For empty, foam-in-place and empty-bottle filled cases, tags facing inward and tags facing downward had the greatest effect on the readability of RFID tags; tags facing forward, upward and outward read 100 % of the time.

Case Location in Pallet Stack. The location of the case on the pallet played a role in the ability of the RFID tag to read consistently. Cases were grouped based on the tier where they were located, the row where they were located, and in what column they were located.

No statistical analysis was done on the data obtained from the evaluation of this information. However, it should be noted that case location appears to play a role in the readability of RFID transponders. The following analyses and breakdown are general observations and should be viewed accordingly.

With this antennae set-up (portal arrangement) the tier, or layer, of the cases on the pallet plays a role in the readability of the tags. The lower the layer, the less likely the RFID tags are to read.

The row in which a case was located also played a significant role in the readability of the tags, with certain product types. The middle rows had a greater number of no-reads than did the outer rows. Because the middle row tags were not in the direct line-of-sight of the system antennae, the radio waves had to penetrate more material to reach the transponder, and thus it is likely that more interference due to the product and/or package materials was experienced. This occurrence was not consistent across all product types and was generally observed when the product being tested was not radiolucent.

The effect of orientation on the readability of RFID tags is closely associated with the product being tagged. When the product being tagged is radiolucent (RF signals can easily penetrate their materials) orientation plays a smaller role than when RF signals cannot pass through the product. The ability to read tags on non-radiolucent products is due to tags being in the direct line-of-sight of the system antennae and not having to penetrate the product, making those orientations with a greater number of tags in the direct line-of-sight of the system antennae more effective.

The column in which the cases were located also had an effect on the readability of the transponders. The closer the RFID tags are to the pallet jack or forklift, the less likely they are to be read. This is likely due to the close proximity of these cases to the electronic pallet jack and the resultant interferences from metals or the power source of this machine.

In other instances, the readability of the tags could be increased based on the column position. For instance, when reading cases filled with water bottles having the tag orientation facing forward, column four, the front most column, experienced 100 % reads. All other columns had 0 % reads. This observation is also found in evaluation of trays of produce. Experiments on pallets of cased lettuce, peaches and strawberries found similar results. (Figures 10.5, 10.6, 10.7 and 10.8). In these figures, white represents 100% reads, and solid red represents 0 % reads in 25 replications. Shades of pink are denoted by the percentage

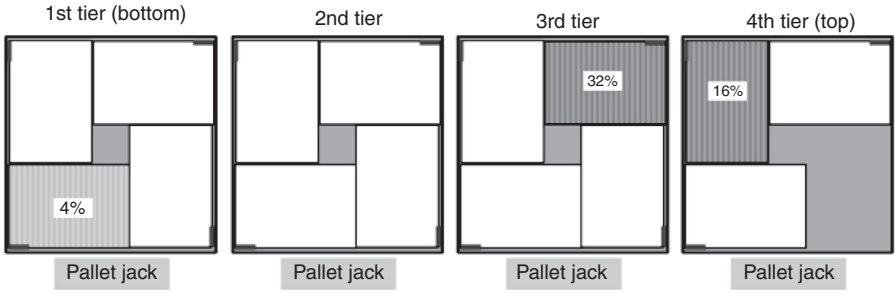


Figure 10.5 Lettuce cases tagged on long side, externally.

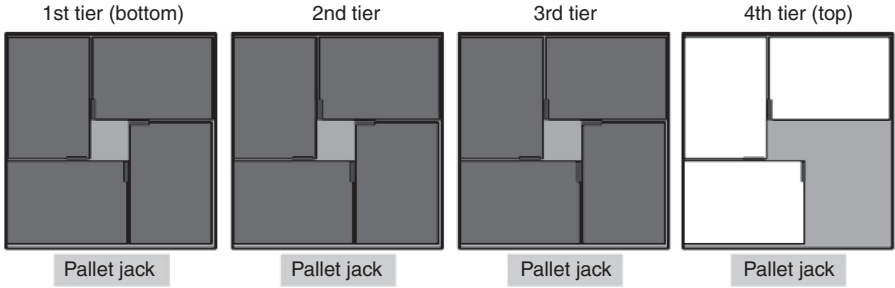


Figure 10.6 Lettuce cases tagged on short side, internally.

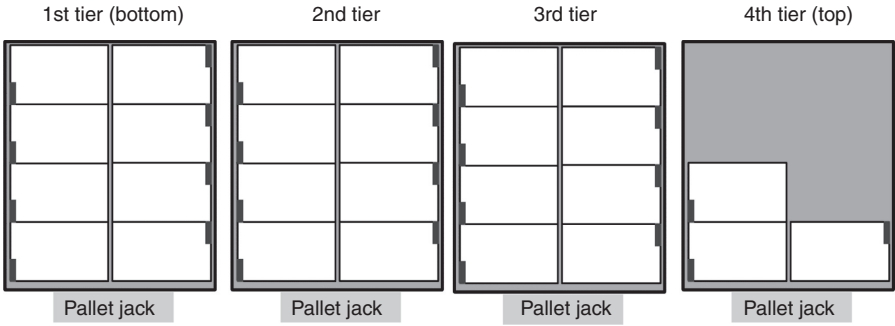


Figure 10.7 Strawberry cases tagged on short side, externally.

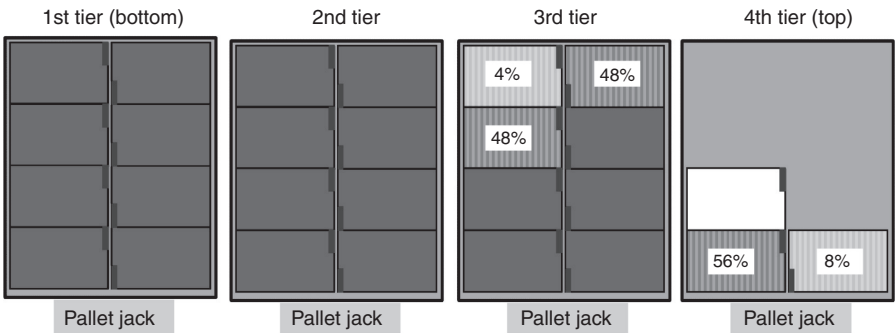


Figure 10.8 Strawberry cases tagged on short side, internally.

of successful reads. The top tier of the internal tags allowed signal access, thereby allowing successful reads for those cases.

From the information and evaluation of the case location data, a general conclusion can be made. For certain pallet patterns, strategic tag orientation and/or locations can overcome or minimize limitation problems based on physics. Taking this a step further, it becomes imperative that each and every product/package combination be tested to insure that the pallet pattern, and tag location and orientation are operational throughout the respective supply chain.

10.5.2 Conveyor Speed, Tag Location, Package Materials, and Package Shape as They Influence Readability

Since the first mandates put forth by Tesco, Metro, Marks & Spencer, Wal-Mart, and the US Department of Defense, the use of UHF radio frequency identification (RFID) has been implemented into supply chains with mixed results. When working optimally, RFID can provide valuable information regarding inventory data and shipment locations. However, tag readability issues exist due to a variety of reasons: product and package interference, RFID equipment set-up locations, and even frequency allocations, depending on the country of use.

It is almost inevitable that a package will travel on a conveyor at some point during the manufacturing and distribution process. Since tracking product movement is one of the key aspects of RFID, it is important to determine if RFID antennae are able to track tagged packages on conveyors.

There is no one specific method for using RFID technology, nor is there one specific solution to be applied across industries. For RFID to work most advantageously within an organization's supply chain, the implementer must think of each product on an individual level. An RFID tagged product, Product A will not function equally to a tagged Product B if there are differences in the product composition and the package system. Additionally, optimal tag type, tag location and orientation, antenna location and orientation, reader location and broadcast strength, and even the cord length between the reader and the antennae, are among the variables that implementers of the technology need to consider when trying to optimize the readability of an RFID tagged product.

In the event that a retailer has implemented RFID mandates to suppliers, both shipper and receiver must work collectively to optimize performance and usefulness in the supply chain. Specifically, the read location (where the tag is to be detected) can have a significant impact on successful RFID utilization. Suppliers will have to ensure that they have tested their product at each read point in the supply chain process in order to avoid failing to meet mandates that could lead to financial losses. Traditional read locations for RFID tags are warehouse dock doors, stretch wrappers and fork trucks, or conveyors.

RFID Read Locations. It is evident that retailers, suppliers, and organizations are working with RFID systems across the globe. However, the point in the supply chain where implementers determine to set up an RFID system to gather data, known as read point or location, varies. In retail applications, an obvious point to set up an RFID system and collect data is by a dock door. The purpose of a dock door is to provide a medium where all products

arrive and depart, making it an excellent location for tracking inventory. Generally, a portal contains, but is not limited to, four antennae positioned in various locations around the door, in order to detect accurately tags entering and exiting the facility.

A shrink-wrap station is another typical data collection point. This is an excellent data capture point because most stretch wrappers offer 360 degrees of visibility of the product (more importantly, of the tags), and, the stretch wrapping process takes more time than walking through a dock door, which increases the chance that all tags are detected. Multiple stretch-wrap machines exist, and how they operate determines where the RFID system will be set up. In some instances, a portal similar to that used in the dock door situation can be placed around the stretch wrapper. Other stretch-wrap machines are equipped with an arm that rotates around the pallet, in which case an RFID antenna can be affixed to the arm itself.

Fork trucks, used to transport product into, out of, and within warehouse facilities, provide another medium for an RFID system placement. An antenna placed on the front of the fork truck is capable of reading the tags located on the pallet load, ensuring that drivers are carrying the correct product and placing it in the desired area, whether it is the back of a destination-bound truck, or in storage.

Of all the examples discussed, dock doors, stretch wrappers, and fork truck read locations focus on the detection of products on a unit load, like a pallet. Unit loads generally contain a large number of case loads, which contain the individual product(s). During the distribution process these case loads either need to be placed onto, or removed from, the unit load. DCs generally use conveyors to move the case loads to and from storage [43]. Thus, conveyors offer an excellent location for a RFID read point by confirming that the correct case has been pulled from storage, and is bound for the correct re-palletization area.

Types of Conveyors. Conveyors generally operate by using either gravity or power to move an object from point to point. A wide variety of conveyors exist, each performing a specialized function. Some of the most common types of conveyor are those containing either a belt or roller bars.

A belt conveyor is composed of fabric, rubber, plastic, leather, or metal and operates over drive, tail end and bend terminals [45]. Belt conveyors are versatile, provide a continuous flow of product, and are low maintenance. They are mainly used for carrying units, cartons, and bags. However, a modern-day example is the use of the belt conveyor as a people mover in high traffic areas such as airport terminals.

Roller conveyors tend to use gravity for product movement. On a roller conveyor the load is supported over a series of rolling bars, turning on fixed bearings that are mounted between side rails at fixed intervals. Product moving on a roller conveyor requires three rollers under the load at all times. Product movement is controlled by gravity; therefore, heavy loads on roller conveyors can be dangerous, as they could accelerate beyond control. Slides in parks for children are often built in roller bar conveyor form, because the acceleration due to gravity can be a source of excitement [45].

A wide variety of other conveyor types exists, including bucket, chain, chute, pneumatic, screw, vibrating, and wheel conveyors. Although they are mainly used for material handling, conveyors also function throughout society as people movers. Ski chair lifts on mountains are another functional example [46].

10.5.3 Procedure for Testing RFID-Tagged Case Loads on Conveyor

In this section, the methods and apparatus used to determine if conveyor speed, packaging materials, and product have an effect on the readability of RFID transponders is examined. The variables for this testing were conveyor speed [300 feet per minute (fpm), 600 fpm], package type [case of chips in plastic tubs, case of chips in metalized spiral wound fiberboard containers (MSWFC)], package shape (case of metal cans, case of metal bottles, and case of metal tins), product type (case of bottled ketchup, case of bottled motor oil) and tag generation (Alien Gen 1, Alien Gen 2) [43].

In total, seven different consumer products were used to evaluate the effect of the five variables tested. To test the product effect a case of ketchup was compared to a case of motor oil. To test the package effect, a case of potato chips in a metalized spiral wound fiberboard container was compared to a case of potato chips in plastic tubs. To test the effect of package shape, three products were used; a case of metal cans, a case of metal tins, and a tray of metal bottles.

Throughout the testing of the seven products, both the tag type and equipment used were held constant throughout the entire testing procedure. Two procedures were performed on the cases.

The product, package and case were tested in a warehouse. In addition, two other variables were tested: speed [600 and 300 feet per minute (fpm)] and tag type (a Generation 1 tag and a Generation 2 tag). Each test consists of 30 trials (per changed variable) for statistical needs.

Prior to testing, the tag ‘sweet spot’ for the individual cases were determined [47]. In actuality, this testing looked for hotspots where RF energy was sufficient to activate a tag (Figure 10.9). Changing the product, package material, or package shape will probably require a new tag location for optimal reads, given a properly designed package. Defining one tag location for all products, materials or shapes is dim-witted at best, and will likely cause poor reads throughout the supply chain.

In general, a red response is a poor location to place a tag, a white response is an okay position to place a tag, and a green response is an excellent location to place a tag. The variance in color is due to a variety of interference possibilities due to packaging materials or product content.

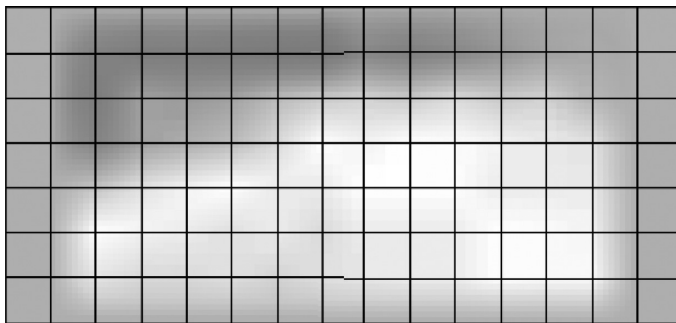


Figure 10.9 Example RFID hotspot result for one side of a case [46].

The results demonstrate that a simple test can be used to identify the RFID tag hotspots. Furthermore, rigorous experiments can be performed to determine if conveyor speed, package type, package shape, and product type all have significant effects on the average amount of tag reads per trial [43].

The results of the testing described in the previous chapter show that conveyor speed had a significant impact on the average number of tag reads per trial for RFID transponders on packages. Additionally, product type, package type, and package shape all had a significant impact on the average number of tag reads per trial for RFID transponders on packages moving on a conveyor. The results also show that the tag type had a significant effect on the average number of tag reads per trial for product type (ketchup and motor oil), and package shape (cans, bottles, and tins), but did not have a significant impact on average number of tag reads per trial for RFID transponders that were placed on the package effect products [plastic tubs and metalized spiral wound fiberboard containers (MSWFC)]. The outcomes of the evaluation are listed in the following section.

10.5.4 The Effect of Conveyor Speed on the Product Effect Test. Ketchup and Motor Oil: Two-Way Interactions

Product by Speed. In studying the difference in the average number of tag reads per trial between products by speed, some overall conclusions can be formed:

- When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.
- When *products* and *speed* were the two variables, speed was the dominant variable, making either product average more tag reads per trial when moving at 300 fpm compared to the product moving at 600 fpm.

Tag Type by Speed. In studying the difference in the average number of tag reads per trial between tag types by speed, some overall conclusions can be formed:

- When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.
- When *speed* and *tag types* were the two variables, speed was the dominant variable, making either generation of tag average more tag reads per trial when traveling at 300 fpm versus 600 fpm.

10.5.5 The Effect of Conveyor Speed on the Product Effect Test, Ketchup and Motor Oil: Three-Way Interactions

Ketchup–Ketchup Interactions. In studying the difference in the average number of tag reads per trial between product (ketchup) by tag types by speed, some overall conclusions can be formed:

- When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.

- When *speed* and *tag types* were the two variables, speed was the dominant variable, making either generation of tag average more tag reads per trial when traveling at 300 fpm versus 600 fpm.

Ketchup–Motor Oil Interactions. In studying the difference in the average number of tag reads per trial between products (ketchup and motor oil) by tag type by speed, some overall conclusions can be formed:

- When the *products* and *speed* were the two variables, speed was the dominant variable, providing more average reads per trial for the product moving at 300 fpm compared with the product moving at 600 fpm.
- When *products*, *tags*, and *speed* were all variables, speed was the dominant variable, providing more average reads per trial for the product and tag moving at 300 fpm, compared with the product and tag moving at 600 fpm.

Motor Oil–Motor Oil Interactions. In studying the difference in the average number of tag reads per trial between products (motor oil) by tag type by speed, some overall conclusions can be formed.

- When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.
- When *speed* and *tag types* were the two variables, speed was the dominant variable, making either generation of tag average more tag reads per trial when traveling at 300 fpm versus 600 fpm.

10.5.6 The Effect of Conveyor Speed on the Package Effect Test. Chips in Plastic Tubs and Chips in MSWFC: Two-Way Interactions

Product by Speed. In studying the difference in the average number of tag reads per trial between products by speed, some overall conclusions can be formed:

- When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.
- When *product* and *speed* were the two variables, speed was the dominant variable, making either product average more tag reads per trial when moving at 300 fpm compared with the product moving at 600 fpm.

Tag Type by Speed. In studying the difference in the average number of tag reads per trial between tag types by speed, some overall conclusions can be formed:

- When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.
- When *speed* and *tag types* were the two variables, speed was the dominant variable, making either generation of tag average more tag reads per trial when traveling at 300 fpm versus 600 fpm.

10.5.7 The Effect of Conveyor Speed on the Package Effect Test. Chips in Plastic Tubs and Chips in MSWFC: Three-Way Interactions

MSWFC–MSWFC Interactions. In studying the difference in the average number of tag reads per trial between product (MSWFC) by tag types by speed, some overall conclusions can be formed:

When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.

When *speed* and *tag types* were the two variables, speed was the dominant variable, making either generation of tag average more tag reads per trial when traveling at 300 fpm versus 600 fpm.

MSWFC–Plastic Tub Interactions. In studying the difference in the average number of tag reads per trial between product (plastic tubs and MSWFC) by tag type by speed, some overall conclusions can be formed:

- When the *product* and *speed* were the two variables, speed was the dominant variable, providing more average reads per trial for the product moving at 300 fpm compared with the product moving at 600 fpm.
- When *product*, *tags*, and *speed* were all variables, speed was the dominant variable, providing more average reads per trial for the products and tags moving at 300 fpm compared with the products and tags moving at 600 fpm.

Plastic Tub–Plastic Tub Interactions. In studying the difference in the average number of tag reads per trial between products (plastic tubs) by tag generation by speed, some overall conclusions can be formed:

- When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.
- When *speed* and *tag types* were the two variables, speed was the dominant variable, making either generation of tag average more tag reads per trial when traveling at 300 fpm versus 600 fpm.

10.5.8 The Effect of Conveyor Speed on the Package Shape Effect Test. Metal Bottles, Metal Cans, and Metal Tins: Two-Way Interactions

Product by Speed. In studying the difference in the average number of tag reads per trial between products by speed, some overall conclusions can be formed:

- When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.
- When *product* and *speed* were the two variables, speed was the dominant variable between only bottles and cans. The product moving at 300 fpm always averaged more tag reads per trial than the product moving at 600 fpm.

Tag Types by Speed. In studying the difference in the average number of tag reads per trial between tag types by speed, some overall conclusions can be formed:

- When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.
- When *speed* and *tag types* were the two variables, speed was the dominant variable, making either generation of tag average more tag reads per trial when traveling at 300 fpm versus 600 fpm.

10.5.9 The Effect of Conveyor Speed on the Package Shape Effect Test. Metal Bottles, Metal Cans, and Metal Tins: Three-Way Interaction

Bottle–Bottle Interaction. In studying the difference in the average number of tag reads per trial between products (bottles) by tag types by speed, some overall conclusions can be formed:

- When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.
- When *speed* and *tag types* were the two variables, speed was the dominant variable, making either generation of tag average more tag reads per trial when traveling at 300 fpm versus 600.

Can–Can Interaction. In studying the difference in the average number of tag reads per trial between products (cans) by tag types by speed, some overall conclusions can be formed:

- When *speed* was the only variable, 300 fpm always averaged more tag reads per trial than 600 fpm.
- When *speed* and *tag types* were the two variables, speed was the dominant variable, making either generation of tag average more tag reads per trial when traveling at 300 fpm versus 600 fpm.

Tin–Tin Interaction. In studying the difference in the average number of tag reads per trial between products (tins) by tag types by speed, some overall conclusions can be formed:

- (i) When *speed* was the only variable:
 - With the case of tins traveling 300 fpm and the case of tins traveling 600 fpm equipped with a Gen 1 tag, there was no statistical difference in the average number of tag reads per trial.
 - With the case of tins traveling 300 fpm and the case of tins traveling 600 fpm equipped with a Gen 2 tag, speed was the dominant variable, with the case of tins moving at 300 fpm averaging 40.4 more tag reads per trial.
- (ii) When *speed* and *tag types* were the two variables:
 - With the case of tins with a Gen 1 tag was moving 300 fpm, there *was not* a significant statistical difference in the average number of tag reads per trial compared with the case of tins with a Gen 2 tag moving 600 fpm.
 - The case of tins with a Gen 2 tag moving 300 fpm, averaged more tag reads per trial than the case of tins with a Gen 1 tag moving 600 fpm.

- Since the dominant tag type and dominant speed prevailed in this particular scenario, it is difficult to say that speed or tag type was the dominant variable in this three-way interaction.

Bottle-Can Interactions. In studying the difference in the average number of tag reads per trial between two products (bottles and cans) by tag generation and by speed, some overall conclusions can be formed.

- When *products* and *speed* were the two variables, speed was the dominant variable, providing more average reads per trial for the product moving at 300 fpm compared with the product moving at 600 fpm.
- When *products*, *tags*, and *speed* were all variables, speed was the dominant variable, providing more average reads per trial for the product and tag moving at 300 fpm compared with the products and tags moving at 600 fpm.

10.6 Chapter Summary

This has been a review of the influence of product and package materials characteristics on RFID readability. Both can, and do. Keep in mind, RF is just a technology and that other technologies can and do work.

Backup for most RFID systems is a bar code, and 2-D systems can carry as much data, and have serialization. One *must* take the systems approach and look at system costs, not just price. As with any technology, it is difficult to use with a global supply chain, since a faulty link results in system error and inefficiencies. This is still not ready for prime time (in packaging), in spite of earlier hype. Still, one should plan for actions should failures occur, but it is appropriate to use if an ROI is present, or if mandated by retailers or government.

With the knowledge that conveyor speeds can potentially have a drastic effect on RFID tag readability, it is crucial that suppliers meeting RFID mandates communicate with their retailers regarding their distribution center and conveyor speed operations. Armed with this information suppliers can guarantee that their tagged product will be detected at retailer RFID checkpoints, ensuring payment for their product. With retailers having knowledge of the tagged product's location, they are less likely to incur a situation in which a product is out of stock, and through this, retailers are able to increase product sales.

The results of the last testing described in the chapter show that conveyor speed had a significant impact on the average number of tag reads per trial for RFID transponders on packages. Additionally, product type, package type, and package shape all had a significant impact on the average number of tag reads per trial for RFID transponders on packages moving on a conveyor. The results also show that the tag type had a significant effect on the average number of tag reads per trial for product type (ketchup and motor oil), and package shape (cans, bottles, and tins), but did not have a significant impact on average number of tag reads per trial for RFID transponders that were placed on the package effect products [plastic tubs and metalized spiral wound fiberboard containers (MSWFC)].

In the product effect, package effect, and package shape effect tests, conveyor speed had a significant effect on the percentage readability of transponders. The average amount of

tag reads per trial with the conveyor operating at 300 feet per minute (fpm) was always significantly greater than the average amount of tag reads per trial with the conveyor operating at 600 fpm.

In all two-way and three-way interactions involving conveyor speed, speed had a significant effect on the average number of tag reads per trial, acting as the dominant variable in the interactions for the product effect products, the package effect products, and the product shape effect products (not involving tins).

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11

How Marks & Spencer is Using RFID to Improve Customer Service and Business Efficiency: A Case Study

James Stafford

RFID (radio frequency identification) is the latest technology to be used by leading retailers to improve their operations. Within Marks & Spencer the technology is being used to speed up some processes and to make others more accurate. Improvement to speed and accuracy of information, particularly information on stocks, is a key way of improving customer service.

This technology works through the use of a small electronic microchip connected to an aerial. This combination is generally known as an RFID tag. The most common type is called a passive tag, which contains no battery and only starts to work in the presence of an RFID tag reader. The reader emits a very low power radio wave that is picked up by the tag and converted to an electric current. The current 'wakes-up' the tag and in turn it sends a weak radio signal back to the reader containing some basic information that has been held in the tag memory. The reader can then pass this information back to a central data base and, in some cases, write some new information to the tag memory. As soon as the reader moves away from the tag it stops working as it has no independent power source, but it will still retain some information in memory (Figure 11.1).

This technology is not new as it has been around since 1940 when it was developed for aircraft identification. What is new is its affordability and miniaturisation, which has enabled it to be used in everyday items such as car keys and rail travel passes.

It may seem surprising that such an apparently new technology should be of interest to a retailer of clothing, foods and home items. The reason is that Marks & Spencer, like

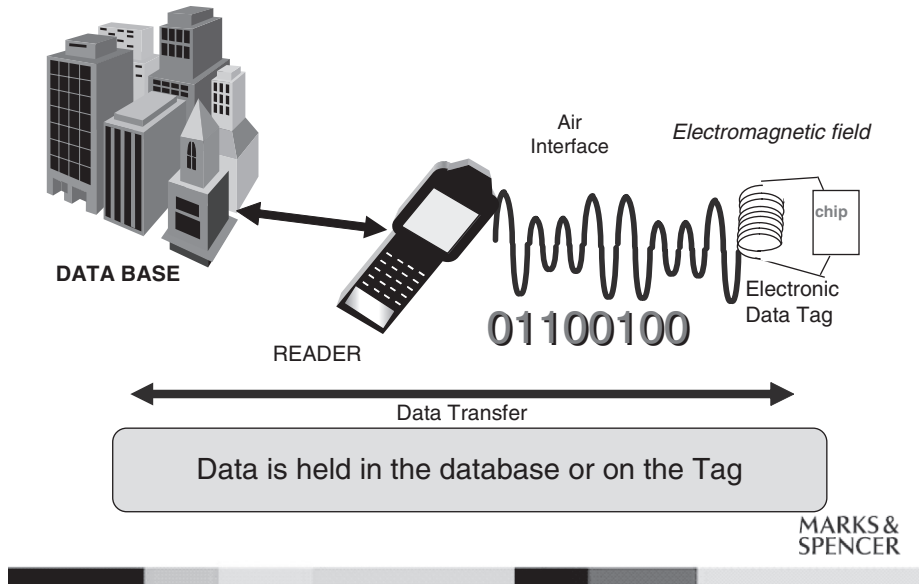


Figure 11.1 *RFID technology.*

most big retailers, has to deal with millions of items each year. Anything that can make the handling of these items more efficient immediately creates benefits. In particular, some items, particularly in the clothing area, are very size complex.

Imagine a customer coming into buy a two-piece suit for a man or woman. Apart from liking the colour style and fabric type, they also want the exact waist size, and leg length, plus the correct jacket size and arm length. Typically M&S will offer this sort of garment in over 30 size variations. Unless the correct size combination is available when and where the customer wants it, they may be disappointed and leave empty handed.

So how does RFID help to solve this problem? It does this by enabling each object to which the microchip is attached to be given a separate identity, and for those identities to be read quickly and remotely using an RFID reader. This information can then be fed into a stock management data base.

11.1 Marks & Spencer Foods

Retail is detail. Knowing that a plastic delivery tray contains chicken breast fillets from a particular source with a specific use by date is much more useful than just knowing that it is a plastic tray containing poultry. Although some of the required information can be contained within a bar code this information can only be read relatively slowly using a bar code scanner. Bar code scanners need to be able to ‘see’ each individual combination of printed stripes. In the case of RFID tags this information can be read very quickly and

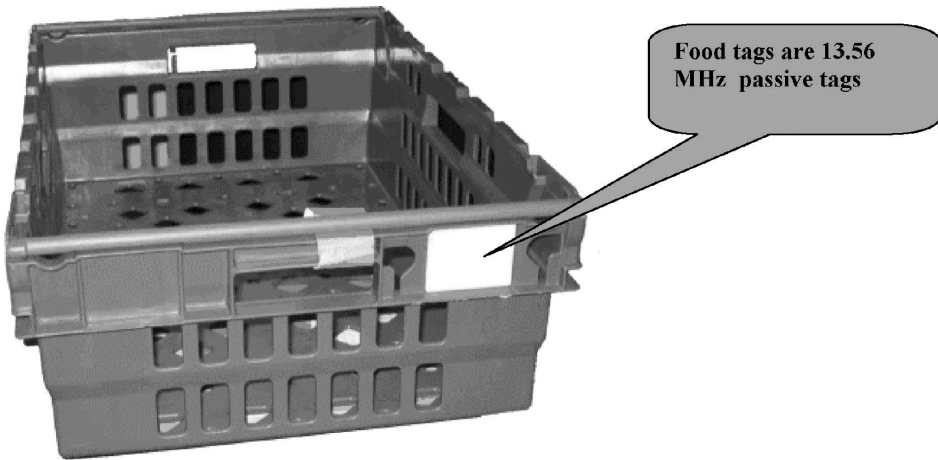


Figure 11.2 Plastic returnable tray with waterproof label.

virtually simultaneously by a reader that is in close proximity to the tags but not in direct line of sight with each one.

Because of these advantages, late in 2000 M&S took the decision to start using RFID tags on the plastic returnable trays it uses to deliver fresh food items in its stores. All new trays were to be fitted with a high frequency (13.56 MHz) rewritable RFID tag contained beneath a waterproof plastic label (Figure 11.2).

The timing of this decision was governed by the imminent need to replace the existing stock of over 4 million returnable trays. The use of these returnable trays was pioneered by M&S in the early 1970s and saves around 30 000 tonnes of cardboard each year. However over the years the transport fleet had migrated from British imperial measurements to modern metric units. In consequence the older trays were no longer an efficient fit into the lorries and there were new additional features needed to improve handling efficiency in the depots. The time had come progressively to grind up all the old trays and use this plastic to make new metric trays. This was the ideal time to start installing RFID tags on the trays. The process started in 2001 and was eventually finished in December 2003.

Each fresh food supplier draws trays from a central pool managed by M&S's food distributor, Gist plc. The supplier washes and dries the tray and then fills it with fresh food items (Figure 11.3).

After the trays have been filled, the supplier writes key information about the food items in the tray to the RFID tag attached to the tray. The RFID tags are 'written to' by specialist readers at the food factories. This process has been refined and improved, and in 2006 over 100 factories are writing information to the tags, which are being routinely read by readers in all the food depots (Figure 11.4).

The trays are then delivered on refrigerated transport to one of seven M&S dedicated Gist food depots. On arrival in the depot the tags are read by mobile RFID readers in the doorway (Figure 11.5), and the information used to confirm delivery accuracy. The depots record the delivery of these trays and then, within a few hours of receipt, sort them and



Figure 11.3 *Tray wash at food supplier.*

send them onwards to the final destination, which will be one of M&S's 475 stores selling fresh food. The store unloads the food from the trays onto the counter, and the empty trays are returned to the depot on the next vehicle for onward transmission to the food suppliers, where the cycle begins again. Each tray, on average, goes through this cycle two and half times per week and has a design life of 7 years although many last much longer.



Figure 11.4 *RFID tray writing at supplier World Wide Fruit.*



Figure 11.5 Depot fixed RFID reader with mobile reader in the foreground.

Speed is the essence of this operation as M&S prides itself on selling only very fresh food and restricts the display life of most food products to only a few days. The use of RFID tags on the trays has meant that the intake process can now take place six-times faster than using conventional bar codes. Currently almost 2 million trays per week are being RFID read in the food depots.

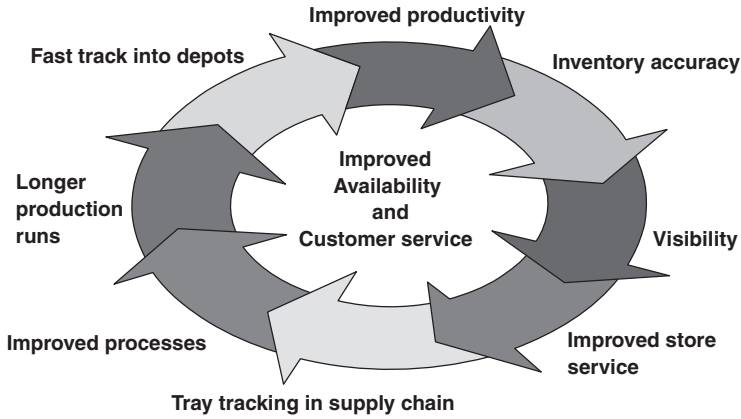
In future, M&S is planning for all the trays to be read in the depot on out-loading before they are placed on the final delivery vehicle. This will further guarantee that the right food items arrive at the right store, thus helping to improve the availability of fresh food items for our customers (Figure 11.6).

11.2 Marks & Spencer Clothing

Clothing differs from foods in that garments are normally delivered as individual items from the distribution centre to the store. In consequence the application of RFID to clothing has been at individual item level rather than in trays or cartons (Figure 11.7). The higher price of clothing in comparison with foods has also enabled disposable RFID labels to be economically applied to individual garments.

In the case of clothing, the major application of RFID is to improve stock accuracy and to improve availability of sizes and hence service, to the customer. Since 2003 M&S has been trialling the use of this technology within the paper size and price labels attached to garments. These special RFID labels are called Intelligent Labels™ (Figure 11.8).

M&S sells 450 million garments each year through a system that needs to be able to handle 600 000 different style, size and colour variations at any one time. Stores get multi-deliveries of garments each day, plus a constant flow of new lines, coupled with the need



M&S

Figure 11.6 Benefits of RFID tray tagging.

to return goods to the distribution centre for consolidation and redistribution. This creates a challenging environment for the maintenance of an accurate stock file for each store.

Although bar-code scanning at the till point gives an accurate picture of what has been sold, figures for the stock position in each store have to be deduced from an aggregation of sales and all stock movements. This inevitably leads to a level of inaccuracy in precise stock figures. Whilst this inaccuracy may not matter that much for simple items sold in



Figure 11.7 Garments in store.



Figure 11.8 Intelligent label on a garment.

few sizes, it becomes critical for size complex garments where each store may only have a small number of each size variation. Two extra items of one size could lead to there being no stock of another size available even though the system showed all stock available in the store. The ability of RFID to connect the real world stock and the system stock lies at the heart of its ability to correct system accuracy. This is what Nicholas Negroponte, Director of the Media laboratory at the Massachusetts Institute of Technology, calls ‘Connecting the bits and the atoms’. It exploits the ability of each microchip to contain a unique reference number, which, when attached to a garment or any other object, can be used to identify that item uniquely.

This uniqueness extends below the normal level of identification provided by bar codes. For example, a bar code will say that this item is an emerald dress in size 12, but it will be identical for all similar emerald dresses in size 12. An RFID chip will give a unique and separate identity to all these dresses. In fact the technology today enables the creation of 10^{27} unique numbers, which is 10 followed by 26 zeros, a very large number indeed (for reference, scientists estimate that there are 10^{22} stars in the universe and 10^{24} grains of sand on every beach in the world).

Having a unique identity means that garments can be counted without the need to worry about counting duplicates. A good analogy here is the problem of a shepherd trying to count seemingly identical and moving sheep. How can he tell if he has counted the same one twice? With difficulty, unless he knows his sheep very well, but if he is able to identify the unique characteristics of each animal, he will be able to do this.

The unique identity contained in each label, coupled with the ability to read this identity using a radio scanning system has enabled M&S to develop a novel and efficient stock taking system based on its Intelligent labels (Figure 11.9).



Figure 11.9 *Hand-held intelligent-label scanner.*

The results from this RFID scanning are used to update the central stock file for each store creating a very accurate picture of what stock is really present in each store. This information is not just about the number of garments present, but about the style, size and colour of each garment.

M&S started to trial RFID stock counting in one store in 2003. Garments were fitted with removable paper labels containing a UHF (869.5 MHz) chip and antenna. Originally the scanner was built into a food trolley and powered by a car battery (Figure 11.10)!

Today's purpose-built equipment evolved from this early prototype. It is now deployed in 42 major stores with plans in place to roll out the technology to 120 stores by spring 2007. The range of garments fitted with Intelligent labels will also increase to cover 12 major merchandise areas by autumn 2007.

The mobile scanning unit contains a screen and a separate wireless hand-held RFID scanner (Figure 11.11). The hand-held scanner emits a low powered radio wave to read the tags and then transmits the tag identification to the mobile base unit using a wireless Blue Tooth connection similar to that used by mobile phones and digital organisers. The mobile base station passes this information over the store wireless network to the store server computer, which in turn is linked to all the central stock control systems in M&S.

Once a week for each department where the merchandise is fitted with Intelligent Labels, the staff move the scanner out onto the sales floor, and start to scan the merchandise using the hand-held scanner (Figures 11.12, 11.13 and 11.14).

The system has been designed so that when the scanner reads an Intelligent label for the first time in the counting process, it emits an audible bleep. When it reads it subsequently, no bleep is emitted. This means that the customer assistant carrying out the scan only has to continue until no more beeping is heard. They are then free to move on to another section of merchandise.



Figure 11.10 Original prototype RFID scanner.

The trials to date have proved highly successful. Using this system staff can accurately count around 6000 garments per hour in a store and around 10 000 garments per hour in a distribution centre where the merchandise is laid out in long straight aisles. This is much faster than bar code scanning, as the need to read the bar code on each item (Figure 11.15), and to take great care to avoid scanning the same item twice slows up the process. Typical stock taking speeds in a store using a bar-code scanner would be around 60 garments an hour.

The improved accuracy of information fed to the central data base has enabled any missing sizes and styles to be identified and quickly replaced. This in turn has resulted in an improved range of sizes being available in the store, which has impressed both our customers and store staff. One major store recently commented that 'RFID has resulted in improved stock accuracy and availability leading to more satisfied customers and increased sales'.

One of the characteristics of the M&S clothing system is that no garment details are written to the tag (unlike the food system). This avoids the need for a worldwide network of garment suppliers having to invest in RFID technology. The system utilizes the fact that a unique number is encoded into each chip during manufacture. Once the chip has been made into a tag it is laminated into a size label that is shipped to various printing hubs around the



Figure 11.11 *Mobile RFID scanning unit.*



Figure 11.12 *Hand-held scanner being removed from mobile scanning unit.*



Figure 11.13 Hand-held scanner being used to scan jackets.



Figure 11.14 Scanning ladies jeans.



Figure 11.15 *Bar code scanning.*

world. These printing hubs routinely finalise the printing process by adding to each label, details about the style size and colour of the garment for which the label is intended. They also add the standard bar code.

The special characteristics of the RFID label printer are that it also reads the unique number on the RFID chip. It then creates a data file that associates the garment information with the unique chip number and sends this combined packet of information back to M&S's central secure RFID data base in the UK. Whenever the label is scanned at any point in the supply chain or in store it is only the unique number that is read, but the central data base is able to translate this number into garment details using the association information provided from the printer in the hubs (Figure 11.16).

Another important characteristic of this approach is that no garment information can be obtained directly from the label. This offers a further degree of privacy protection for the customer as it is not possible to obtain any useful information about a customer's purchase habits by scanning discarded labels, as these only contain the unique number (Figure 11.17).

From the beginning, M&S has tried hard to inform its customers about the new use of this technology. For any new technology to succeed, consumers need to be engaged and reassured that the benefits outweigh any real or perceived disadvantages. In particular M&S has engaged in an open dialogue with many of the groups concerned about privacy, which has occasionally come up as an issue with various applications of RFID.

We all have a right to privacy and this is enshrined in the UK Data Protection Act. Privacy is best seen as a tradable right which means we all trade a little of our privacy for

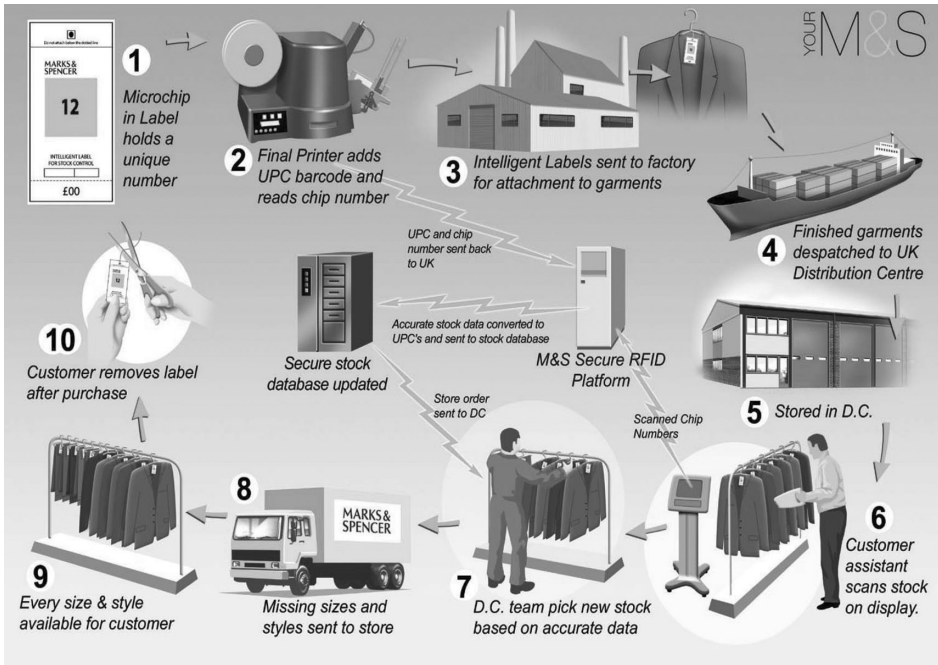


Figure 11.16 How the intelligent label is used for stock control.

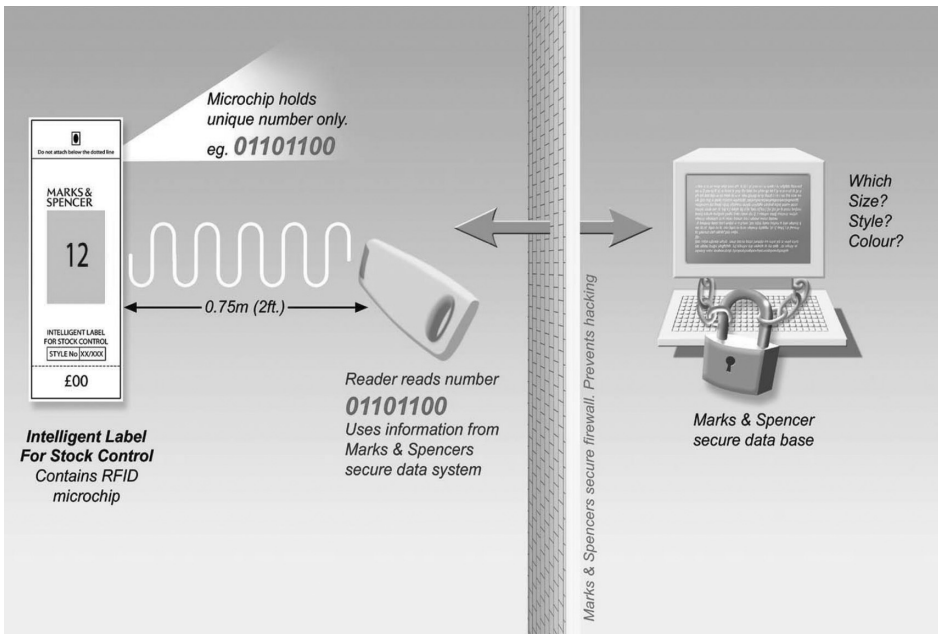


Figure 11.17 The Intelligent Label.

the convenience of using credit cards or for feeling more protected in the streets. This does not mean however that we are willing to give it up just to make life easier for commercial organizations.

At Marks & Spencer we aim to demonstrate that we use technology in a responsible way for the benefit of our customers. We have found that a policy of openness with our customers coupled with a clear explanation of why and how we are using technology works well. For example we do not scan the RFID tags at till points, they do not emit signals or contain batteries and they can be removed at any point during the purchasing process. The label clearly states 'Intelligent Label for Stock Control', which is exactly the purpose for which they are being used. If the customer returns the garments without the intelligent labels this does not prevent them obtaining a refund. Additionally, stores using the technology have an explanatory leaflet available for customers and our privacy policy is shown on the corporate web site.

In summary M&S can demonstrate that RFID technology can make a significant contribution to increasing business efficiency and improving customer service. We firmly believe that it is an important technology that will positively influence operations at many more retailers in the future.

12

Smart Packaging Technologies for Beverage Products

Maurice G. O'Sullivan and Joseph P. Kerry

12.1 Introduction

The beverage industry has always been quick to adopt new technologies as they relate to innovative packaging solutions. Today, beverages are more than simply products that quench your thirst and there is much activity in adding nutrient and 'wellness' components to beverages. Milk-based and juice-based beverages, which continue to grow in popularity, are seen as the ideal carriers of such components. The development of beverage lines where flavour, as well as other organoleptic properties, needs to be created or controlled is equally another important area of development in the beverage industry. In the future, nanotechnology promises to yield new solutions to key challenges for the beverage industry, just as it is likely to impact the food industry. Research and development underway includes the development of functional beverages, nutrient delivery systems and methods for optimizing beverage appearance, such as colour, flavour and consistency (ElAmin, 2006).

A relatively new and growing area for fragrances is the use of smart packaging as a novel marketing tool for bringing products to the consumers' attention, particularly in food and beverage packaging (Markarian, 2006). Also, as people increasingly ignore commercials and spread their attention across many types of media, traditional television, radio and print advertising is losing effectiveness, and marketers are looking for new ways to get noticed. One promising way appears to be targeting as many of the five senses as possible via the package itself (Webb Pressler, 2006). Issues pertaining to luxury, high-end, beverage products such as reinforcement of consumer appeal, tamper evidence, counterfeiting and brand protection, are also highly topical areas of interest within the beverage industry. Many

of these issues are being addressed through the use of smart packaging technologies and these are presented in the following sections.

12.2 Gas Release Packaging

One of the most widely adopted forms of innovative packaging is the gas-releasing 'widget' developed originally for canned and bottled beer products, such as Guinness (Robertson, 2006). This technology was developed to give the consumer the draught beer experience in the comfort of their own home, with the beer having a thick and creamy head. The function of the widget is to release CO₂ from some of the beer in order to create the head. The widget consists of a hollow nitrogen gas-containing plastic sphere, 3 cm in diameter, with a tiny hole in it. The sphere is added to the can before the can is sealed, and floats on the surface of the beer, with the hole just slightly below the surface (Anon., 2007a). Prior to sealing the can, a small shot of liquid nitrogen is added to the beer; this evaporates during the rest of the canning process and pressurizes the can. As pressure increases in the can, beer is slowly forced into the sphere through the hole, compressing the nitrogen inside the sphere. When the can is opened, the pressure inside the can immediately drops and the compressed gas inside the sphere forces beer out through the tiny hole into the additional surrounding beer (Figure 12.1). This agitation causes a chain reaction of bubble formation throughout the beer, and the CO₂ that is dissolved in the beer forms tiny bubbles that rise to the surface, forming the head. The presence of dissolved nitrogen allows smaller bubbles to be formed with consequent greater creaminess of the subsequent head (Anon., 2007a). This is because the smaller bubbles need a higher internal pressure to balance the greater surface tension, which is inversely proportional to the radius of the

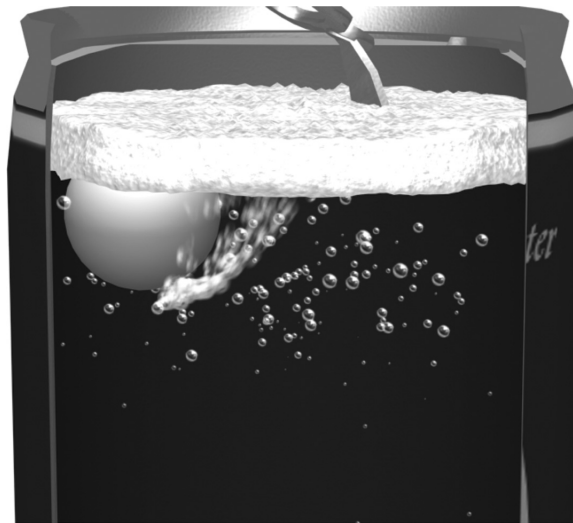


Figure 12.1 *A widget operating in a can of stout. Reproduced with permission from Packaging Materials and Technologies Ltd.*

bubbles. Achieving this higher pressure is not possible just with dissolved carbon dioxide because the much greater solubility of this gas compared with nitrogen would create an unacceptably large head. The result, when the can is then poured out, is a surging mixture in the glass of very small gas bubbles and liquid, just as is the case with certain types of draught beer. Not only does the nitrogen make the beer creamier, and produce a better head, it also protects against oxidation. The brewer can therefore permit the beer to be less carbonated (Anon., 2007a). The 'canned draught' products have levels of carbonation similar to those in cask-conditioned ales, and less than half those in some bottled beers.

Apart from Guinness, other breweries have since come up with their own widget designs that were introduced to draught beer in 1992, lager in 1994, and cider in 1997. In 2002 canned milk coffee containing a widget was marketed (Robertson, 2006). The Kenco Ice Cappio coffee drink from Kraft Foods was launched in this innovative container in the UK in 2002. When the can was opened, the widget produced a creamy head of froth on the beverage (Anon., 2003a). This technology also lends itself to application in other segments such as mixed milk drinks and milk shakes, yoghurt drinks and coffees. For Kenco Ice Cappio, Ball Packaging Europe also inserted plastic capsules in 0.25-litre cans. A relatively new cappuccino cocktail is focused on the Ball Packaging Europe can: 'Cafe Kiss' is a cappuccino drink, with a lacing of vodka, which was launched on the United Kingdom market in a 200-ml Slimline can in 2006. A capsule (widget) inside the can ensures the typical cappuccino froth head when the can is opened. The coffee cocktail, aimed at the 25- to 45-year-old group of consumers, is currently on sale in selected bars and clubs and also from the British retail chains Tesco and Spar (Anon., 2006a).

Future developments of the widget may incorporate elements of nanotechnology, for example, the external surface of the widget could be expected to provide a site for nucleation, or a liquid or active agent could be encapsulated within the widget. The widget could prolong bubble release and create other 'theatre effects' during opening and consumption (ElAmin, 2006).

12.3 Flavour Release Packaging

Packaging devices may also be used to release aroma or flavour into beverage products at the point of consumption, and to create or maintain product intensity and quality. Companies are incorporating scents directly into plastic bags and bottles, so a consumer can smell shampoo or chocolate without opening the top. Newly developed scented ink, meanwhile, is allowing advertisements and catalogues to capture a consumer's attention with an unsuspecting whiff, using a technology beyond your father's scratch-'n'-sniff (Webb Pressler, 2006). Fragrances and deodorants for plastics are used in a variety of applications and are playing a growing role in marketing food and beverage packaging and in consumer products for the home (Markarian, 2006). Olfactory scientists say that using scent is smart marketing. Of all the human senses, smell has the most direct pathway to the emotional centre of the brain (Webb Pressler, 2006).

The incorporation of aromas into the polymer material can be used to attract consumers when the package is opened, and also to balance any detrimental effects of aroma loss (Koontz, 2006). AddMaster recently developed a chocolate fragrance masterbatch for use



Figure 12.2 *Aroma Water, LLC, licenses the technology from ScentSational Technologies to produce Aroma Water™. The cap emits an aroma (lemon-lime or mandarin orange scent) that tricks the taste buds into believing the water is flavoured. Used with kind permission of ScentSational Technologies (www.Scennt.com).*

in polyethylene packaging of chocolate-flavoured, milk-based, drinks that is intended to create an ‘in-store awareness’ of the product (Markarian, 2006). Also, a new aroma- and flavour-releasing technology for packaging is being tested in consumer trials for bottled water and nutritional food packaging applications in the US (Anon., 2003b). US company, ScentSational Technologies, is behind the product, which is also known as ScentSational (Figure 12.2).

This patented brand-enhancing flavour packaging incorporates aromatic qualities directly into closures (Todd, 2003). Pasteurization generally burns off what’s known as top notes, or the aroma notes in beverages traditionally associated with freshness (Todd, 2003). Also, while aromas in packaged foods can break down and start to smell different, the ones ScentSational uses stay fresh because the molecules are, essentially, encased in plastic (Webb Pressler, 2006). ScentSational puts these top notes back in by taking food grade flavours that are FDA-approved Generally Recognized As Safe (GRAS) and mixing them with polymers at the time of injection moulding and adding them to the plasitol liners of metal closures (Todd, 2003). The plastic gradually gives off aroma ‘volatiles’ that last about a month and give scent to whatever food or liquid is nearby (Webb Pressler, 2006).

In the polyethylene terephthalate (PET) bottled water trial, the technology is incorporated into the lid. Other applications could include flavoured and scented bowls for ready to eat cereals, soup and instant meals, flavoured bottles for nutraceutical applications and flavoured lids for dairy product packaging (Anon., 2003b). ScentSational’s technology is

based on the premise that foods and beverages contained in packaging that smells better will taste better. The technology works using the science of taste. With the exception of sweet, sour, bitter, salt and Umami, all other taste is a result of the sense of smell. When someone drinks a beverage, the liquid creates vapours inside the mouth that travel up the retro-nasal canal where it eventually hits the olfactory bulb. It is here that these flavour vapours are interpreted as taste by the brain (Todd, 2003).

NutriSystem, a leading marketer of weight management products, recommends that users of its products drink at least eight 8-ounce glasses of water daily to help flush out toxins produced when body chemistry changes as weight is lost (Anon., 2004b). To make the challenge a little easier, the company sells a water bottle fitted with a closure infused with another product produced by ScentSational Technologies. This product, CompelAroma[®] technology, encapsulates substances within the structure of a plastic package that emit an aroma during heating, after opening. This gives the water added to the bottle taste, even though no flavourants are added (Anon, 2004b). A Pennsylvania based beverage firm, Aroma Water, LLC, licenses the technology from ScentSational Technologies to produce Aroma Water[™] in either a lemon-lime or mandarin orange scent. Both 'flavors' are approved by the Food and Drug Administration (Figure 12.2). The aroma of a particular flavour can affect the sense of taste. For NutriSystem, CompelAroma[®] is added to the closure of the water bottle as it is injection moulded. The closure emits an aroma (currently lemon, peach or berry) that in effect deceives the taste buds into believing the water is flavoured, enhancing the consumer's enjoyment of water without adding calories, sweeteners or preservatives (Anon., 2004b).

A recent innovation to make milk more popular with children has been developed by Unistraw Intl. Pty Ltd, Australia. This company has been engaged for the last seven years in perfecting a milk-flavouring solution that is mess-free, convenient, wholesome and tasty (Mohan, 2006). The patented Unistraw[™] system enables flavour 'beads' to be dissolved in a beverage as the liquid passes through the straw. The system has three elements, a straw, filters and flavour beads (Figure 12.3). The system's first component, the straw, is made from transparent, recyclable, food-grade polypropylene (PP), mixed with a food-grade plasticiser/toughener that prevents the straw from cracking or splitting. The straw measures approximately 0.26 inches in diameter and is 7.08 in long. Filters are heat-welded into both ends of the straw and use a patented cone shape that allows an optimal flow of liquid through the straw, while keeping the company's UniBead flavour beads inside (Figure 12.3). Each straw holds approximately 4 g of UniBeads, which are 0.08-in diameter, round beads that can be dissolved into a beverage to add flavour, vitamins or other ingredients. The UniBeads are manufactured at Unstraw's facility in New South Wales, using processes and equipment developed by the company (Mohan, 2006). In Australia, the straw is sold under the brand name 'Sipahh[™]'. These milk flavouring straws were designed for the 5–15 year old target market. The original launch flavours of chocolate, banana, caramel and strawberry have already been joined by toffee apple, cookies and cream, and choc-mint. Other applications envisioned for the Unistraw[™] system include the delivery of vitamins and other nutrients, nutraceuticals and bioactive ingredients or pharmaceuticals into beverages (Mohan, 2006). Already on sale in a number of countries around the world, Sipahh[™] is expected to be on sale in more than 80 countries during 2007 (Anon., 2007c). Another positive feature is that the product is free of preservatives and artificial aromatic substances and is made exclusively from natural colourings (Bornholdt, 2006). Sipahh[™]



Figure 12.3 The patented Unistraw™ system, which enables flavour ‘beads’ to be dissolved in a beverage as the liquid passes through the straw. The system has three elements, a straw, filters and flavour beads. The straw is sold under the brand name ‘Sipahh™’. Used with permission of Unistraw International Limited.

fits perfectly into the global trend towards healthier and convenient products that deliver nutritional benefits in a fun and novel way (Anon., 2007c).

Choice enabled packaging (patent pending) is now being marketed by IPIFINI, Inc., a Boston based innovative consumer technology company, for flavour and aroma additions into liquids (Figures 12.4 and 12.5). IpiFINI’s technology allows consumers the ability to personalize their products at the point of use. As well as giving users choice, it can be used to deliver products that are susceptible to degradation when blended with the other material or stored in the bulk container. Depression of a button containing the additive pushes the flavour into the bulk product. Previous innovations have suffered from being susceptible to tampering on the supermarket shelf, but this range of products has a method for overcoming this (LeGood and Clarke, 2006). For carbonated drinks, only when the pressure is released can the flavour be added. Alternatively, the buttons can be screened as part of the packaging design. Some advantages of these products could be the provision of multiple flavour choices for each can and the choice given to the consumer, by pressing a button on the can, as to which flavour they would like to try. This also allows the consumer the possibility of exploring multiple combinations of these flavours (LeGood and Clarke, 2006).



Figure 12.4 Pictured is the Choice enabled packaging (patent pending) which is now being marketed by IPIFINI, Inc. (www.ipifini.com) for flavour and aroma additions into liquids. As well as giving users choice, it can be used to deliver products that are susceptible to degradation when blended with the other material or stored in the bulk container. Patent pending. Reproduced with permission from IPIFINI (www.ipifini.com).

12.4 Nutrient Release Packaging

As well as adding flavours directly to beverages, products have been developed that add a segregated nutrient that otherwise cannot be preserved in liquid solutions. In effect they only become added at the point just before consumption. The Ball packaging group has developed 'Fresh Can[®]', which is geared toward the health, wellness, and sports drink markets. Developed jointly by Ball Packaging Europe (BPE) and Degussa FreshTech Beverages LLC, FreshCan[®] Wedge technology is a patented delivery system that enables dry sensitive ingredients, such as vitamins, to be dispensed into a canned beverage only when the can is opened (Mohan, 2006). With Fresh Can[®], sensitive substances such as vitamins, probiotic additives, or trace elements, can be stored in a can in a dry state and remain unmixed with the beverage until the can is opened (Anon., 2005a). This technology is a patented beverage can that was specifically developed to contain an air- and water-tight plastic container called

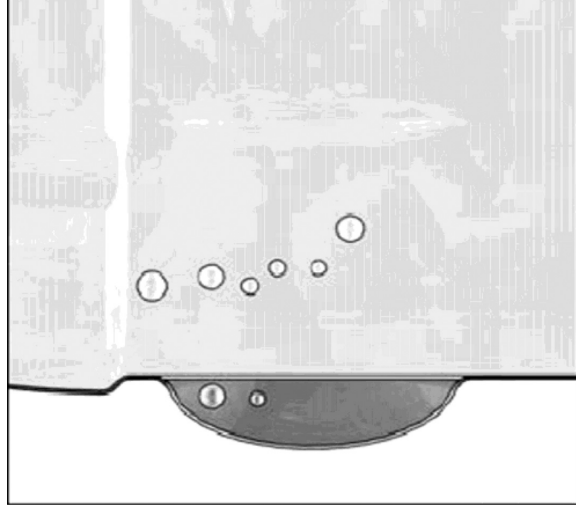


Figure 12.5 Pictured is a cross section of a cherry flavoured additive that when pressed will release into a cola beverage. Choice enabled packaging (patent pending) which is now being marketed by IPIFINI, Inc. Patent pending. Reproduced with permission from IPIFINI (www.ipifini.com).

a 'wedge'. When the consumer opens the can, the pressure decreases, causing the wedge end to spring open. Thus, sensitive substances are not dissolved in the beverage until it is consumed. What's more, nutritional additives that the consumer could previously only take in powder or tablet form can now also be sold as a drink, making it a more convenient form of ingestion for certain types of consumers, in particular in the sport and fitness sectors (Anon., 2005a). According to Ball, the wedge capsule floats freely in the can, i.e. it is not fixed to the base, but nevertheless has a reliable opening mechanism. This feature provides logistical benefits for the container-filling process because the wedge and the can are delivered separately to the beverage producer.

The first commercial application of the wedge became available with the launch of the new Defense^(TM) Vitamin & Mineral Supplement beverage line from New York based Brain Twist, Inc. Offered in natural orange and lemon-lime flavours, Defense combines zinc, pectin, calcium, vitamin C and vitamins A, B2 and E in a beverage formulated to combat the germs that cause the common cold and flu (Figure 12.6).

FreshCan[®] Wedge technology was selected for use with the product to maintain the effectiveness of the drink's vitamins and minerals (Mohan, 2006). Defense is packaged in a traditional, two-piece aluminium can holding 14.5 oz of the beverage. Inside resides the FreshCan[®] Wedge, a two-compartment, polypropylene device containing 10 mL of dry ingredient cylindrical in shape and having a total volume of 25 mL.

Atlantic Multipower Germany, Europe's leading supplier in the sports food sector, is introducing a ready-to-drink creatine product in Germany, UK and Austria. Cranberry-flavoured Crea Max contains 4.6 g creatine citrate, a natural dietary supplement, which enhances the performance of those engaging in sports involving intensive muscle workout,

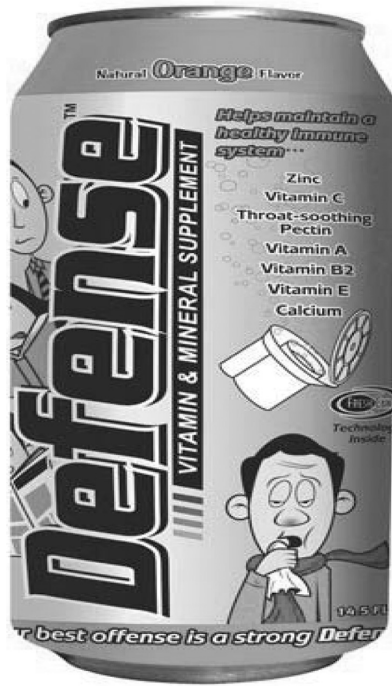


Figure 12.6 Defense[™] citrus flavoured vitamin and mineral supplement beverage line from New York-based Brain Twist, Inc., which is formulated to promote consumer ‘wellness’. Image from Brain Twist, Inc.

and which increases the effectiveness of weight training. With wedge support, the creatine is freshly mixed with the drink when the can is opened. The advantage for the consumer is the added convenience because creatine was previously only available to sports people in tablet or powder form and not as a drink (Anon., 2006b; 2007b)

A further example of the employment of this technology is Swiss company, Emmi. They too turned to packing innovation to overcome stability issues with a nutrient known as CoQ10. Its ‘LactoTab’ performance drink, based on milk serum, has CoQ10, vitamins and minerals contained within a tablet sealed in the lid of the bottle (Figure 12.7) (Halliday, 2006). A powerful antioxidant, CoQ10, plays a vital role in the production of chemical energy in mitochondria – the ‘power plants’ of the cell – by participating in the production of adenosine triphosphate (ATP). It has been studied for its role in cognitive health, heart health, and anti-ageing (in oral and topical formulations). This packaging format protects the nutrients from degradation by light and oxygen, since they are only mixed with the liquid just prior to consumption (Halliday, 2006). The directions for opening are ‘the closure is twisted quickly in the direction of the arrow, as a result of which the tamper evident seal is broken, while the protective aluminium cover is slit open at the same time and the tablet in the blister is pressed in to the bottle’ (Anon., 2006c). Four products are currently available in the range; Energy, Sport & Body, Mineral Ca and Mg, and Vitamin Plus.



Figure 12.7 'LactoTab' performance drink, based on milk serum, has CoQ10, vitamins and minerals sealed within a blister compartment in the lid of the bottle. When the cap is twisted, the tamper proof seal deactivates and the tablet is released from the blister into the milk serum. Reproduced with kind permission of the Emmi Group.

Another company, called Portola, has introduced the Fusion cap, which allows beverage consumers to add a flavour or vitamin to a bottled beverage by simply twisting the cap. This two-piece, resealable cap is designed to keep a flavour or vitamin powder, tablet, or liquid separate from the beverage until the consumer is ready to drink it (Anon., 2004a). Similarly, the New Zealand-based company Alto, who designed the Technology cap and which was commercialised by Rio beverages for its IKon energy drink, has also developed the Freshmix cap, which contains the feature of a fizzing tablet dispenser. This feature allows the active ingredient to remain fresh and inactive within an aluminium foil compartment in the closure until the point of consumption, when the tablet is released into the beverage to provide a fresh and fizzy drink on demand.

12.5 Pro-biotic Release Packaging

Orchard Maid is the first drinkable yoghurt to be equipped with the probiotic Life Top Straw™ Straw (Anon., 2002a). The product first appeared in the UK and was developed by BioGaia and marketed by Tetra Pak, both located in Skåne Sweden (Figure 12.8). Orchard Maid fruit yoghurt drinks are packaged in regular single-serve cartons with straws (Anon., 2002b). The probiotic bacteria are only released when liquid passes through the straw at the point of consumption. These probiotic straws can be attached to ambient packaging



Figure 12.8 This unique and patented technology from BioGaia consists of a telescopic polypropene drinking straw, with a Reuteri[®] oil droplet attached to its inner part. Drinking 100 ml will release the required dose. The straw is packed in a printed polyester/aluminium/polyethylene laminate to ensure stability and can be attached to a drink package. It has a shelf life of 12 months at room temperature. Used with kind permission of BioGaia (www.biogaia.com).

and contain the lactic acid bacterium *Lactobacillus reuteri* (ReuteriTM). Aseptically processed and packaged, the drinkable yoghurts have an ambient shelf-life of 12 months. Scientific research has shown that *L. reuteri* helps to reduce the risk of gastrointestinal disorders and contributes to the body's immune defence system (Anon., 2002a). To ensure probiotic viability and effective dosage, the probiotic remains separate from the drink until consumption by the consumer. The product provides convenience for manufacturers in that existing packages can be used and also probiotics can be added to virtually any beverage, without compromising on ingredients or taste. The straw eliminates production concerns such as accurate blending, controlled dosage and heat damage (Anon., 2002a). Manufacturers know that consumers are getting an effective amount of the probiotic, the straw delivers 99 million active *L. reuteri* bacteria and is said to be safe for all healthy or immuno-compromised children and adults (Anon., 2002a). *L. reuteri* produces reuterin, a substance demonstrated to inhibit harmful bacteria from growing inside the body. It is also claimed that it supports the immune system, improves nutrient absorption and contributes to intestinal wellness (Anon., 2002a).

12.6 Enzyme Release Packaging

Several categories of antimicrobial have been tested for antimicrobial packaging applications: organic acids, fungicides, bacteriocins, proteins, inorganic gases, species, silver substitute zeolite, and enzymes (Han, 2000; Suppakul *et al.*, 2003; Cutter, 2002). One form of active packaging utilizes the incorporation of enzymes to facilitate in-package processing (Brody and Budny, 1995). Enzymes are very useful in food processing; however, in foods

like 100 % natural juice or milk, consumers do not want to read on the ingredient panel that such things have been added (Berry, 2000). Active packaging technologies that employ bioactive compounds such as enzymes and peptides typically immobilize the moiety via entrapment or physical adsorption. However, there are advantages to covalently attaching the compound to the packaging film. From a regulatory standpoint, if it can be established that a compound is highly unlikely to migrate from the polymer to the food, it may not need to be considered a food additive (Anon., 2005b). Cornell researchers have successfully impregnated polymers in film material with enzymes that are very specific in their function (Berry, 2000). Soares and Hotchkiss (1998a) showed that the bitterness associated with certain citrus juices could be significantly reduced using CA (cellulose acetate) films containing immobilized naringinase. These films reduce bitterness by hydrolysis of naringin and sorption of limonin. Comments from panellists used suggest that this reduction in bitterness would be perceived as an increase in sweetness by untrained panellists (Soares and Hotchkiss, 1998a). In order to be practical, an improvement in enzyme activity per unit area may be required so that a lower film area to product volume ratio can be used. This work also demonstrates that an active packaging system based on immobilization of enzymes to product contact layers of packaging may be feasible. Unlike the current situation where most foods deteriorate in quality during storage, products exposed to enzymes bound to packaging might improve during storage (Soares and Hotchkiss, 1998b). Appendini and Hotchkiss (1997) investigated the efficiency of lysozyme immobilized on different polymers. It is known that cellulose triacetate (CTA) containing lysozyme yields the highest antimicrobial activity. The viability of *Micrococcus lysodeikticus* was reduced in the presence of immobilized lysozyme on CTA film (Appendini and Hotchkiss, 1997). Goddard *et al.* (2007) also showed that this concept also works with removing lactose from milk. Instead of adding lactase to milk or using an immobilized enzyme reactor that can foul or clog, lactase can be incorporated into the container's wall. A British patent assigned to Tetra Pak International AB describes incorporation of lactase into pasteurized or sterilized milk prior to packaging to split the lactose after packaging (Brody and Budny, 1995). With sufficient activity, the lactose concentration of the milk during shipment could be reduced (Berry, 2000; Goddard, 2007). Lactose intolerance, or mal-digestion, is the reduced ability to hydrolyse lactose and affects individuals with insufficient lactase activity in the small intestine. It is a dietary problem affecting a minor but nevertheless substantial fraction of the population (Brody and Budny, 1995). The result is varying degrees of abdominal cramps, gas, and nausea (Anon., 2005c). Goddard *et al.* (2007) used a yeast-derived β -galactosidase that was covalently attached to a surface-modified polyethylene film and sustained enzyme activity over a range of temperature and pH similar to that of free lactase enzyme (Goddard *et al.*, 2007). These data suggest that enzymes that may have applications in foods can be covalently attached to inert polymer surfaces, retain significant activity, and thus have potential as non-migratory active packaging materials. Also, Hotchkiss states that, in theory, there are enzymes that metabolize cholesterol, and they could be used in a manner similar to lactase in order to reduce the cholesterol in a product like milk (Berry, 2000). Brody and Budny (1995) suggest a system whereby active packaging and the technology of a company called PharmaCal Ltd, allows the incorporation of the enzyme, cholesterol reductase, into the packaging structure of, for example, a milk product. Untreated milk could be packaged and in the time taken to transport the package to the consumer, it conceivably could become free of cholesterol.

12.7 Odour Removal Packaging

Flavour scalping, or permeation of aroma components, may result in loss of flavour and taste intensities and/or change in the organoleptical profile of a beverage product (Nielsen and Jägerstad, 1994). The development of unpleasant flavours as a consequence of processing can be the result of thermal degradation of components, such as proteins, or of reactions such as the Maillard reaction (Rooney, 2005). Oxidation of fats and oils is also accelerated at processing temperatures. Besides these reactions there can be a slow generation of unpleasant flavours when fruit components are disturbed from their structural components in the fruit. The bitter principle, limonin, builds up in orange juice after pasteurization, and renders juice from some cultivars undrinkable. Chandler and Johnson (1979) showed that substantial quantities of limonin could be removed by acetylated paper, following earlier work involving cellulose acetate gel beads (Chandler *et al.*, 1968). The concept of odour removal using chemical affinity was further developed by Brodie and Visioli (1994), who used the reaction of aldehydes with amino polymers. Odours that result from aldehydes such as hexanal and heptanal, which are formed from the breakdown of peroxides created during the initial stages of autoxidation of fats and oils can be removed from package headspaces by active packaging (Robertson, 2006). Synthetic aluminosilicate zeolites, which have a highly porous structure, have been incorporated into packaging materials to adsorb odourless aldehydes (Day, 2000). Such compounds formed in dairy-based and beer-based beverage products could be removed, and thus improve sensory quality.

In the case of beer, a number of commercial oxygen scavenging technologies have been developed to be incorporated into PET bottles. The Oxbar system (Constar International, USA) consists of an aromatic polyamide (MXD-6) with reducing properties that can be blended in any proportion. By inclusion of a layer of MXD-6 within two layers of PET and using a cobalt salt as a catalyst, structures suitable for the manufacturing of bottles for beer, wine, or sauces can be designed (Miltz *et al.*, 1995).

Sulfites have also been proposed as active substances for use in plastic gasket liners of bottle closures, as liquid trapped between sheets of flexible packaging material, or directly incorporated into plastic film structures to pack products such as wine or ketchup. Other more recent developments of integrated systems include oxygen scavenging labels such as Freshmax (Multisorb Technologies, Inc., USA) and incorporation of O₂ scavengers in closure seal liners for beer and soft drink bottles such as Smartcap (a development of Advanced Oxygen Technologies, Inc., USA) or OxbarTM (Carnaud Metal Box, UK), which is specifically designed to be incorporated into PET bottles. A typical oxygen scavenging structure used in beer bottles is presented (Figure 12.9).

12.8 Thermochromic Labelling

The technology to make thermochromic inks (that change colour when exposed to heat) and photochromic inks (that change colour when exposed to light) has been around since the mid-1970s (Agosta, 2002). Thermochromic technology for beverages first became popular with wine labelling (Robertson, 2006) to indicate to the wine drinker when the product was at the correct temperature to drink (Agosta, 2002), but are also found now on many beer

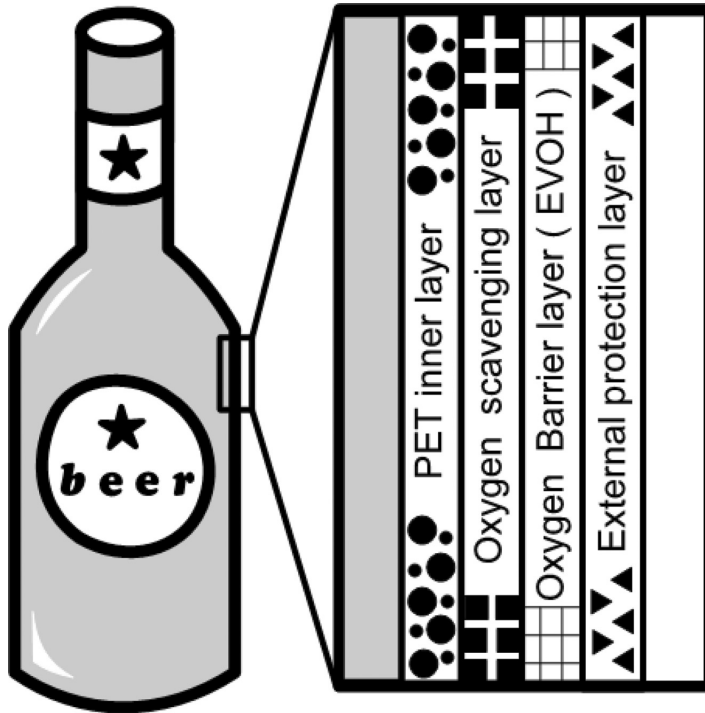


Figure 12.9 Typical oxygen scavenging multilayer structure used in PET bottles for beer. Image used with permission of Alberto Bertolín Terrádez.

products. The whole label or just a small part can change colour at a selected temperature, using inks developed by B&H Colour Change Ltd, to show when the beverage is the correct temperature for serving/drinking, for example, Coors Fine Light Beer, now being sold, has a temperature-sensitive logo that turns from white to blue when the bottle is cold enough to drink (Anon, 2005d) (Figure 12.10a). Similarly, labels for wines have been developed to indicate that the correct chilled drinking temperature has been achieved. (Figure 12.10b) (Anon, 2001). Thermochromic inks can be printed onto labels or containers that are to be heated or cooled prior to consumption to indicate the ideal drinking temperature of the product (Robertson, 2006).

Similar beer examples can be found on supermarket shelves with labels that incorporate thermochromic-based designs to inform the consumer when a refrigerated beer is cold enough to drink. Hite beer, from Korea, utilizes thermochromic inks for beer bottles and cans. At low temperatures the green ink on beer bottles indicates the optimum temperature for consumption and on beer cans it also indicates the level of cold beer inside the can (Han *et al.*, 2005). An example of the thermochromic technology available from Chromatic Technologies, Inc., demonstrates its use in determining the proper drinking temperature of a beverage. A stripe appears on a can indicating that the product is in the proper range and only that range (Agosta, 2002). Depending on their composition, the inks will change



(a)



(b)

Figure 12.10 The whole label or a small part will change colour at a selected temperature to show when the beverage is the correct temperature for serving/drinking. Shown are examples for (a) beer and (b) wine. Bottle shrink sleeves can be preprinted with thermochromic inks prior to sleeving. Used with kind permission of B&H Colour Change Ltd (www.colourchange.com).

colour at specific temperatures, and if appropriate colours are chosen, then hidden messages such as 'drink now' or 'too hot' become visible (Robertson, 2006).

A Colour Changing Disposable Lid from Smart Lid Systems™ provides consumers with a visual indicator of product temperature for beverages in paper or polystyrene coffee cups. Infused with a colour changing additive, the Smart Lid™ coffee-cup lid goes from 'coffee-bean brown' to glowing red after being placed on a cup containing a hot beverage (Mohan, 2006). A further visual indicator ensures that the lid has been placed securely on the cup. When the lid changes colour, a dark ring forms around its edge if it is attached to the cup properly. The lid is made from virgin high-impact PS, which is mixed in the cold-pellet state with a colour-changing additive from Matsui Intl, that has been approved for food contact by the US Food and Drug Administration. Another aspect being promoted by Smart Lid Systems™ is the lid's potential as a marketing tool, whereby an advertising message could be printed on the lid that would only appear once the lid changes colour. For example, text printed in brown ink on the lid or on a clear sticker applied to the lid would only be visible when the lid was in a hot, or red, state (Mohan, 2006). Huhtamaki, a Finnish packaging company, uses what it calls 'Heat and Reveal' temperature-responsive labels. This uses thermochromic technology to reveal a hidden message or strap line incorporated into the cup's design. The heat of the drink determines when the ink is made visible. Such messages could provide instant-win opportunities; for vending operators and branders, the technology allows the competition and winning message to be kept secret until the moment a beverage is dispensed. Similarly, the device can also reveal a surprise slogan or message that will only become visible once a drink is poured (Anon., 2006d).

12.9 Smart Branding

The competition for the consumer's attention on-shelf has never been more intense and innovative beverage packaging companies are interested in packaging that captures the attention of the consumer (Mohan, 2006). Manufacturers are spending more to design packages that blink, beep, yell and waft scents at shoppers (Webb Pressler, 2006). UK-based Cognifex Ltd, is shining a fresh light on brand marketing. Using a tiny, electronic unit with an LED and silicon chip, with a self-contained button-cell power source, they have found a way to illuminate plastic and glass beverage bottles for marketing and promotional purposes (Mohan, 2006). In development for three years, the Cognifex unit is designed to fit on the bottom of a standard-sized beverage bottle and can be triggered in a number of ways. These activation methods could include manual depression of a switch, pulling of a tab, removal of the cap or lid with a special opener, an infrared (IR) signal, magnetic switching or an external radio-frequency (RF) signal. Once triggered, the LED will illuminate the bottle and its contents for a predetermined period of time. Depending on what the brand owner is trying to achieve with the illumination effect, the device can be designed to function for anywhere from a few minutes to several months. Another possible application envisaged is for sweepstakes or promotional campaigns, where bottles could be illuminated remotely to indicate a winning package, or winning bottles could emit a different colour than do regular bottles.

AriZona Beverage Co. is at the forefront of a new wave of high-tech packaging in consumer products. As people increasingly ignore commercials and spread their attention

across many types of media, traditional television, radio and print advertising is losing effectiveness, and marketers are looking for new ways to get noticed (Webb Pressler, 2006). Some companies have created paper-thin, flexible video displays and tiny speakers, but aroma seems to be the biggest payoff in packaging, thanks to its powerful link to memory and emotion (Webb Pressler, 2006). Coming down the road are computer chips embedded in packaging that can communicate with a shopper's PDA or cell phone to give additional product information. Miniature sound systems on boxes and bottles will give people spoken tips and ideas. The German electronics giant Siemens AG has developed a flat electronic display that can be applied to boxes like a label, allowing for tiny lights, miniature games or flashing messages (Webb Pressler, 2006).

Finally, in what might be the first instance of naming a wine for its packaging, Don Sebastiani & Sons released Plungerhead in March 2006. The Dry Creek Valley zinfandel is named for a 'zork' closure from Australia (www.zork.com.au) composed of a polyethylene cap and plunger that 'pop' when opened (Anon., 2006d). The closure is favoured not only because it eliminates the possibility of cork taint but also because it retains the sense of celebration in opening a bottle of wine (Anon., 2006d).

12.10 Anti-counterfeit Beverage Packaging

A concern among packagers and their customers worldwide is the growing incidence of counterfeit products making it into the market. Experts estimate that in Europe as much as 7 % of the branded consumer products market is lost to counterfeit products (Anon., 2005e). The amount of fake food and drinks entering the EU grew by 200 % in 2004, with the higher quality of counterfeits making detection more difficult (ElAmin, 2005a). Counterfeiters are shifting their attention into the mass market goods categories and packaging is in the front line in fighting this loss (Anon., 2005e). Lipton, Coca Cola and Nestlé products topped the list of faked food and drink items seized at the EU's borders, according to the European Commission when announcing new measures to crack down on the problem (ElAmin, 2005). In many Western nations, such as the UK or US, the quota of counterfeit products is about 10 %. China accounted for most of the total faked goods seized in 2004. Russia's economic collapse in 1998, however, offered food fraud the opportunity to fill empty shelves with cheap, counterfeit goods (Anon., 2005f). Condensed milk is a big culprit with producers often making cheaper versions using vegetable fats, yet still putting condensed milk on the label. Some even falsify factory identification codes on packs to try and escape safety authorities (Anon., 2005f). Fake mineral water is also a big problem, with around three quarters of mineral water sold in Russia thought to be fake and counterfeit bottles controlling half of the more developed Moscow market, despite regular checks by police (Anon., 2005f). Counterfeiting and tampering can undermine consumers' trust in the quality and safety of a branded food product, leading to a loss in market share. In response, companies have turned to new forms of smart packaging and labelling to ensure that consumers and customs can check for authenticity (ElAmin, 2005).

Protection against theft and counterfeiting is a highly developed area for high value goods such as electronics and clothes. However it has not found widespread application in the beverage industry because of the comparatively low unit value of packaged foods (Robertson, 2006). Many anti-counterfeiting devices did not work in the past because they



Figure 12.11 A whiskey product printed with a hologram as an optical deterrent. Image from JDS Uniphase Corporation (www.jdsu.com).

were too costly to duplicate. Now the emphasis is on technology, including the use of Radio Frequency Identification (RFID) tags, security-smart printing techniques and use of special inks (Anon., 2005e). To date RFID technology has been used to increase convenience and efficiency in supply-chain management and traceability, being normally applied to secondary and tertiary packaging (Robertson, 2006). However, RFID technology may play an increasingly important role as a security countermeasure for counterfeiting, theft and tampering of beverage products.

High-resolution printed intertwining lines known as guilloches, already used successfully on banknotes, can be printed on primary packaging and/or labels. Microtag particles can be printed using multiple ink layers that combine to form unique code or holograms (Figure 12.11) can be integrated into primary or secondary packaging (Anon., 2005e; LeGood *et al.*, 2007).

Microtrace offers a variety of identification and authentication labelling in the form of compounded plastic resins, films, adhesives, paper, security labels and now security inks (ElAmin, 2005b). A new series of microtaggant security inks will allow any printer to apply the anti-counterfeit technology to packaging using flexographic or screen printing processes. In basic form, microtaggants are a unique numeric code sequence in a multiple coloured layer format. In more complex forms, microtaggants deliver multiple layers of security through the incorporation of several taggant technologies (Anon., 2007e). The ink gives products and packages a unique numeric code sequence in a multiple coloured layer format. The codes will be unique for each manufacturer. Once a formulation is produced for a customer it becomes their exclusive 'fingerprint' (ElAmin, 2005b). The acetate films containing microtaggants can be used to produce authenticated, finished holograms.

Thermosensitive inks change colour when a packaged product has been exposed to predetermined temperatures, often a sign that it has been counterfeited and introduced into the supply chain. UV inks fluoresce under ultraviolet light and infrared inks can only be

detected using a special camera, offering security that does not interfere with the graphic appeal of the package. Metameric inks look identical, but are revealed to be different under a special filter. Scented inks offer both a shelf appeal and security protection (Anon., 2005e).

Biowell Technology, a Taiwan based biotechnology company, has perfected the world's first DNA-tagged anti-counterfeit label. By using bioengineered DNA as an invisible and highly-specific identification tag, forensic-level authentication of a tagged item is possible. DNA tagging has the ability to protect brand name products, documents, artworks, ID cards, and so on, from counterfeiters' tools of the trade: precision computer scanning and printing equipment. DNA tagging provides an extremely high counterfeit barrier, because the unique DNA sequence that identifies a tagged object can never be replicated by a counterfeiter (Anon., 2002d). This DNA anti-counterfeit label has been applied in luxury brand protection by wine, tobacco and pharmaceutical industries (Anon., 2002d).

Kodak is using new, high-tech, anti-counterfeiting technology to help several Napa Valley vineyards in the fight against wine fraud (Park, 2007). Kodak's web site says the company's Traceless system, marketed as an anti-counterfeit solution to the drug industry, could be used to protect 'premium wines'. It uses invisible markers that can be mixed with printing inks or paper and are detectable only with proprietary portable readers. These are leased to clients and can't be opened without being damaged (McCoy, 2007). Industry experts estimate the problem could affect up to 5 % of wines sold in secondary markets (Park, 2007).

12.11 Tamper-proof Packaging

Knowing whether a package has been tampered with is equally important to consumers (Butler, 2001). The main purposes in lowering the risks of tampering are first to eliminate tampering and secondly to locate the already tampered products on the shelf by integrated identification (Han *et al.*, 2005). Tamper evidence technologies that cannot easily be replicated, e.g. based on optically variable films or gas sensing dyes, involving irreversible colour changes, will become more widespread and cost-effective for disposable packaging of commodity items (Butler, 2001). Piezoelectric polymeric materials might be incorporated into package construction so that the package changes colour at a certain stress threshold. In this way, a 'self-bruising' closure on a bottle or jar might indicate that attempts had been made to open it. The new packaging is a natural red to light-pink colour (Butler, 2001). When punctured, light and air react with the packaging in a process called photochemical oxidation, which forms a type of bruising (Anon., 2002e). This is a form of smart packaging that indicates when the integrity of the barrier has been breached. This breach could be from a malicious tamperer, an insect or an inadvertent rupture of the package by poor handling. Packaging protection is an increasingly important part of packaging design. Consumers are now far more aware of product safety and they want to ensure that the packaged beverage they are consuming is as safe as possible (Anon., 2002e). Additionally, aluminium and plastic closures can help customers identify if the package has been opened. The tamper proof band will split when the package is opened, which provides tamper evidence to the consumers (Han *et al.*, 2005). Risks include what the industry terms malicious and non-malicious tampering. The former is an increasing threat, particularly in the light of increasing terrorist activities and the potential for sabotage attacks on packaged beverage products (Anon., 2002e).

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13

Consumer Benefits and Convenience Aspects of Smart Packaging

Paul Butler

13.1 Introduction

Up to now packaging has done an excellent job in preventing waste and getting products to customers in good condition, but we live in a rapidly changing world where yesterday's status quo is no longer good enough. The consumer/package interface has remained unchanged for decades. At the retail store or supermarket, a sea of coloured noise greets shoppers – row upon row of near identical products that fail to engage the senses, lift the spirits, educate, inspire or entertain. Desperation appears to be the major driver in today's new product/package introductions. The strategy of just throwing new products at consumers needs to change, and for real packaging innovation to move up marketing and advertising budgets in terms of importance. Smart packaging can be considered as a natural progression in package innovation for many consumer products. After all, competition for shelf space has never been more intense, and the competition arena is increasingly moving from media to the point-of-purchase, making packaging more important than ever before.

In the home, consumer's expectations and other social factors are pressurising packaging as in other products to improve and support rather than impede the way we choose or have to live our lives. A 2004 UK poll of 2000 *Yours* magazine readers found that 99 % thought packaging had become harder to open in the past ten years. In fact, 71 % of readers of the magazine, aimed at the over-50s, said that they had been injured as they struggled to open food packaging, and 97 % thought there was just 'too much excess packaging'. Against these new standards, present day consumers have much to be unhappy about in current packaging once they get it home. Consumer smart packaging has the potential to meet

at least some of these future aspirations in improved packaging by placing the packaging user interface and consumer experience at the heart of both product purchase and product utility. This in turn will provide new levels of consumer convenience in areas such as efficient and effective product use, in storage and disposal, and in bringing new forms of useful functionality to help support consumers in their day-to-day lifestyles.

13.2 Evaluating the Consumer Value Proposition

Future packaging must offer and deliver a more compelling value proposition to consumers, who increasingly are not particularly impressed if a product just works – this is a given. The ‘wow’ factor will be as important in commodity packaging as it is in determining why people buy a certain brand of car. Consumer benefits driving a smart packaging development must be clearly communicated but those that are promoted as having consumer benefits but in reality are thinly disguised supply chain management improvements will likely struggle to gain acceptance.

For smart packaging targeted at the consumer, the consumer benefits need to be paramount for a successful new consumer product introduction. A common pitfall when new technology is to be introduced, in packaging just as in other sectors, is to revel in the bells and whistles of a new technology without considering what are the important factors to consumers at each stage of a product’s lifecycle. This was the starting point for a useful methodology for evaluating the benefits of products and services, developed by Lim and Mauborgne (2000), based on identifying where and how the new product or service will affect consumers, and displaying the results as a matrix of utility versus the various stages of buyer experience. A product or service could offer improved convenience simply by being easy to obtain or use, or improve customer productivity by helping them to achieve things faster, better, or in different ways.

Purchase, use and disposal are generally the most important stages for packaging, so by placing a new smart packaging concept in one of these spaces, innovators can clearly see how a new idea creates a different utility proposition from existing products. Smart packaging can significantly extend the scope of buyer experience, and can move a product from being solely convenient to buy to new levels of interactivity with the consumer during use and disposal, as the examples in Figure 13.1 illustrate.

Convenience in use for consumers is a major space in which smart packaging innovations can be developed. There is a growing societal demand for packaging that revolves around the need for more and more convenience, and the search by consumers for packaging/product offerings that save the consumer time. A discussion of current successful examples and future possibilities will be the focus for the rest of this chapter.

13.3 Improving Convenience in Product Use

When consumers find a highly functional packaging of a popular branded product in a new packaging system that answers their needs for convenience, portability, easy opening, etc., their reaction tends to be ‘Why didn’t they think of that before?’ This is the power of consumer smart packaging where the design and function of the package is ‘smart’.



Figure 13.2 *The Dulux plastic Easycan™ puts the consumer needs first. It is shaped to fit the hand whilst painting, has an easy-to-open screw top lid and a rim on which to rest the brush.*

The second example is from the international drinks industry – Sheridan’s Perfect Pour. Sheridan’s is a two component drink where a white vanilla creme liqueur is floated on the surface of a dark coffee-chocolate liqueur, resulting in a drink similar in appearance to an Irish coffee, developed by IDV (Grand Metropolitan), now Diageo. The original packaging system consisted of two separate but joined bottles with separate screw cap closures that gave consumers problems in pouring the correct ratio of white and dark liqueurs and in floating the white liqueur over the black.

A smart closure system was required that removed these problems, and this was developed for IDV by PA Consulting Group. The first phase of PA’s design work established the feasibility of dispensing both liquids simultaneously, in the proportion required, in two separate layers. The viscous qualities of both fluids were considered, and also the control of the return air flow. Finally, the closure mechanism had to fit on to two joined bottles and meet the usual consumer requirements for liquid-tight sealing and ease of use. The Sheridan’s Perfect Pour unit was introduced on time to a worldwide market (see Figure 13.3), enabling IDV to build a substantial new drinks sector and brand around the novel smart closure concept.

The third example can be found in the dispensing of sauces, dressings and ketchups from squeeze plastic containers, where problems arise because of the tendency for product to collect around the orifice and build up as an unsightly crust after repeated use, and for certain products such as ketchup and mustard to initially dispense a small quantity of watery material (serum) that collects on the surface of the product. Smart closure packaging designs have been applied to solve these problems and put an end to messy sauce bottle tops (see Figure 13.4).



Figure 13.3 The smart closure on Sheridan's coffee layered liqueur allows controlled dispensing of both components to create the perfect drink.

What is required is a self-sealing valve that opens forward under the positive pressure of the squeeze and yet pulls back and self-seals when the pressure is released, cutting off the product flow. Inspiration can be found in the one-way flap valves that control blood flow through the human body in the design of a closure containing a silicone valve with a crosscut orifice. A quick squeeze of the package opens the valve and dispenses the product.



Figure 13.4 An end to crusty sauce bottle tops with the smart closure that self-seals even when used inverted.

When released, the valve cleanly cuts off the product flow and then reseals. This unique self-sealing valve offers quick and easy one-handed access with a smooth, even product flow to allow controlled dosage, and allows squeeze sauce bottles to be developed in the now-familiar inverted format.

13.4 Improving Convenience for On-the-go Food and Drink Consumption

Less inclination and time to cook in the home means eating out more often, a trend that is most advanced in the USA, where meals eaten away from home account for almost half of the food budget, nearly double the proportion spent in 1970. Unfortunately in conjunction with the car culture and distances travelled, it has also spawned the hugely undesirable practice of eating and drinking in cars. In the USA, the car is fast becoming an integral part of places to eat and drink. According to a University of Michigan research paper, almost 10 % of all meals in America are now eaten in a car, but figures as high as 20 % have also been quoted. Eating or drinking in a moving vehicle is not very smart, but it is a phenomenon that is occurring with growing frequency. What will also likely grow is the use of the stationary car as a place to eat.

Such growing demand presents packaging opportunities for well designed, easy-to-open and dispose of packaging appropriate for the stationary vehicle environment. Examples include smart packaging, such as self-heating and self-cooling beverage containers, discussed later in this chapter, and innovative packaging designs that permit a one-handed meal that fits easily into a car cup holder to be consumed without creating a mess. These trends are all part of an overall picture of increasingly hectic lifestyles that is creating a demand for new food and beverage products packaged in a way that offers user convenience.

To meet these challenges, many lightweight, single-serve containers that are easily consumed on-the-go are being developed. Soup is a favourite with packaging designed for on-the-go portability with an easy-open, microwaveable, package that provides a quick meal; a self-heating smart packaging for soup under the Chef Jay brand is commercial in the USA. Other examples include grab 'n go squeezable yogurt in a tube, and fruit to go in single-serve easy peel clear plastic bowls.

13.5 Adding New Convenience Functionality – Self-Heating and Self-cooling Packaging

It is a statement of the obvious perhaps that when smart packaging brings cost to the consumer – as it clearly does in self-heating and self-cooling forms of packaging – it must also bring useful and valued functionality that the consumer is prepared to pay for. For this type of smart packaging the functionality is obvious and it is not difficult to appreciate the usefulness of a self-heating or self-cooling beverage for today's busy consumer, engaged in seemingly permanent on-the-go lifestyle activities, leisure pursuits and perpetual travel. The challenge is to create low-cost heating or cooling technologies that can be conveniently incorporated into packaging, are reliable, effective and do not have a great environmental impact. From a technical point-of-view, there is a range of options available to heat or cool packages, and their key characteristics will now be considered.

13.5.1 Self-Heating Technologies

The only viable form of heat engine for self-heating is an exothermic chemical reaction. A number of options is available with varying degrees of heat output, but the most reactive are also the most dangerous, using potentially toxic chemicals and producing undesirable gaseous by-products. The exothermic chemical reaction of choice for consumer packaging is lime reacting with water because it generates substantial heat output. Lime is cheap and readily available, and the by-products of the reaction are environmentally acceptable. An alternative reaction is the hydrolysis of calcium chloride, which has the advantage of no reaction by-products but generates a lower heat output.

One of the most successful self-heating beverage containers was launched in the UK in 2001 in test markets, as a joint venture between Crown Cork and Seal, Thermotics Development and Nestlé. The product 'Hot When You Want' Nescafé canned coffee heated about 200 ml of hot coffee, with an occasional shake, to around 40 °C above ambient in about 3 minutes. More recently, there has been a major launch of self-heating gourmet lattes in the USA, with a range of 10-ounce Wolfgang Puck gourmet lattes being available through Kroger grocery stores in 32 states (Figure 13.5). Based on the calcium oxide/water reaction, the container is portable, fits into a cup holder and heats the coffee to around 145 °F (63 °C) in 6 minutes and stays hot for 30 minutes. The foam insulated label permits printing in up to six colours.

In many Mediterranean countries, small quantities of strong espresso coffee drunk at medium warm, not boiling temperatures is the beverage of choice. Caldo Caldo, an Italian



Figure 13.5 Wolfgang Puck gourmet lattes come in a range of four flavours and rely on the exothermic reaction between calcium oxide and water for their self-heating.

development, uses the exothermic reaction between anhydrous calcium chloride and water. When the substances are mixed, heat swirls around the aluminium cup and is conducted into the beverage. The consumer shakes the container for 40 seconds before peeling off the lid and a temperature rise of around 23 °C is achieved. This beverage is a niche market product sold across Europe in sports venues, motorway rest areas and many other outlets. Hot drink variants are coffee, cappuccino, chocolate, coffee with grappa, and tea with lemon.

When it comes to food, spin-off technology from the military MRE programmes using highly reactive exothermic reactions based on magnesium oxidation or the reaction between potassium permanganate and glycerine has created a niche but growing market for self-heating food products for emergency services and the outdoors sector.

The increasingly convenience-orientated domestic market requires a means to heat all types of food and beverages including high viscosity liquids and solid products, i.e. thick soups, snacks including wraps, fajitas, stuffed pitta bread, ready meals, pasta, rice and stews. To date, the technologies for self-heating have been confined to lime/water reactions, where heat output is lower but the reaction is safer. Heating times can be long for solid food products since heat is transferred from the heating source to the product purely by conduction.

By ensuring that excess water is present with the lime/water reaction, a new heat transfer process is being developed by Thermotic Developments – that of direct steam heating. This highly efficient system transfers heat to the product by injecting steam directly into and through the food. Steam is a very effective medium for transferring energy with 1 g steam theoretically possessing 2 kJ of energy.

13.5.2 Self-Cooling Technologies

Notions of self-chilling packaging continue to excite investors and marketers alike, and the brief sounds easy. ‘Design a self-cooling device for beverages such as colas, beer and fruit juice of 330 and 500 millilitre capacity that will decrease the temperature from the existing value to around 4 °C in a convenient (say 3 minute) time period. Do this at a moderate on-cost and without compromising existing environmental considerations, safety, portability or recycling and untold riches will be yours’.

Technology choices in practice boil down to two – endothermic chemical reactions and heat pump technology using water vapour as the heat transfer fluid. Forms of gaseous high pressure expansion can provide effective and rapid cooling but can quickly be ruled out on environmental and safety grounds.

Endothermic reactions tend to be weak but this has not stopped the commercialisation in Italy of self-cooling coffee – ‘Freddo Freddo’ which employs the endothermic reaction between sodium thiosulfate pentahydrate and water. By contrast water evaporation can be a powerful cooling process, as stepping out of the shower on a cold day demonstrates. The evaporation of 10 ml of water can theoretically cool 330 ml of water by 18 °C.

For single serve containers, the technically viable heat pump technology has not yet become commercial. High cost and lack of reliability appear to be the key factors, but the technology is finding commercial success in party keg sizes of beer. The German CS-Metallbau Company has developed the world’s first self-chilling refillable keg using zeolite heat pump technology. The technology is licensed to Cool-System Bev. GmbH and is being

used by Germany's Tucher Bräu brewery for 20-litre take home kegs of beer in refillable stainless steel kegs.

13.5.3 Future Outlook

For self-heating packaging, technical developments are expected to continue with the focus being on lime/water and calcium chloride/water chemical reactions with the provision of a temperature control feedback system so the devices create a maximum temperature for the drink regardless of the ambient temperature. Thermochromic temperature labels will be incorporated to indicate when a product is hot. Costs will come down and product quality will go up, so the future is promising, particularly for direct steam heating.

It is predicted that individual self-cooling beverages will be reasonably commonplace by 2010. This will require the development of cost-effective miniaturised 'drop-in' modules using heat pump technology where the heat produced inside the beverage container can be absorbed by phase change materials.

The global market for beverage cans is estimated to be approximately 400 billion pieces per year and is projected to grow by about 10 % every year. The lure of a cost-effective self-cooling beverage can has resulted in many unsuccessful ventures so far (Figure 13.6), but the vision remains strong, and the market penetration of the self-cooling can, as forecast by prominent market research organizations and beverage companies, will probably increase to about 5 % of total can consumption while the unit price of the self-cooling can is expected to fall to around 20–25 cents. If this happens, world market share of the self-cooling can



Figure 13.6 Field of opportunities or graveyard of dreams for self-cooling beverage containers?

will be 20 billion cans per year and amount to about US\$3.5 billion per year. Whether this is a field of opportunity or a graveyard of dreams for investors remains to be seen.

13.6 Improving Openability in Packaging

'Wrap rage' is the new term that has been coined to describe the build-up of frustration that can occur when packaging is difficult to open, but frustration is only one problem – it can lead to consumers suffering injury as they resort to the use of knives and other sharp implements to open difficult packaging. Hard-to-open packaging discriminates against the weak and is a real barrier to consumer choice and negatively affects repeat purchasing.

The situation is becoming dire. In the USA, *Consumer Reports* looks annually at the most difficult to open packages and awards the dubious honour of 'Oyster Awards' for the worse culprits, generally won each year by the ubiquitous welded hard-plastic clamshell packaging for consumer goods. In the UK, the consumer magazine *Health Which?* contacted 1000 readers to ask if they experienced problems with food and drink packaging. Of the 235 respondents, the noteworthy finding was that 45 % reported avoiding particular types of packaging because they find them difficult or impossible to open.

Designing easier-to-open packaging is generally not rocket science, just good design, which adds little if anything to the package costs. The underlying philosophy of 'design-for-all' is the introduction of changes – often very small changes – into the designs of consumer products so that the greatest number of members of society can use them. These small design changes made with consumer openability in mind, fit into the category of smarter packaging.

An example is the packaging industry's recent introduction of a new range of easy-to-drink- from closures for beverage and water bottles, carried by athletes and cyclists. With one hand, a sportsperson can open these tops by pulling them with his/her teeth, squeeze a shot of drink into their mouths, and close the bottle again by pushing the tops against the chin. There has been a significant adoption of this type of drink container by the elderly and disabled because of this mode of operation. This example illustrates the wider opportunities that are available for introducing minor design changes to provide significant gains for consumers, in the application of the 'design-for-all principle'.

Simple designs tend to be the best, and packaging for Nestlé Maggi range of bouillon cubes, available in Germany is a good example of great design at zero on-cost. The flat cardboard pack is perforated across one of the flat sides and down the corresponding two edges. A sharp tap along the back of this line hinges open the pack, allowing individual cubes to be easily removed, and the pack to be reclosed (Figure 13.7).

The message is that small design changes can make large differences to openability. Rigid containers are sometimes difficult to grip and nearly all package closures are round so they are difficult to grip without resorting to the variety of opening aids presently available on the market. Some packages have 'non-round' tops on products such as paper-whitener so that able-bodied people can get a better grip when the top sticks to its base. The German company Gerresheimer has developed a cap that is designed to improve handling for elderly or infirm users. Viewed from above, the cap looks like a plus sign with arms reaching out from the centre of the cap. This design greatly reduces the force required to open the



Figure 13.7 A package can be easy to open through ‘smart’ design. Tapping this soup bouillon pack on a hard surface breaks the pack in half so it can easily be hinged open to remove a single portion.

container. Bottles can also be stood cap side down, allowing the user more effectively to empty viscous materials.

Squeezeopen™ is an innovative design solution to many of the problems of openability. The closure consists of a lid that is a press snap fit onto a base that serves as the container and opening is performed simply by gently squeezing the lid’s sides and releasing the pressure. A multipurpose inner symmetrical ramp system guides and joins the components together (creating an effective seal) when the lid is pressed onto the base and helps to force the components apart when the lid sides are compressed.

Finally the metal can has made great strides in openability with ring-pull, easy-open, ends appearing on more and more products. Metal closures on vacuum-packaged products in glass jars remain an openability obstacle to many consumers but technology is available to solve even this problem, as developed by Metalgrafica Rojek SA, a family-owned business based in Sao Paulo, Brazil. The innovative Rojek closure fits both cans and glass jars and has a peelable elastomer seal over a small aperture in the top of the closure. Pulling the seal releases the vacuum and the container can then easily be opened, without the requirement of great manual strength or any opening devices like can openers or knives.

In the future, developments in low peel-force adhesives and structures, even smart packages that are self-opening, but still tamper-proof, are likely. As an example, the incorporation of smart adhesives in bonded, rather than mechanically seamed ends, might allow the development of ends that open via debonding of the adhesive on application of current from a small battery pack. Such adhesives have been developed, e.g. the electrically disbonding epoxy system, ElectRelease™. Alternatively, we might envisage a shape memory material acting as a metal rubber band to retain an end or closure that vents or opens automatically with change in temperature, e.g. on microwave heating. Other convenience-driven smart packaging concepts that improve ease of use are being considered, such as the development of ‘dial-a-dose’ smart caps and closures that allow the safe dispensing of exact controlled quantities of product, e.g. pharmaceuticals, cleaners, and other potentially hazardous materials. As always however, there is a fine line between ‘easy to open’ and ‘easy to tamper with’.

13.7 Making Packaging Reusable for Other Functions

Smart packaging could just be simply a great package design that works well for its original purpose but provides additional convenience and usefulness once it is empty. Not only would this give consumers a new benefit, but would also support sustainability via reuse and reduce the amount of packaging going to waste.

Packaging like this that has outlived its intended primary function lives on in almost every household, whether as empty glass jam jars to hold dirty paintbrushes or empty yoghurt pots in which to plant seeds. Elements of structural design can be used to design packaging to be creatively reused by consumers, or that could be part of the product – say an electronic dispenser that can be refilled. For example, a freezer pack could be made collapsible after emptying to become a freezer thermometer; the secondary packaging from a radio could be turned into an auxiliary speaker – both environmentally sound approaches.

The opportunities are many, the examples today are few. Clearly, for everyday packaging there is a limit to reuse, since how many yoghurt pots to use as seed germinators does one household need? Nevertheless for items purchased on special occasions, there is the possibility of the packaging fulfilling dual purposes. Take for example a large container of chocolates for Christmas, normally packed in a tinplate container or plastic tub that is frequently discarded after use. One manufacturer has combining the initial container for chocolates with a reusable champagne or wine cooler, see Figure 13.8, a play on the brand name ‘Celebrations’.



Figure 13.8 *Smart packaging design can give new life to the package once the contents have been used. This plastic tub of chocolates when empty can be used as a wine cooler.*

In the future it is expected that tear-offs will become greatly valued thanks to smart packaging technology. Increasingly they will consist of electronic devices that cost 10 dollars or more to buy separately not so long ago, such as radios, wristwatches, calculators and many other things. In 2002, it was reported that a patent had been granted for a disposable paper cellphone and that backing from General Electric had been agreed to commercialise them. Initially they would have conventional components but be cheap enough to be disposable. For example, the cellphone would come with 60 minutes talk time for someone travelling perhaps to a foreign country or needing a mobile phone for some emergency. Perhaps that could be a tear-off on the packaging of travel products.

13.8 Summary

Of all the drivers for the development of smart consumer packaging, user convenience is king. Within user convenience, packaging must play to one or more of three key central themes – save me time, save me money, or support me by making things easier for me in my life. Consumers are tired of packs that make demands on their time and attention, they want first and foremost improvements that save time, are easy to use and reduce stress on an already busy life. Increasingly hectic lifestyles are creating new consumer demands that rely heavily on packaging that is lightweight, portable, easy-to-open without the aid of tools, but also resealable. Even on its final journey to the rubbish or recycling box, if the packaging is not reusable, the package ideally should crush easily, or be easily cleaned and safe to handle – if not, this provides one last negative memory for the consumer.

Societal trends will impact on packaging as in other consumer products in many different ways. The overall picture is one of increasingly hectic lifestyles that are creating a demand for new food and beverage products and innovative packaging, particularly in terms of user convenience. On-the-go as a way of life seems to show no signs of abating and in all likelihood, consumers will become even more mobile and time pressured. In this brave new world, untapped opportunities exist for smart packaging to offer new and improved levels of consumer benefits and convenience.

Reference

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14

Smart Packaging Technologies used with Aerosol and Household Cleaning Sprays

Lindsey Gaunt

14.1 Introduction

The advantages of electrostatic spraying, whether the spray is liquid droplets or dry powders, are well known, well documented and exploited in such applications as crop spraying, spray painting and ink-jet printers. Improvements in efficiency and performance arise through higher transfer efficiency, a more even distribution on the target, and the coating of surfaces not in the direct line of fire as a result of a phenomenon known as wrap-around. There are inevitably also disadvantages, although almost exclusively associated with the increased cost, complexity and bulk of the equipment required. To deliver the required level of charge in industrial applications a power supply is used, charging the spray by either induction or corona. This limiting factor can be overcome by exploiting natural charge separation phenomena to deliver a spray with sufficient electrostatic charge to achieve the benefits of electrostatic spraying. This has been implemented in a commercial insecticide aerosol spray, shown in Figure 14.1. The electrostatic charge associated with the aerosol droplets results in substantially increased deposition of the droplets onto insects in flight and a subsequent improvement in product performance.

In this chapter, some fundamental processes of electrostatics are introduced to give a background to the advantages of electrostatic spraying and to explain natural charge separation phenomena. The natural charge separation phenomena of frictional charging and flow electrification are exploited to achieve passive charging of sprayable products,



Figure 14.1 Commercial insecticide aerosol spray incorporating passive electrostatic technology. Used with permission from Packaging Materials & Technologies Ltd.

such as aerosols and household cleaning sprays. Passive charging does not require a power supply or battery to impart high levels of charge to sprays, and thus allows application in a wide range of products, especially those for the consumer market. Some examples are also given of the benefits achieved by implementing the technological concepts described in various areas.

14.2 Electrostatic Spraying

The advantages of electrostatic spraying arise from the attractive forces between the charged droplet or particle and the target surface. Coulomb's law states that the magnitude of force between two electrical charges depends on the magnitudes of the charges and their spatial separation, as shown in Figure 14.2. The magnitude of the force, F , between point charge q and point charge q' located at distance r is given by:

$$F = qq' / 4\pi\epsilon\epsilon_0r^2$$

In electrostatic spraying, the best case scenario exists where the target surface is oppositely charged to that on the spray particles, as in Figure 14.3(a). The forces of coulombic attraction increase deposition efficiency. In the next best scenario the target surface is conducting and earthed. In this instance, as the charged particle nears the surface, a charge equal in magnitude and opposite in sign is induced in the target, and is indeed an image of the approaching charge. For this reason the term 'image charge force' is coined to describe this scenario, which is illustrated in Figure 14.3(c). Where the target surface is conducting

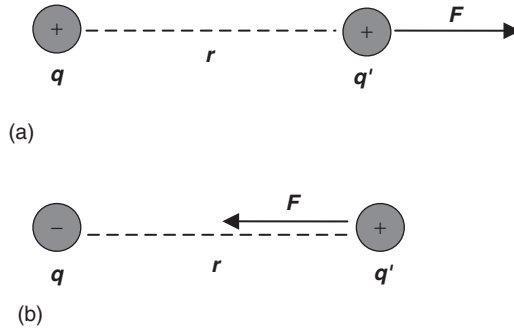


Figure 14.2 The direction of electrostatic force, F , acting on a point charge $+q'$ in the field of a point charge q where (a) q is positive, or (b) q is negative.

yet electrically isolated, an image charge is induced by polarisation as the charged particle approaches, as shown in Figure 14.3(b). The worst case scenario arises where the target to be sprayed is insulating, yet here too electrostatics spraying can still deliver some improved performance. No polarisation or image charge can be induced in an insulating surface. Such surfaces can exhibit long-lasting surface charges arising through triboelectrification with objects they have been in contact with, and this can result in coulombic forces of attraction. Where a surface does not retain a surface charge opposite in polarity to the spray droplets, deposition efficiency can still be increased where the two are at different electrical potentials, and thus droplets will deposit on the surface to equalise this difference.

A sufficient level of charge on the spray is a prerequisite for performance improvements to be demonstrated. For the charge on a particle to influence its trajectory in the air, the forces of attraction or repulsion must overcome gravitational and inertial forces. It is generally considered that only above a charge-to-mass ratio of $100 \mu\text{C kg}^{-1}$ will electrostatic forces start to influence the trajectory of droplets (Gaunt *et al.*, 2003a; Singh *et al.*, 1978; Splinter, 1968).

The charge-to-mass ratio of typical off-the-shelf domestic aerosol products is in the region of $0.01 - 1 \mu\text{C kg}^{-1}$, and in exceptional cases is as high as $10 \mu\text{C kg}^{-1}$ (Gaunt *et al.*, 2003a,b). Similar charge levels are recorded for other household spray devices. This

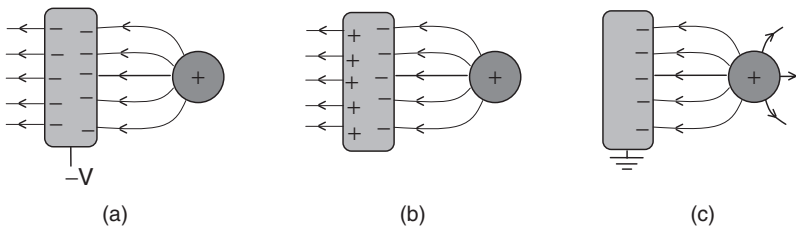


Figure 14.3 Attractive forces between a charged droplet or particle and a target surface. (a) The target is maintained at the opposite potential to the charged particles. (b) The isolated surface is polarised in the field of the charged particle. (c) The target surface is connected to earth so as the surface is polarised the negative charge is conducted away so as to reduce the potential to zero.

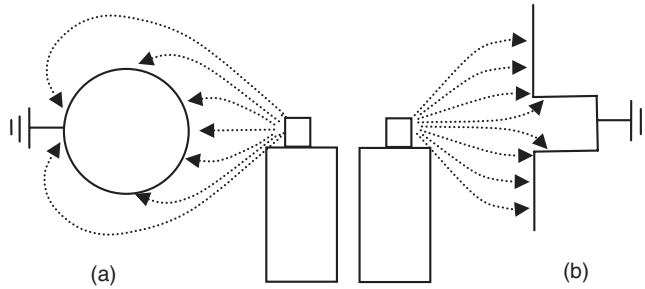


Figure 14.4 *Electrostatic spraying (a), wrap-around, (b), Faraday cage effect.*

charge level is insufficient to influence the trajectory of spray droplets. However, sprays incorporating designs that include passive charging technology or promote natural charge separation phenomena, as discussed in the following sections, can produce higher levels of charge, sufficient to demonstrate the benefits of electrostatic spraying.

The benefits of electrostatic spraying arise when particles follow electric field lines to a target. This results in high deposition efficiency and particles reaching the back of the target, which is usually shielded, as shown in Figure 14.4(a). However, because particles follow field lines it is difficult to coat inside recesses due to a Faraday cage effect (Figure 14.4b). Estimates from the paint spraying industry suggest that electrostatic spray systems deliver improvements from 40 % efficiency to 70 % efficiency on flat surfaces (Cross, 1987).

14.3 Natural Charge Separation Phenomenon

When liquids or solids come in contact with dissimilar materials, separation of positive and negative charges readily occurs at the interface. Consequently, one of the materials becomes positively charged and the other negatively charged. This process can occasionally lead to significant static problems but can also be exploited for industrial purposes. Industries that rely on static charge to achieve a particular process require controlled sources of static charge, so they generally make use of corona or induction charging, powered by an active power supply. However, it is possible to exploit the natural charge separation phenomena to good effect, giving reliable operation over long periods of time yet eliminating the need for bulky, expensive power supply equipment. The process for charge separation in liquids is known as flow electrification and for solids it is called frictional or triboelectric charging.

The natural charge separation phenomena of tribocharging and flow electrification are rarely exploited in industrial processes. However, suitable levels of charge can readily be attained by appropriate techniques and used to generate charged sprays. Employing passive charging realises the advantages of electrostatic spraying whilst eliminating the disadvantages associated with power supply equipment. In delivering passively charged sprays, the spray device usually requires little modification, or demands a novel design that can be little more costly or complex than a conventional system. What can be necessary is more careful attention to quality control and the need to earth components of the spray device, usually through the user.

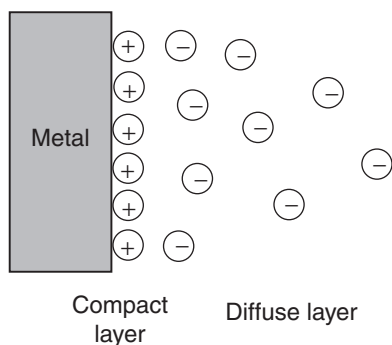


Figure 14.5 Schematic diagram of the electrical double layer of a solid–liquid interface.

14.4 Flow Electrification for Charge Separation

Flow electrification, sometimes known as double-layer charging, is a phenomenon whereby liquids accumulate charge as they flow. The phenomenon is observed during pumping and transport of petroleum products, where it can be particularly hazardous if uncontrolled (as reviewed by Klinkenberg and Van der Minne, 1958). Electrification in liquids can also be exploited to generate naturally highly charged liquid sprays.

Charge reorganisation occurs on a microscopic scale in liquids at any interface, with a solid, a gas or another liquid. One polarity of charge is held relatively tightly bound at the interface, known as the compact layer, with ions of the opposite polarity held much more weakly as a diffuse layer. The immobile ions of the compact layer and the diffuse layer of counterions in the liquid together make up the electrical double layer, as represented schematically in Figure 14.5. The nature of the electrochemical reaction at the interface depends upon the interaction between the solid and liquid constituents, and this determines the net flux of electrical charge comprising the double layer. The distance that the diffuse layer extends into the bulk of the liquid depends on the liquid's conductivity. For water based liquids where conductivity is greater than 10^{-6} Sm^{-1} the diffuse layer is only a few molecules thick. For liquids where the conductivity is of the order of 10^{-11} Sm^{-1} , the diffuse layer may extend a macroscopic distance from the interface. When the liquid is moved across a surface, such as during spraying, the diffuse, weakly bound, layer of charge is entrained within the liquid bulk, leaving the compact charge layer attached to the solid. As charge from the diffuse layer is entrained, the electrical potential in the bulk liquid rises, and when the liquid loses contact with the surface, such as on atomisation, the charge is retained on the droplets. If the charging process is to continue, then the charge at the surface must be replenished by moving through the walls of the pipe. In a metal pipe, current of the order 10^{-9} to 10^{-14} A is recorded. Such low levels of current are able to flow through some insulating pipes and not limit charge separation. Alternatively, the more conducting boundary layer at the solid–liquid interface can also provide a conduction path to earth and thus allow charging to continue indefinitely.

The amount of charge accumulated by liquid flowing in a pipe is limited by liquid conductivity, among other factors. A highly conducting liquid cannot accumulate charge

as the rate at which ions diffuse to the pipe wall to be discharged is very rapid. A perfectly pure insulating liquid will not charge because there are insufficient dissociated ions to carry the charge. The conductivity over which charging is observed is 10^{-13} to 10^{-7} Sm^{-1} , while the charge generation rate reaches a maximum at the order of 10^{-10} Sm^{-1} (Cross, 1987).

Flow factors are equally important in determining the charge levels attained. Liquid charging increases with increasing flow velocity and turbulence. During laminar flow there is little or no radial movement of the double layer. With the transition from laminar to turbulent flow, the diffuse layer of charge begins to be distributed across the bulk of the liquid by turbulent transport, and as turbulence increases the thickness of the laminar sublayer at the solid surface is reduced. The presence of a filter, valve or pump in the flow line can also enhance charging by several orders of magnitude, due to increased turbulence and the increase in surface contact in relation to the volume of liquid.

14.5 Frictional Charging

The effects of contact and frictional charging can be easily observed when scraps of tissue paper are picked up after rubbing a comb, from the small electric shocks delivered when touching a door handle after dragging your feet across a carpet, or the crackle heard as a woollen jumper is removed on a dry day. When two solids come into contact, charges are exchanged as shown in Figure 14.6. This represents an over simplification of the situation, as both surfaces retain areas of negative and positive charge, yet one charge predominates. Charge reorganisation at the interface brings the materials into thermodynamic equilibrium, and as the surfaces are separated the excess charge is retained.

The amount of charge transferred during contact is determined by a number of factors. In a simple, non-sliding, contact the amount of charge transferred to an insulator is generally proportional to the work function of the materials, and can be influenced by surface imperfections and impurities (Cross, 1987). In practice charging is often achieved when surfaces are rubbed together and in this case the energy of rubbing is more influential than the nature of the materials. From knowledge of the materials it is seldom possible to predict how much charge will be transferred in a particular circumstance since the frictional charging process is so complex. It is possible though, within limits, to predict the relative

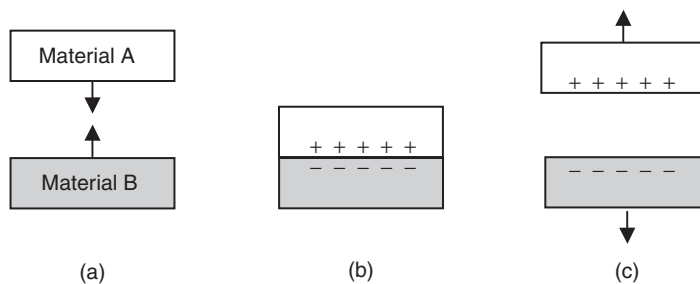


Figure 14.6 The three stages of triboelectric charging: (a) two dissimilar materials are brought into contact; (b) charge transfer occurs at the interface; (c) separation of the surfaces each with its excess charge.

Table 14.1 *Triboelectric series. Materials at the top of the table charge positively when rubbed against materials below them in the series (from Taylor and Secker, 1994).*

Material	
+	Asbestos
	Glass
	Human hair
	Nylon
	Wool
	Lead
	Aluminium
	Cotton
	Steel
	Copper
	Silver
	Sulfur
	Polyester
	Polyurethane
	Polypropylene
	PVC
	Silicon
-	Teflon

polarities of the materials using a triboelectric series, such as given in Table 14.1. Materials tend to charge positively against materials below them in the series, and this prediction is more reliable the further apart the materials are from each other. The series does not give any predictions relating to the magnitude of charge transferred, however. This is shown when samples of identical materials are rubbed together, and substantial charge transfer can occur. Many triboelectric series exist, and can differ from each other in some respects due to small differences in the basic material and the test procedure used. However, it is possible to identify trends. Contact between a metal and a plastic surface invariably leaves the metal with a net positive charge and the plastic with a net negative charge. A rubbing contact will impart several orders of magnitude more charge than will a simple, non-sliding contact. Since charge transfer depends on the force and velocity of the contact, the charge acquired by a particular material depends much on the energy of rubbing. As an example, the level of charge generated during powder handling by grinding is in the order of 0.1 to 1 $\mu\text{C kg}^{-1}$ and by pneumatic transfer in the order of 1 to 100 $\mu\text{C kg}^{-1}$.

14.6 Domestic Aerosol Sprays

Passively charging domestic aerosol sprays have recently been developed and successfully marketed for the household pest control sector. The technology (Gaunt and Hughes, 2003b), although challenging to implement, represents one of the most significant technical

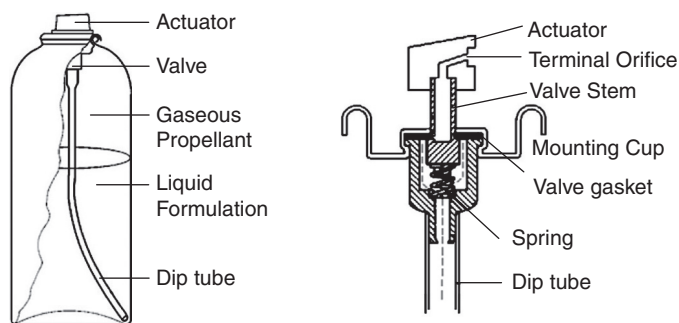


Figure 14.7 Schematic drawing of the main components of a domestic aerosol product and a valve in the open position.

advances in aerosol technology since the invention of the pressure-pack spray in the late 1800s (Sanders 1970). Sprays with optimised formulation and pressure parameters fitted with an actuator that promotes shearing of the electrical double layer can produce higher levels of charge, sufficient to demonstrate the benefits of electrostatic spraying. Charging is achieved by exploiting flow electrification. Formation and shearing of the electrical double layer at the liquid/solid interface is maximised to promote the level of charge carried on the formulation as it is atomised. Factors that affect the level of charge accumulated include the electrochemistry of the liquids and solids interacting, flow parameters such as turbulence and velocity, and the contact area between liquid and solid (Gavis and Koszman, 1961).

The modern domestic aerosol comprises a propellant, a solvent and an active, ingredient packaged in a container equipped with a valve for discharging the liquid formulation when required and an actuator for delivering the desired spray characteristics of flow rate, droplet size distribution and cone angle. The main components of a typical dispenser are shown in Figure 14.7. The propellants commonly used are liquid hydrocarbon gas (butane/propane mix) or compressed gas. The formulation can be a homogeneous or a heterogeneous emulsion, the latter either having a water or oil continuous phase. Spray characteristics are critical to good spray performance, and largely determined by actuator parameters such as swirl chamber geometry, orifice dimensions and also by propellant type and pressure.

The conductivity of the formulation is one important factor in successfully delivering this electrostatic technology. It is the conductivity of the formulation that determines the depth of the electrical double layer that forms at the interface of the liquid and solid, and thus the level of electrification of the liquid. The range of conductivities over which charging is observed is between 10^{-7} and 10^{-13} Sm^{-1} , where the double layer may extend a macroscopic distance from the interface (Cross, 1987). Where the formulation must comprise a significant percentage of water for reasons of economy and performance, this seems impossible to achieve. The conductivity of tap water is typically in the order of 10^{-2} Sm^{-1} and deionised water is in the order of 10^{-4} Sm^{-1} , resulting in a double layer only a few molecules thick. In overcoming this, the properties of emulsions can be exploited. By enclosing the water in a water-in-oil emulsion, it is possible to obtain a formulation of more suitable conductivity, such that formation of the double layer is promoted and a high water content can be retained.

To maintain formulation conductivity within suitable boundaries, it is also useful to use liquid hydrocarbon gas (LPG) propellants rather than compressed gas. The conductivity of a butane/propane mix, being of the order of 10^{-8} Sm^{-1} , makes LPG a suitable ingredient. Conversely carbon dioxide, a commonly used compressed gas propellant, dissolves in and increases the conductivity of the water phase. The use of liquid hydrocarbon propellants is also important in maintaining a high and constant pressure, ensuring consistent charging for the lifetime of the product. LPG propellants also contribute to generating an aerosol product with a small and even droplet size distribution. This is important as a higher level of charge would be required to impart electrostatic benefit to larger diameter droplets.

Selection of the dispenser components primarily influences shearing of the double layer. Promoting flow velocity, flow turbulence and increasing the contact area between liquid and solid can increase the charge imparted to the spray on atomisation. As charge accumulated in the liquid bulk always has an opportunity to relax further along the system, it is the modifications made at the actuator level that are most influential in determining the ultimate charge imparted. Thus, selection of actuator orifice diameter and swirl chamber configuration can affect the charge-to-mass ratio by over two orders of magnitude. To increase further the contact area between liquid and solid at the point of atomisation, novel terminal orifice designs have been developed. A standard circular orifice has the lowest possible area of contact, so any deviation from this can be expected to promote charge levels. For example, Figure 14.8 shows the commercialised novel actuator orifice design along side a conventional orifice delivering the same flow rate.

Through combinations of suitable formulations and actuator selections, charges in excess of $100 \mu\text{C kg}^{-1}$ can be attained. Such systems consistently generate this level of charge for the lifetime of the product due to the stability of an optimised assembly. Variations in ambient temperature and relative humidity affect charging very little. Once generated, aerosol droplets in the air do not lose their charge. As a droplet evaporates, charge is retained on the droplet and thus the charge-to-mass ratio actually increases, enhancing electrostatic effects.

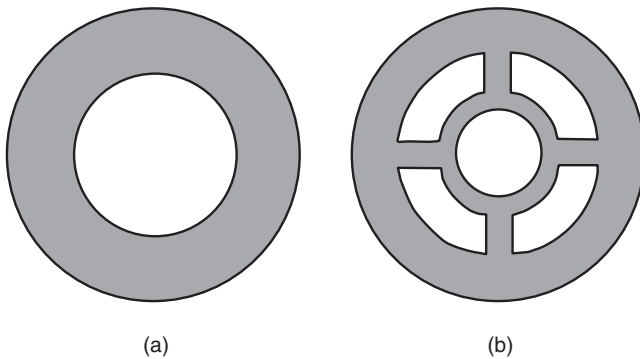


Figure 14.8 Actuator orifice shapes: (a) a conventional circular orifice; (b) a charge-promoting segmented orifice with the same cross-sectional area as (a). The grey shaded area represents the solid parts.

14.7 Induction Charging for Charge Separation

Exploitation of the flow electrification phenomenon is not suitable for all spray applications. Where very high water content formulations are to be used, or where a liquid hydrocarbon propellant in a pressurised device cannot be used, an alternative charging method is required. In industrial applications, charging is usually achieved by corona or induction charging. Corona charging is not appropriate for a passive charging technology, as the high electrical potential required to drive a corona discharge can realistically only be achieved using a conventional power supply. A system using induction charging can be designed, exploiting only natural charge separation phenomena. Real charges induce image charges in adjacent conductors, as shown in Figure 14.3(c). This can be used in spray applications by atomising a conducting liquid in an electric field, as shown in Figure 14.9. The liquid will be earthed and act as the earth electrode to create the electric field. As the liquid filament enters the electric field region, charges flow into the liquid from earth. Once the liquid is atomised into droplets, the excess charge is retained and a charged aerosol is produced. The principle determinants of charge are the liquid's conductivity and the voltage between the two electrodes. This technique is suitable for devices such as pump- and trigger-actuated sprays of the type used for some domestic cleaning products and beauty and personal care products.

In conventional induction charging spray devices, the voltage on the induction electrode is achieved with a power supply. In a passive system however, it can be charged by triboelectrification (Gaunt and Hughes, 2003a,b). The charge imparted to spray droplets is highly dependent upon the design of the induction electrode, but a charge in the region of 1–100 nC on the induction electrode is sufficient to achieve charge levels on the spray in excess of $100 \mu\text{C kg}^{-1}$. 1–100 nC of surface charge can be readily attained by tribocharging between two materials. The induction electrode when appropriately designed and constructed from a conducting material allows intensification of an electric field at the point where a liquid filament fragments into droplets. The induction electrode must be electrically isolated to minimise leakage of static charge. Contact or rubbing with a suitable polymer or other insulating material then imparts high levels of surface charge to the induction electrode.

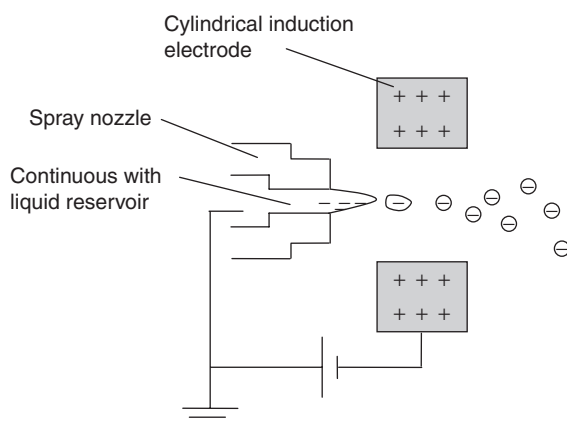


Figure 14.9 Schematic representation of induction charging of a liquid aerosol.

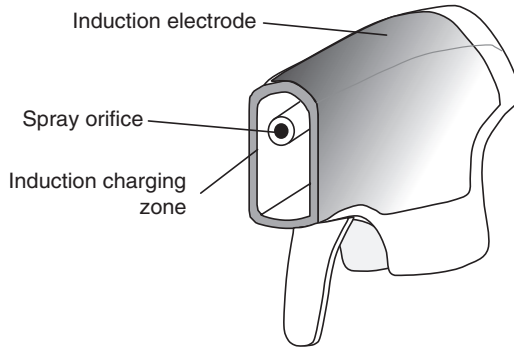


Figure 14.10 Schematic drawing of the passive-charged trigger-actuated spray device.

In pilot studies, an induction electrode of aluminium was electrically isolated using a polymer-supporting base. The induction electrode surrounds the components making up the spray device, such that the electric field is intensified around the point of liquid atomisation. The induction electrode is conducting so that charge is mobile in the material, allowing the electric field to intensify in the desired location. A prototype device is shown in Figure 14.10. The induction electrode is charged by rubbing with an insulating material. It is preferred that this material be relatively insulating in order to maximise the level of charge imparted. A charge of 20 nC on the induction electrode charges a spray of water to a charge-to-mass ratio of $140 \mu\text{C kg}^{-1}$, which compares with a conventional charge level of $5 \mu\text{C kg}^{-1}$ when there is no static charge on the electrode. Higher electrode charges generate higher spray charge-to-mass ratio values.

The design of the electrode with respect to the point of liquid atomisation is critical in maximising aerosol charging. Droplets must break away from the grounded liquid filament at the point of highest electric field in order to maximise charge levels. One advantage of this device is that charge is retained on the induction electrode rather than being lost or given up during spray generation. Surface charge will decline with time due to relaxation and surface leakage, and thus spray charge levels will similarly decline. This is reflected in Figure 14.11, which shows how successive atomisations from a trigger-actuated spray are charged without the level of charge on the induction electrode being topped up. The implications for the technology here are that for each successive spray achieved by trigger actuation, the charge on the induction electrode only needs to be topped up and not totally generated in each actuation.

This technology is not currently restricted from commercial applications by the ability to impart charge to the droplets, which can readily be achieved. Instead it is the pump- and trigger-actuated spray technology which presently limits application of this technology. The droplet size distribution of the aerosol produced from these types of spray is relatively large, having a MMD (mass median diameter) in the region of 50 to 150 μm compared with 20 to 50 μm for LPG-pressurised aerosols. In order to realise the benefits of electrostatic spraying, droplets of this size would require a charge-to-mass ratio exceeding that reasonably achievable by passive charging techniques. As better spray technology inevitably becomes available, two-stage passive charging by triboelectrification and induction will become worthwhile.

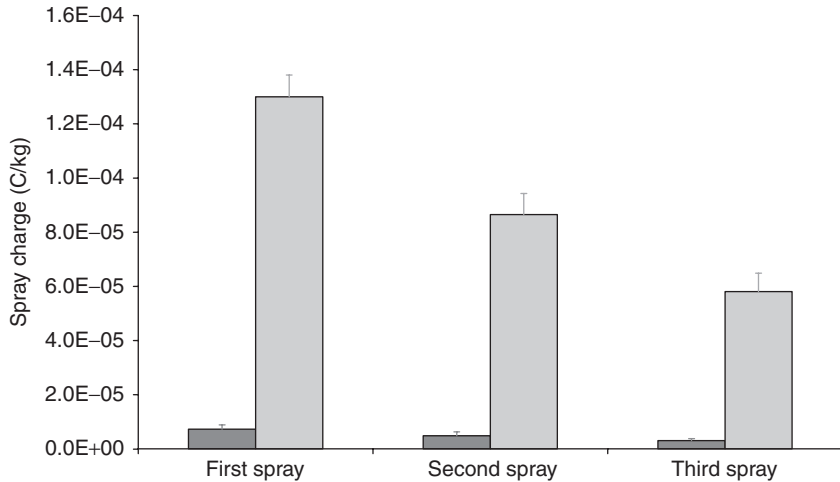


Figure 14.11 Charge-to-mass ratio of successive trigger sprays of water. The induction electrode is charged once by triboelectrification to 0 C □ or to 20 nC □.

14.8 Realised Benefits

Modern domestic aerosols are widely used to deliver air fragrances, insecticides, deodorants, household surface care and other products. In the majority of these applications the purpose is to deliver an active ingredient onto a surface, and therefore electrostatic spraying will achieve a performance enhancement as a result of attraction of the spray onto the surface, and a more even coating and deposition of droplets onto surfaces not in the direct line of fire by wrap-around.

A case study of charged domestic insecticide aerosols provides evidence for the level of efficiency improvements attainable. In this example, the bioefficacy of a commercially available insecticide aerosol with a charge-to-mass ratio of $20 \mu\text{C kg}^{-1}$ was compared with the same product, which had been modified according to the principles described above to give a charge-to-mass ratio of $200 \mu\text{C kg}^{-1}$. In two bioassays using house flies and mosquitoes the rate at which the insecticide spray took effect was increased by 25 % (Gaunt *et al.*, 2003a). The bioassay mimics the use of an insecticide spray against insects in flight, so involves releasing 50 insects into a room in which a spray of insecticide has recently been introduced. A typical result for the rate of knockdown (a state of paralysis in which the insect is incapable of coordinated movement) in house flies is shown in Figure 14.12. The charged aerosol consistently achieves faster knockdown than the conventional spray, signifying a faster rate of deposition onto insects in flight.

Insects in free flight are electrically isolated, conducting, targets. Charged droplets in close proximity to an insect will cause local polarisation of charges, as indicated in Figure 14.3(b). Attraction of droplets to the insect in this way will increase deposition efficiency. Space charge forces within the cloud of charged aerosol droplets will disperse the spray to a greater degree into all areas of a space. Typical behaviour of insects means that they tend

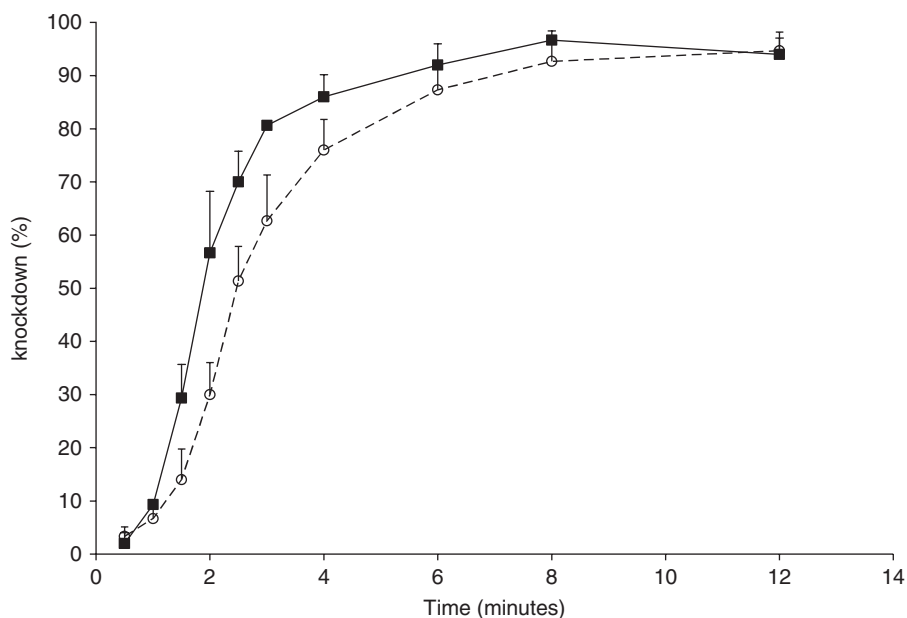


Figure 14.12 Rates of knockdown of house flies (*Musca domestica*) by a conventional insecticide aerosol ○ ($q/m = 20 \mu\text{C kg}^{-1}$) and an electrostatically charged insecticide aerosol ■ ($q/m = 200 \mu\text{C kg}^{-1}$). (Reprinted from L.F. Gaunt *et al.*, *Journal of Electrostatics*, 57, 35–47. Copyright 2003, with permission from Elsevier).

to spend more time in the upper portions of a room. Thus, space charge dispersion makes the availability of the insecticide spray in a room more biologically appropriate.

The advantages of charged domestic sprays do not only pertain to improved targeting and coverage of a surface. There are also benefits for the ubiquitous air freshener. In a similar manner to electrostatic precipitators, charged sprays can also be used to control airborne particulate pollutants and allergens in the domestic environment.

A fine spray of water droplets is a well-known and industrially implemented method for removing airborne particles. The fine sprays produced by domestic aerosols can also deplete the concentration of dust particles, and this effect is increased where the spray is electrostatically charged. As in the previous case study, a commercially available air freshener spray with a charge-to-mass ratio of $14 \mu\text{C kg}^{-1}$ has been compared with the same product, which had been modified to deliver a spray with a charge-to-mass ratio of $14 \mu\text{C kg}^{-1}$ (Gaunt *et al.*, 2003b). Using an air particle counter to record the airborne concentration of particulates, a conventional air freshener removes up to 60 % of dust particles in a room immediately after use. The same spray when charged removes nearly 80 % of particles, as shown in Figure 14.13. Further analysis shows that the most significant effects are seen with small particulates below $5 \mu\text{m}$ in diameter, and that charged sprays demonstrate the greatest percentage improvement over the effect of conventional sprays on submicrometre ($<1 \mu\text{m}$) particles.

A fine spray of water droplets removes airborne particulates as a result of contacting them by interception and inertial impaction as they move through the air. As the droplets settle

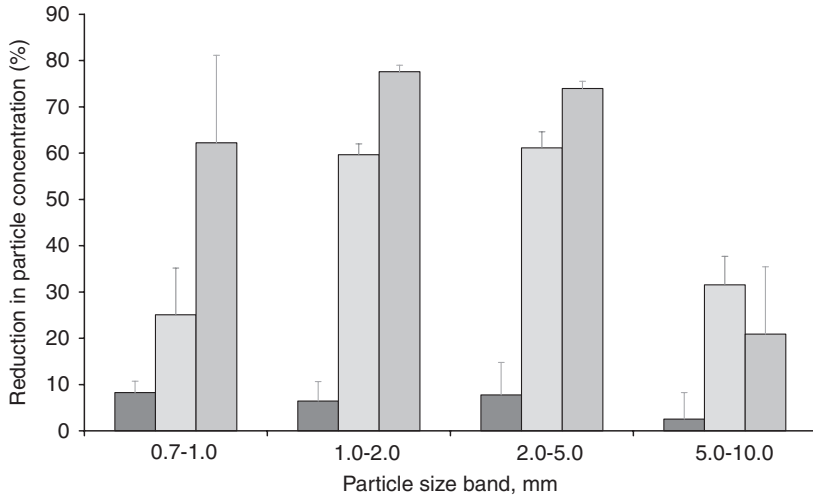


Figure 14.13 Rate of depletion of 2.0 to 5.0 μm diameter particles by a conventional aerosol \square ($q/m = 14 \mu\text{C kg}^{-1}$) and an electrostatically charged aerosol ($q/m = 140 \mu\text{C kg}^{-1}$) compared with the natural rate of particle depletion \blacksquare . (Reprinted from L.F. Gaunt, et al., *Journal of Electrostatics*, 58, 159–169. Copyright 2003, with permission from Elsevier).

onto surfaces, particles are removed. Enhanced particle removal by charged sprays arises due to enhanced particle collection by the charged droplets, arising from the attractive force. The attractive force will also reduce the chance of particulates bouncing off the droplets when contact is made. Space charge forces will improve the dispersal of the spray droplets through the room, allowing cleaning of a greater volume of the air.

Electrostatic spraying is recognised as offering significant performance benefits. When spraying a product onto a surface, the charge on the droplets causes attraction to surfaces leading to higher deposition rates. The mutual repulsion of like-charged droplets also causes them to be evenly distributed in space, so deposition is more even.

14.9 Conclusions

The advantages of electrostatic spraying are well exploited in a number of industrial processes, yet rarely available in consumer products due to the technical and cost-related issues surrounding provision of a power supply. By exploiting natural charge separation mechanisms such as frictional charging and flow electrification, electrostatic spraying becomes available to a diversity of product categories. Delivering electrostatic technologies in this way demands an understanding of the principles of the charging processes and the influential factors. Armed with this knowledge it becomes a relatively simple design process to incorporate charging into product design.

The benefits are numerous and visually demonstrated to the consumer. Attraction of charged droplets or particles to surfaces results in increased product contact with target surfaces, up to three times that achieved without charge. Electrostatic spraying also delivers

wrap-around, where surfaces not in the direct line of fire are coated as particles deviate from their straight line trajectory to follow electric field lines onto the rear of target objects. In this way the difference between a conventional and electrostatically charged spray become immediately apparent, due to the presence of product where it was not aimed. The evenness of coating with the latter is also clear. Space charge forces cause the like-charged particles to be repelled from each other. In so doing they become equidistant in their distribution in the space, and thus impact a surface more evenly distributed. The real advantages have been demonstrated for a number of household products, including insecticide sprays, surface cleaners and air freshener sprays, although this is not a comprehensive list.

Acknowledgments

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15

Smart Packaging in the Health, Beauty and Personal Care Sectors

Paul Butler

15.1 Introduction – Drivers and Packaging Needs

15.1.1 Health

Packaging is being challenged to support the health industry in the problem of patient medication compliance, to provide more effective and convenient forms of product delivery, and to help strengthen product authentication. There has been, and still is, significant activity in innovative packaging solutions that address these issues and positive cost/benefit trade-offs for the use of smarter packaging can generally be established. Increasingly a pharmaceutical package has to be much more than just a container for pills.

Patient Compliance and Product Delivery. Non-compliance is a serious health and cost issue in virtually all countries and has the greatest effect in terms of health on the ageing population. According to IDTechEx, a Cambridge UK-based consultancy, medication non-compliance costs the US alone about \$100 billion and 125 000 deaths yearly. It is responsible for 10 % of hospital and 23 % of nursing home admissions, affecting in excess of 3.5 million patients.

Clinical research trials used to test new pharmaceuticals is also an important area where non-compliance is a serious problem. The essential need is for reliable clinical data and this is directly related to patient compliance in taking drugs according to the established protocols of the trial. On the basis of the results of such trials, new medications are either approved for general medical use or abandoned.

Over the years, the healthcare and pharmaceutical industries have devoted much effort to the development of packaging delivery systems that aid compliance. A significant trend has been towards the blister pack, with the assumption that this form of convenient packaging with intuitive graphics can improve medication compliance, but without remind and record functionality, only limited improvements are possible. Smart packaging technologies are now emerging with these improved functionalities, including the tracking of actual medication use and communication with the healthcare provider.

A further area affecting non-compliance is the difficulty many people have in reading or understanding the contents and instructions of prescription medications. The small print and look-alike packaging of medicine vials can lead to confusion and mistakes, particularly in those with sight impairments, dyslexia, or reading problems. Many people want the packaging to explain more clearly how a drug works, suggesting that it would probably be beneficial if the pack used visual rather than text-based instructions and explanations. Improved on-pack communication will be one of the principal features of electronic smart packaging. Branded pharmaceutical packaging with built-in smart features such as moving colour images accompanied by a sound track in the language of choice could have a dramatic effect on assisting the old and infirm to take their medication, help encourage compliance and make it harder for generics to copy a product.

Authenticity. Authentication issues are – for obvious reasons – even more important with pharmaceuticals than they are with food and beverages. The World Health Organization estimates that counterfeit drugs cost the pharmaceutical industry \$40 billion yearly and the US government has already issued guidelines for the use of electronic pedigree systems for the pharmaceutical supply chain. These systems may use RFIDs or bar codes on item-level packaging that record the details of every transfer by wholesalers and re-packagers, until the final sale or use of the drug. Alarmed by the increasing cases of fake Viagra, Pfizer has announced in January 2006 that it will use RFID tags on all Viagra bottles in the US to authenticate the products. The subject of RFID on packaging and authenticity is an important subject in its own right but lies outside of the scope of this chapter.

Authenticity is key to the market branding of leading products, and the issue of product counterfeiting has long been a problem for certain luxury and high-end consumer products. Smart RFID tags confirming product authenticity, and other difficult-to-copy technologies offering high security, will become commonplace, initially in combating stock loss of high value products, such as spirits and perfume.

'Health in the Home' Concepts. Future growth opportunities exist in 'health in the home' concepts, where low-cost, convenience, portability and ease-of-use will drive the development of smarter packaging and product delivery devices, empowering people to take more responsibility for the state of their health. The challenge will be to develop new methods of diagnosing or predicting illness early, in order to prevent or reduce the subsequent costs of diagnosis and treatment. Smart medical packaging will give the consumer greater control and the ability to easily, accurately and quickly personally monitor their condition in the home. In the longer term, the integration of health information provision and monitoring will enable individuals to become custodians of their health and that of their families.

15.1.2 Beauty and Personal Care

Enhanced Quality of Life. Many consumers want value-added cosmetics that offer the advantages of the prestige brands, but cost less and are available in convenient mass market outlets. Young women are looking for trendy, portable products to suit their hectic lifestyles, offering all kinds of opportunities for consumer smart packaging. Just as for pharmaceuticals, delivery systems based on packaging will continue to play a dominant role in cosmetics and personal care products.

Anti-ageing Formulations. The ageing population in the developed world has increased the need for technologies and products such as anti-wrinkle products, hair regrowth, cosmetics with vitamins, nutritionals, sunscreens, herbs and various anti-ageing ingredients. Anti-ageing treatments already account for the major share of growth in the skin care market. Consumers expect fast, visible results in the form of healthier, and particularly younger-looking, skin. To deliver these results there is a growing trend by companies to rely on the use of advanced technologies. Much of this development will be in formulation, but innovative delivery systems designed to deliver active cosmetics ingredients into the skin using smart packaging technologies such as iontophoresis will find increasing application.

Fragrances Aimed at Younger Consumers. Fragrances aimed at this growing part of the market now need to perform to lifestyle expectations by using new technologically based packaging delivery systems designed specifically with the younger consumer in mind to help a fragrance and its wearer stand out from the crowd.

15.1.3 Summary of Drivers and Packaging Needs

The importance of smart packaging in the health, beauty and personal care markets is greater than in almost any other sector. The higher than average margins that generally characterise the sector should enable more innovative packaging to be developed and introduced, having strong emotional branding appeal or offering new levels of convenience and functionality for the consumer. Some future key drivers and their associated packaging needs are shown in Table 15.1.

15.2 Current Smart Packaging Examples

15.2.1 Innovative Product Delivery and Dispensing

Dual Dispensing Packaging – Fixed Ratio. Smart packaging designs have been developed that allow two incompatible products to be kept separated and only mixed at point of use. This concept has been exploited in the cosmetics and personal care markets with tube-within-tube packaging for complex and fragile formulations. A major advantage offered is the potential development of innovative dual-phase formulations that would not be stable as intimate mixtures.

As an example, Procter & Gamble's Crest Dual Action Whitening Toothpaste combines peroxide-based whiteners in one formulation together with other sensitive ingredients in a

Table 15.1 Summary of key drivers and packaging needs for the health, beauty and personal care sectors

Driver	Packaging Need
Health	
Patient compliance	Unit dosing Ergonomic packaging designs Non-spill, non-drip Easier portability
Security/Safety	Cognitive child-resistant closures Packaging integrity Label integrity Easy to store
Better, tailored information	Ease of disposal Ease of recycling
'Health in the home'	Personal diagnostic patches and devices, e.g. smart combs Disposable one-shot unit packaging Smart bandages
Beauty/Personal Care	
Convenience	Better, faster, non-messy, delivery systems More powered packaging (like electric toothbrushes)
Ageing population	Easy to open Easy to dispense Easy to read/audiovisual labelling
Aesthetics	Pocket-friendly compact designs Beautiful objects used in public places Communication-capable devices
Sexual attraction	Innovative perfume delivery systems



Figure 15.1 Crest Dual Action Whitening toothpaste comes in a dual tube-in-tube package keeping two active ingredients separate until point of use.

second formulation. The tube-in-tube package is shown in Figure 15.1, where the dispensing nozzle can clearly be seen. The nozzle has three grooves formed into its outer surface, through which product from the outer tube flows and three internal channels through which product from the inner tube passes. When the tube is squeezed, the toothpaste is discharged through the six openings as separate, alternating streams.

Examples of other fixed ratio dual-dispensing packaging can be found in commercial skin-care products such as Coppertone® Endless Summer sunless tanning lotion range, Merck's Exfoliac® Twin AC skin smoothing product, and in certain household cleaning products (e.g. SC Johnson's Drano® and Bissel OxyKic™).

Dual Dispensing Packaging – Variable Ratio. Increased flexibility and control is possible if the packaging allows variable ratio dispensing (Figure 15.2). An innovative dispensing pack that allows dual dispensing in variable proportions from 0–100 % has been developed by the German company Variotec. Termed Dialpack, the packaging requires a simple twisting of a dial to adjust the pump dispensers in each chamber to allow different ratio mixes of two components with high mixing accuracy. The two substances are drawn from their two separate cartridges by the pumps, mixed by a static mixer and then dispensed from a pump- or spray-style closure. Cartridges can be purchased and replaced according to need.

One of the first applications for Dialpack was Variosun, a dual dispense packaging system containing suncream with sun protection factor adjustable from 2 to 30, so that one



Figure 15.2 Examples of dual dispense cosmetic product packaging in the form of a fixed ratio pack from Lablabo (left) and a variable ratio product from Versadial (right).

container for sun protection can be used for the whole family regardless of skin type and sun sensitivity. Fiji Blend™'s Shades of Darkness uses the Versadial concept to package a tanning formulation consisting of a 'light' formula lotion in one half and a 'dark' bronzer containing a higher percentage of the active ingredients including self-tanners and bronzers in the other. The consumer can then decide on the required tanning level.

Ionisation-enhanced Cosmetic Foundation Delivery. A packaging device that generates low energy electrostatic charges to help deliver particulate skincare products onto the face in a safe and effective manner, akin to airbrushing, has been developed initially for the Japanese market but is now available more widely through Procter & Gamble's prestige skincare line SK-II. The SK-II Air Touch Foundation (Figure 15.3) is a light, hand-held disk that houses an ioniser and a sachet of foundation colour. The thumb-operated ioniser positively charges the particles of foundation colour, so they are attracted to the negative charge of hydrated skin and not to the eyes, eyebrows and eyelashes. Application of the foundation is extremely even, producing a natural flawless complexion with no need for blending.

Programmable Delivery of Aerosol Air Freshener. AromaPulse™ is a newly available packaging technology from Hush™ Fragrances (St-Hyacinthe, Quebec, Canada) that delivers programmable air freshening for the home. Long-lasting essential oil aromas in four separate fragrances, Mediterranean Fig, Summer Bloom, Laundered Linen and Thai Coconut Lime, are contained in refillable capsules and are fitted within a conventional metal aerosol container to which is attached a programmable electronic device that controls the delivery of the fragrance throughout the day. The user can choose from three settings to adjust fragrance delivery: the intensity of the spray (small, medium or large), the frequency (time) between each spray and the time intervals during the day when the device is activated. Extra bursts of fragrance are available at anytime by activating the device manually. The



Figure 15.3 *The SK-II Air Touch Foundation dispenser uses ionisation to charge foundation particles so they are attracted to the face without covering areas of hair or the eyes, producing a smooth, blemish-free even application.*

AromaPulse™ system allows the user to add scent to the air in the home without altering the fragrance by burning it or passing it through a wick.

Ionic Charge-enhanced Skin Patch Delivery. Delivery systems based on absorption through the skin have been used for years in the application of medication or cosmetic products. However the skin is an effective barrier to large chemical molecules so absorption is generally poor. The process of iontophoresis improves absorption and is based on the ionic diffusion of charged radicals under a mild electrical current potential, provided by a small flat flexible printed battery located in the skin patch, together with a self-adhesive membrane impregnated with the required ionic formulation as an ointment or gel. Most drug and cosmetic molecules are positively charged; since like electrical charges repel, the application of a positive current will drive these positively charged molecules away from the electrode and through the outer protective layer of the skin (stratum corneum) and into the underlying tissues and eventually the blood (Figure 15.4). Typically the current increases penetration through the skin by around sixteen times.

Pioneering development was done by printed battery specialists PowerPaper of Israel, through PowerCosmetics, a separate division; since then the technology has been taken up by a number of other companies. The initial focus has been on cosmetic formulations for skin lightening and whitening, firming and lifting, moisturizing, slimming, and cellulite reduction, including such problem areas as skin ageing and wrinkling, dark spots or discoloration. A commercial product for facial skin applications is currently being marketed by the Estée Lauder company as Perfectionist Power Correcting Patch.

Iontophoresis is also under study in oncology, lumbar punctures, and as an alternative form of paediatric medicine, particularly for children who fear injections. Another focus of interest concerns medications that cannot be administered in traditional ways. Some drugs, such as insulin, cannot be given orally because they are hydrolysed in the digestive tract. Others are excreted or metabolised, and hence intravenous administration is not effective. This area is developing rapidly and Vyteris of Fair Lawn, New Jersey, USA, has been granted the first FDA approval to use iontophoresis to deliver the pain killer lidocaine. This active patch technology, termed LidoSite®, allows precise dosing, giving physicians and patients control in the rate, dosage, and pattern of pain management that can result

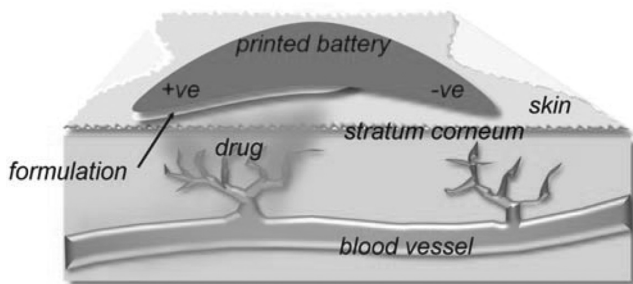


Figure 15.4 A smart skin patch: positively charged cosmetic and drug molecules can be driven through the tough outer skin by the process of iontophoresis.

in considerable therapeutic, economical, and lifestyle advantages over existing methods of drug administration.

15.2.2 New Forms of Consumer Convenience and Functionality

Packaging with Built-in Illumination. On-the-go convenience when using a cosmetic product such as makeup is a major driver in the development of smarter packaging. Poorly lit environments are commonplace in situations where makeup needs to be applied or readjusted, for example in the back of a taxi, and this consumer need has led to the development of a range of light-up cosmetic packaging by Robert DuGrenier Associates under the brand name Litelips. The collection includes packages for lipstick, lipgloss, mascara and nail polish; each has one or two small LED lights incorporated into the packaging, either in the base or cap of the unit that shines directly in line with the applicator, together with a small mirror built into the case (Figure 15.5). Various switch options are offered: a push button at the end of the cap, a sliding switch or an internal switch that is activated as the product is twisted to remove the applicator. The estimated lifespan of the LED lights is 56 hours.

Self-cooling Packaging for Face Cream. Lipids (fats, oils, waxes, etc.), the basic materials used in cosmetic products, are believed to undergo molecular retraction on rapid cooling, which make them penetrate the skin better. Once absorbed, they regain their initial structure and can have an immediate cosmetic uplifting effect on the skin of the face and neck, markedly reducing wrinkles and other blemishes.



Figure 15.5 Application of make-up in poorly lit environments is facilitated by the built-in illumination and mirror of the product packaging in the Litelips range of cosmetics.

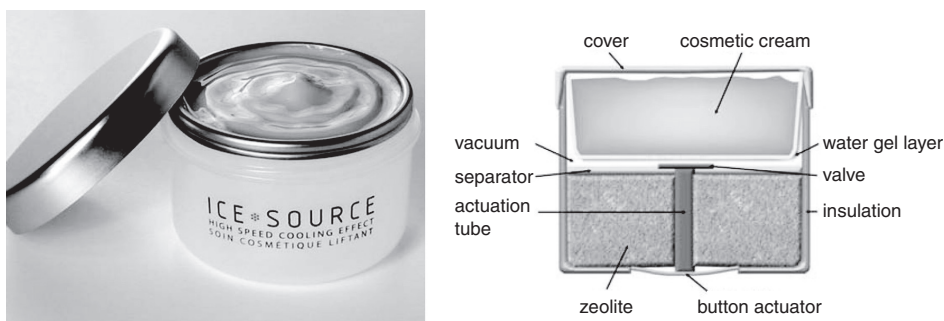


Figure 15.6 Cosmetic face cream in a self-cooling container. Cooling is initiated via a button at the base; this breaks a vacuum seal between an upper chamber surrounding the metal dish containing the cream, and a lower chamber containing zeolite. Water evaporates from the dish surface, cooling the cream.

Packaging for face cream that allows this rapid quenching effect has been developed by Thermagen, based on heat pump technology. The self-cooling packaging contains around 22 ml of Ice Source[®] face cream in the upper container, whose external surface is coated with a water-containing gel, and a zeolite desiccant in a lower chamber (Figure 15.6). To use, a button is pressed at the base of the container to start the cooling process. This opens a vacuum valve between the upper and lower chambers, causing water to evaporate from the gel and be absorbed by the desiccant in the base of the device, leading to a fall in temperature of the face cream of around 20 °C within 2 minutes. The ice-cold cream is then applied to the face and neck and it is claimed to result in a reduction in wrinkles by up to 21 % by relaxing the skin, particularly around the eyes.

15.2.3 Improved Consumer Communication

Packaging that Communicates the Product Attributes. Syrups, elixirs, solutions and suspensions are traditional dosage forms for oral medication, where liquid formulations are typically measured by pouring into a spoon. This approach has the great drawback of spillage, particularly when dosing small children. A no-spill medication for fever/pain and cough or congestion has been developed by Taro Pharmaceuticals in the form of a liquid gel, made by combining a pharmaceutically active ingredient in a liquid base with a thickening agent, so that the medication will stay on a spoon even if it is turned 90 degrees or upside down. The spill-resistant paediatric formulations are designed to provide parents with increased ease and accuracy of dosing. The products using this technology, called NoSpil[™], are sold across the US under the ElixSure brand (Figure 15.7).

In order to signal ‘spill proof’ to the consumer, the paperboard outer packaging features a lenticular graphic on the spoon illustration on the front panel. Initially this produces an attention-grabbing ‘winking’ effect as two images of a spoon flip back and forth as consumers pass by the product on the store shelf. But the secondary communication plays to the product’s unique attribute of spill resistance. One image shows a level spoon with



Figure 15.7 *Increased ease of use and accuracy of dosing is provided by this spill-resistant medicine for children by Elixsure. The outer packaging communicates the no-spill characteristics of the formulation by lenticular graphics.*

product in it, while the other image displays the spoon tipped on its side. The product remains in the tipped spoon.

Packaging that Helps Users Manage Cosmetic Product Application and Shelf Life. An electronic packaging innovation that helps consumers time how long their cosmetic treatment should last, and even alerts them as to the time and date of their next treatment, has been developed by Production Innovations, a California-based packaging technology company. It is claimed that P3 – which stands for Precise, Product, Performance – can help consumers using time-sensitive products to use them more precisely and even more regularly. The innovation incorporates a microprocessor into the packaging cap, complimented by an LED light that blinks, as well as an LCD readout that times the length of the application. The timing mechanism is activated when the cap is opened, and begins when the cap is closed after an application dose has been removed from the packaging. At the end of a preprogrammed time, the cap beeps and the LED flashes. The targeted application products are any time-sensitive cosmetic treatments, such as facial peels, face masques and hair dyes. The product has been designed to have a minimum impact on the appearance of the packaging, blending into the cap in a way that does not detract from branding or the overall design, and can also be retrofitted to a wide variety of packaging styles (Figure 15.8).

Many cosmetic products contain ingredients whose effectiveness ages with time once the packaging is opened, and products that are used infrequently by the consumer may well become ineffective, unsuitable, or even dangerous to health, after long periods of storage. This is because although most cosmetic products contain preservatives that inhibit



Figure 15.8 (Left) Electronic programmed packaging closures that help consumers time the length of a cosmetic treatment, and remind them of the next. Reproduced with permission of production Innovations LLC. (Right) Integrated colour-change label signals consumers to throw away ineffective and possibly contaminated cosmetics that have exceeded their shelf-life. Reproduced with permission from Timestrip Plc.

microbiological growth, eventually bacterial breakdown can occur, leading to possible harmful effects if the product is then applied to delicate parts of the body, such as the eyes. This may be a growing problem with the increased use of ‘natural’ or ‘green’ cosmetics, which may not contain preservatives and therefore once opened may have very short shelf-lives. The issue becomes one of remembering when the product was opened in the first place, particularly for short shelf-life products that are easily contaminated.

The shelf-life for eye-area cosmetics is more limited than for other products. Mascara is a good example. This normally has a shelf life of around 3 to 6 months. Apart from drying out after an extended opening period, the biggest danger is contamination by the pump action of the brush, which can force bacteria into the container where the moist, wet environment is ideal for growth. Subsequent application to the eye area may result in infection, such as conjunctivitis. Moisturisers and creams can also harbour bacteria picked up from the hands and fingers. In development for such products is Timestrip[®], a smart label that monitors how long a product has been open. Once activated, in this case as the cosmetic product is first opened, the label turns progressively red as liquid diffuses from a small reservoir along a porous strip, indicating the passage of time. The strips can be manufactured to measure elapsed time from minutes up to over a year, at various temperatures, and the simple visual signal tells a consumer when to discard a product safely. Concept mascara and lipstick products are illustrated in Figure 15.8 where the Timestrip[®] is integrated within the packaging.

Compliance Packaging for Pharmaceuticals. An example of a simple and cost-effective mechanical closure for medication packaging in bottles, jars and vials has been launched by Neville & More. The closure works by automatically indexing each time it is operated, indicating when the bottle or jar was last opened and acting as a reminder to the patient to take their next dose of medication. The closure supports four different prescription regimes,

from once to four times daily. Increased functionality can be obtained from a packaging closure by incorporating electronic circuitry, simple displays and LEDs, together with a miniature battery power source. Such electronic smart packaging devices are slowly gaining acceptance although cost remains an issue.

Remind Cap[®] closures are simple electronic timing closures that fit vials or bottles and, once programmed for a particular dosing regime, signal to the patient the intervals between doses via a series of beeps and a flashing light. The ScripTalk[®] Talking Prescription Label System has been developed by En-Vision America to improve compliance and safety for patients who have difficulty reading or understanding instructions or warnings on prescription labels. The device has a microchip embedded in the label that is automatically printed, programmed and fixed to the container at the pharmacy. At home, the patient uses a handheld ScripTalk Reader, which is capable of reading the prescription information stored on the microchip in the language of choice using speech synthesis technology, enabling the visually impaired to take their medication correctly.

The Med-ic[™] Smart Package uses an onboard CPU embedded in a blister package to record each time a pill or capsule is removed. The RFID tag records the time for later analysis, such as at repeat prescription time or on a follow-up visit to a health centre, when the information can be downloaded through a 13.56 MHz RF wireless reader and displayed graphically. When used for clinical trials, at the end of the trial period the patient returns the blister package and the information is downloaded to a database.

A second variant has been launched – a smart medication bottle termed eCAP[™]. It reminds the patient when the next dose is due and records the time the patient opens the bottle to remove the tablet or capsule, without active patient input. The information is then retrieved by the reader for review by a doctor or pharmacist. Both variants of these smart pharmaceutical packages are shown in Figure 15.9.

Cerepak[™] by MeadWestvaco employs smart technology to measure and improve patient compliance. It reminds patients when to take medication, records when they do, and



Figure 15.9 Two variants of smart pharmaceutical packaging from Information Mediary – for blister packs (left) and tablets or capsules (right). Reproduced with permission from Information Mediary Corp (IMC).

reports that data back to their doctor or pharmacist. The technology was developed in conjunction with Cypak AB, a Swedish technology firm. Low cost, non-metallic (graphite), non-toxic, screen-printable, conductive inks are used to create the circuit board, sensors and antenna on a paperboard substrate in a single stage production process. The sensors are capable of detecting and recording events – such as a broken seal, an opened lid, or damage to the package – with a timestamp, and can also form an electronic questionnaire for subjective data collection. A small (7 mm²) silicon microchip is adhesively bonded to the printed circuitry having 32 kb of memory (15 pages of information), 32 inputs for sensors detection, a clock, piezoelectric reminder signal and temperature sensor capability. A lithium-manganese dioxide button battery powers the device, which has low power consumption that gives a long operating time using minimal battery power.

Cerepack and the initial Cypak electronic compliance packaging (ECP) use standard blister packaging, and each removed dose is recorded with current date and time-stamped, then transferred to a target database over the Internet, with maximum security. Information from the ECP can be retrieved at any time by placing the wallet onto a scanner connected to a PC.

The Helping Hand™ from Bang & Olufsen Medicom is a convenient packaging device designed to help people to manage their medication. It discreetly reminds the patient when it is time to take a tablet, and also has a guiding function that records how well the dosing schedule has been followed.

15.3 Latest Developments and Future Opportunities

15.3.1 Better Product Protection

Functional three-component polymers have been developed and are starting to be introduced as packaging materials for the pharmaceutical industry. In film, insert or as part of the container, these materials will be capable of absorbing degrading gaseous components, such as oxygen and water vapour, or any other chemically active molecule that might migrate through the interconnecting transmitting channels into the polymer matrix. One potential application is in the packaging of complex and sensitive chemical DNA test strips and diagnostic strips and patches, which will increasingly be found as part of home healthcare diagnostic kits.

CSP Technologies is commercialising a new series of patented polymeric materials consisting of three-phases – a polymer, a channelling agent, and an active component in particulate form, such as silica gel, desiccant combinations, zeolite, cations, biocides, herbicides or pigments. The three components are thoroughly mixed and processed to create a three-phase system that contains a network of interconnecting channels leading from the surface to the entrapped active particles. This unique polymer matrix technology enables active functionality in the control of humidity for containers for pharmaceutical, nutraceutical, and personal care products by maintaining a constant, predetermined relative humidity. Activ-Vial™ is a one-piece, injection-moulded container with a flip-top lid that has been commercially introduced to eliminate moisture damage in glucose strip packaging.

Tamper evidence packaging assurance is a further need. Tamper evidence technologies that cannot easily be replicated, e.g. based on optically variable films, or gas sensing dyes involving irreversible colour changes, are becoming more widespread and cost effective

for the disposable packaging of commodity items, but smart materials might offer a better route. For example, piezochromic polymeric materials might be incorporated into package construction so that the package changes colour at a certain stress threshold. In this way, for example, a ‘self-bruising’ closure on a bottle or jar might indicate that attempts had been made to open it.

15.3.2 Better Product/Packaging Communication

With so much focus on RFID in packaging, the humble barcode is frequently presumed to be on a fast track to obsolescence with nothing new to offer. However, when printed as a two-dimensional data matrix code, content is significantly increased, and although still requiring a line-of-sight reader, these barcodes could offer potential applications in improving the consumer/package interface. As an example, a stand-up retort pouch of Heinz soup sold in Japanese grocery stores has a printed 2-D barcode that when interrogated by consumers via the camera mode on their mobile phones, connects the user to the Heinz website, where recipes, branding information and various downloads can be found. In the future as the amount of legal and discretionary label information grows, there will be a need for supplementary audio and visual components to communication, particularly where the ageing population is concerned, which can have difficulty reading fine text (see Figure 15.10).

In the past, the evolution of electronic smart packaging has been hampered by the lack of small, low-cost, power sources. This translates to relatively bulky and expensive devices that characterise the commercial examples of electronic smart packaging today. In the future, technological developments in piezoelectric materials, organic photovoltaics and thin-film printed batteries are expected to overcome these limitations and become cost effective for



Figure 15.10 *Smart packaging of the future might communicate messages about the product via simple printed 2-D barcodes that can be interrogated and then listened to, with a camera phone.*

packaging applications even of commodity products. On-board power will deliver sound, vision and sensing opportunities for packaging and, in an increasingly track and trace world, active RFID tagging at item level.

15.3.3 Better Product Delivery

The objective of an ideal drug delivery system is to place effective medical agents in specifically targeted parts of the body. From advances in nanotechnology, nanoparticles, microcapsules and nanoemulsion technologies are becoming important as carriers for healthcare, cosmeceuticals, colour cosmetics and personal care products, which in turn require new and innovative packaging delivery systems. More acceptable, effective and convenient packaging devices under consideration include aerosol inhalation devices, forced-pressure injectables, biodegradable polymer networks designed specifically to transport new gene therapies, and transdermal methodologies such as iontophoresis. As an example, new types of electronic aerosol inhaler are being developed that provide not only more efficient delivery but also user-friendly features such as dose counting, overdose prevention, dose-due alarm, breath-delivery coordination and data logging. The need for user effort and coordination is significantly reduced.

One particularly promising technology, TouchSpray™ is an electronic, propellant-free, aerosol for delivering liquid drugs via the lungs and nasal cavity developed by The Technology Partnership (TTP). It uses conventional battery power to activate a piezoelectric element attached to a thin foil membrane containing multiple tiny holes. As the surface of the foil comes into contact with a solution or suspension of drug, the liquid is micro-pumped through the small holes in the foil, an action that converts the drug solution into a very fine stream of low velocity, precisely controlled, droplets (Figure 15.11).

15.3.4 New Forms of Functionality

One of the few objects having acceptable exposure activity in public places for females is makeup, either in the form of lipstick or a small compact. In both instances small,

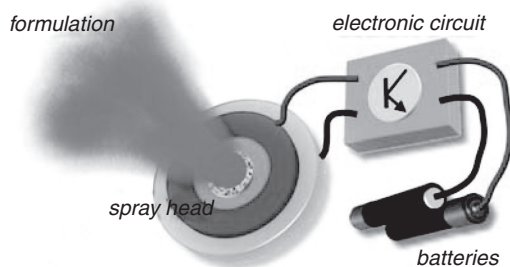


Figure 15.11 Precise droplet control from electronic atomiser technology developed by The Technology Partnership.



Figure 15.12 *Concept design for a smart ladies compact with self-adjusting magnifying mirror and simple message receiving capabilities. Image used with permission of PI3.*

handbag-friendly and aesthetically pleasing packaging is vital. Conceptual design work for a leading fragrance house by PI3 has investigated socio-cultural trends in the evolution of female toiletries and linked these to possible future technological packaging developments.

The concept colour compact (Figure 15.12) has a smart magnifying mirror that can be instantly adjusted by piezoelectric control to make the magnification of the mirror reflection tailored to suit a particular user's make-up application. In addition, the issue of social acceptability in terms of communication in restricted social situations, such as in a restaurant, is addressed in this concept by creating the ability of the compact to double as a communication device and receive limited text messages.

Today's contemporary perfume bottles are beautifully sculpted containers that look desirable on the shop counter or bathroom shelf, but their basic design has been unchanged for thousands of years. Glass bottles containing scent or fragrant oil look fundamentally the same today as they did in ancient Greece, so the manner and processes of applying fragrances to the body have also remained largely unchanged. The female rituals, experiences and the desire for self-expression of the modern world require a more innovative approach to fragrance delivery.

A futuristic smart packaging proposal by PDD, a London-based structural design agency, is SNIF™ – Sexy New Intelligent Fragrance – a concept fragrance system that can be placed anywhere on the body (Figure 15.13). It has dual sensory intelligence and monitors the bodily conditions of the person wearing it, as well as the changing environmental conditions, to release the optimum level of fragrance from three fragrance reservoirs. The device is sensitive to an individual's skin balance, and is as much a fashion accessory as a fragrance product.

15.3.5 Health in the Home

As previously discussed, it is predicted that an important future trend will be the move to give people more control over their own health in their own home, with the help of advanced electronics, computers and the Internet, so that they and their doctors are better prepared to deal with health issues. This will involve the development and transfer of portable, miniature, intuitive and accurate diagnostic smart packaging devices of the type that are currently used in the laboratory into the home. Complex diagnostic tools could very well become affordable hand-held machines in bathrooms in the next 10 years, while portable packaged devices will allow monitoring of health parameters while outside of the home.



Figure 15.13 The SNIF fragrance device (left) can be placed anywhere on the body releasing perfume in accordance with the body conditions of the wearer (right). Reproduced with permission from PDD Ltd.

Smart packaging developments for on-the-go health monitoring are expected in the following areas:

- smart bandages that change colour dramatically to tell you whether you have a serious infection;
- smart skin indicators for alerting of danger to allergic reactions, particularly in young children;
- programmed skin patches using smart gels that rely on changes in skin properties to trigger drug delivery, replacing conventional pill-taking medication.

16

Laser Surface Authentication – Biometrics for Brand Protection of Goods and Packaging

Russell Cowburn

16.1 Introduction

In recent years a number of highly successful human biometric technologies have been introduced, such as fingerprint recognition and iris scanning [1]. These work on the principle that no two people have the same small scale detail in the pattern of their fingertips or irises and that these naturally occurring variations can be used as a unique identifier for the individual. Laser Surface Authentication (LSA) is a new technology that mimics this biometric principle, but applies it to inanimate objects such as documents, goods and packaging [2]. A newly developed laser scattering probe allows the equivalent of a unique fingerprint to be rapidly measured from each item that is to be identified and protected. Like human biometrics, the fingerprint is derived from naturally occurring microscopic randomness that is inherently present in virtually all surfaces.

16.2 Naturally Occurring Randomness

Naturally occurring randomness is an extremely attractive proposition for brand protection. The traditional approach to brand protection technologies is to apply some complex manufacturing process to an item, e.g. a hologram or a special formulation of ink. The security comes from a presumed asymmetry in technical capability between the brand owner

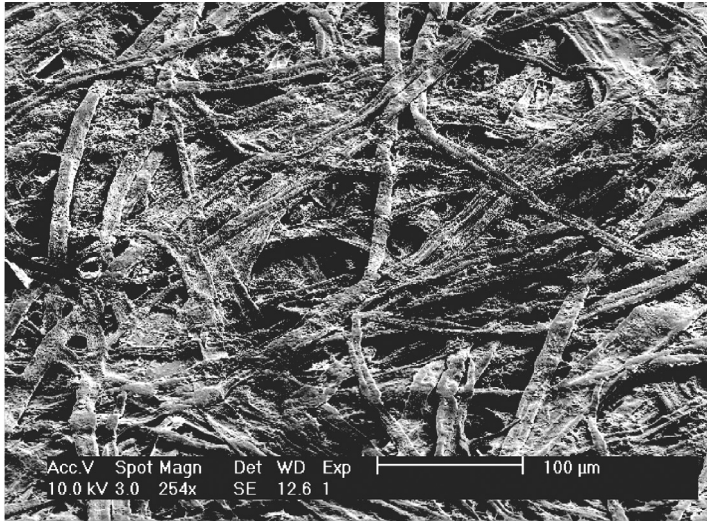
and those who would attempt to counterfeit it. In reality, one finds an arms race of such technologies: a new hologram is introduced in January, the counterfeits are available on the street by June (or in some cases February!). Naturally occurring randomness, be it in traditional human biometric form or the new inanimate biometric technology LSA, uses a different principle. In this case, the security rests upon the asymmetry between reading and writing the security feature. Since the feature is naturally occurring, the brand owner is never involved in writing or creating the identifier – nature does that. The brand owner only ever reads the feature, either at an initial registration time or later when the person or item is to be identified. This is very important, as it changes the nature of the arms race. In order to overcome the technology, it is necessary for the attacker not simply to be as technically capable as the brand owner, but more so. The attacker would be required to learn how to create artificial identifiers, which is something the brand owner was not required to do. We call this principle ‘intrinsically read-only’. The more detailed and complex the naturally occurring randomness, the greater the technical challenge posed and hence the more secure the technology. For example, human fingerprints are relatively coarse and attackers have developed techniques using latex overlays (or even Jelly Baby sweets!).

If naturally occurring randomness is to be used for identifying and protecting documents, goods and packaging, there are three requirements: (i) the items must possess a high degree of microscopic complexity – if it is not microscopic it will be easy to copy and if it is not complex there will not be enough unique combinations to identify each item in a large collection; (ii) it must be possible to read the feature easily and rapidly; (iii) the feature must be robust when subjected to normal or even heightened levels of wear and tear.

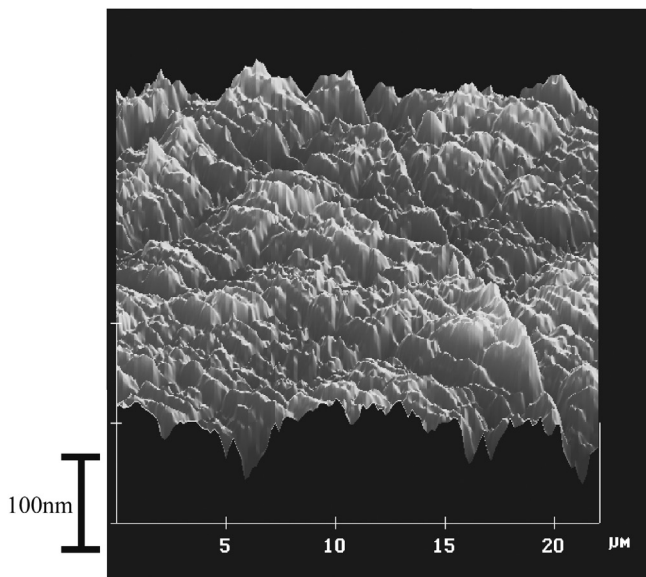
Figure 16.1 shows high-resolution microscope images of the surfaces of normal office paper and a plastic (PVC) card, such as used for bank cards. In both cases one sees a high degree of complexity. The supposedly smooth paper surface upon close inspection actually reveals an intricate tangle of fibres. Similarly, the smooth and shiny plastic surface actually reveals a mountainscape of hills and valleys if viewed with nanometre-scale precision. Although multiple examples of the same type of item would probably exhibit similar average statistics for these features (e.g. the width of the fibres or the average roughness of the surface), the specific pattern formed should be unique to each item since the exact place of each fibre or the exact location of each plastic peak is entirely random.

16.3 Diffuse Laser Scattering

Although high resolution microscopy clearly reveals the naturally occurring randomness, it is too expensive, bulky and difficult to use as a practical brand protection technology. In its place, we have developed a simple, low-cost, portable laser probe that allows much of the same information content as shown in Figure 16.1 to be obtained, but without the expense and complexity of full microscopy. The laser probe uses the principle of diffuse laser scattering, as shown schematically in Figure 16.2. A low-power laser (1 mW, 635 nm, continuous wave solid state) is focused onto a surface at normal (i.e. perpendicular to the surface plane) incidence. Physicists use the Rayleigh criterion to determine what then happens to the beam. The Rayleigh criterion uses the Rayleigh parameter $R_a = \frac{2\pi\sigma}{\lambda} \cos \theta$, where σ is the r.m.s. (root mean square) roughness of the surface, λ is the wavelength of the incident light and θ is the angle of incidence of the light, as measured from the surface



(a)



(b)

Figure 16.1 (a) A scanning electron micrograph of the surface of a sheet of office paper. (b) An atomic force micrograph of the surface of piece of shiny PVC card.

normal. The criterion says that if $R_a < \pi/4$ then the surface can be considered to be smooth and should be treated as a mirror in traditional geometrical optics. This means that the angle of reflection of the laser beam will equal the angle of incidence, and the light should return in the direction that it came from. This is known as ‘specular scattering’. If $R_a > \pi/4$, then the surface is rough enough to influence the reflection of the light, and much of the power

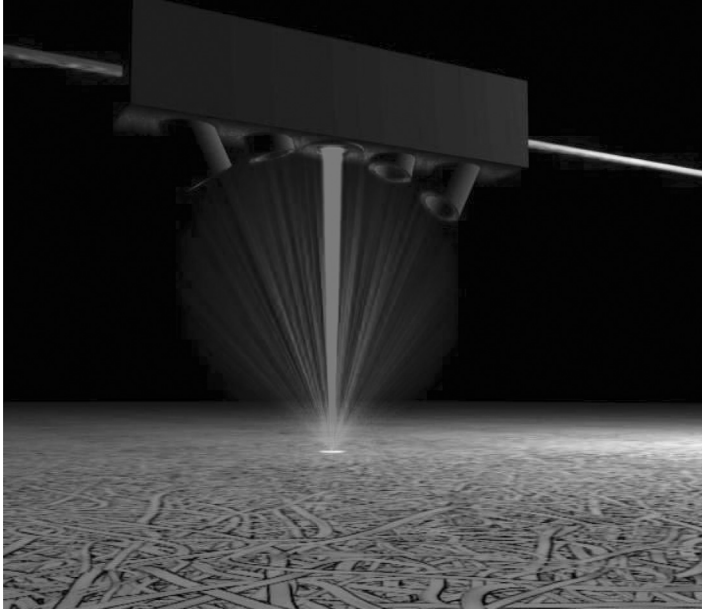


Figure 16.2 *A graphic representation of the LSA technique. A focused laser beam is shone onto the surface. Any imperfections in the surface (shown here as paper fibres) cause some of the light to be diffusely scattered to the sides, where it is captured by photodetectors. The complete sensor is then scanned across the surface of the item.*

of the laser beam will be scattered in directions other than the surface normal. This is what is shown schematically in Figure 16.2 and is known as ‘diffuse scattering’. We experience this effect every day without even realising it. When we look at a sheet of paper, it appears bright white regardless of how we view it. This is diffuse scattering. When we look at a mirror, we see a reflection from a specific angle. This is specular scattering. Setting $\lambda = 635$ nm and $\theta = 0$ allows the Rayleigh criterion to be recast as optically smooth surfaces occur when $\sigma < 80$ nm; otherwise they are optically rough. One sees from Figure 16.1(b) that even very smooth PVC plastic cards have enough surface roughness to be close to the threshold of optical roughness and that one should expect some diffuse light scattering from their surface. Paper and coated paperboard are certainly rough enough to scatter light diffusely.

The LSA laser probe simply places photodetectors at various angles to catch part of the diffusely scattered light, and the intensity at each detector is recorded as the probe is scanned over the surface of the item. Each point in the scan corresponds to a snapshot of a small part of the diffuse scattering from that precise laser position. The complete sequence of recordings is as random as the fluctuations in the surface. Note that this is a one way physical function: because we only record a small subset of the complete diffuse scattering from each position, we cannot infer the profile of the surface from the sequence of recordings, although in principle one could infer the sequence of recordings from the

profile of the surface. Diffuse scattering is therefore no substitute for microscopy if one actually wishes to see the surface. However, since the LSA signal is derived from the profile of the surface, it is as good a unique identifier as the picture of the surface itself would have been, and it is much easier to measure.

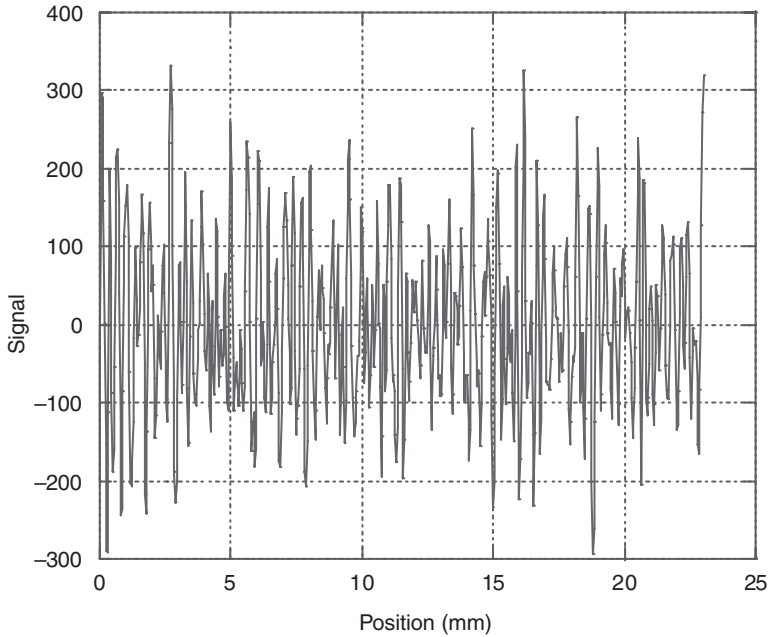
Figure 16.3 shows typical LSA scans obtained from a sheet of normal white office paper, a piece of coated paperboard as used in pharmaceutical packaging and a plastic PVC card. Care was taken in this figure to apply precisely the same signal processing conditions so that the amplitudes of the signals from the different materials can be compared. In all cases, one sees a signal that looks like random white noise. The signal size from the white paper is approximately 10-times stronger for office paper than for the other materials. This is consistent with the roughness amplitudes measured directly in Figure 16.1. The autocorrelation function of all of the scans of Figure 16.3 falls off with a full width, half maximum, of approximately 100 μm , which is comparable to the focused beam size, as would be expected for a random signal. Figure 16.4 shows a close up of part of a scan from office paper where we have overlaid the results from a second scan taken later after the paper had been removed from the scanner, handled and then replaced onto the scanner. One sees excellent agreement between the first and second scan of the same item. The exact degree of match between the two scans in Figure 16.4 is shown in Figure 16.5 where we have computed the cross correlation function between these two scans. The sharp spike in the middle rising to 0.85 shows an excellent match when the two scans are correctly aligned with each other. For comparison, Figure 16.5 also shows the cross correlation function computed between two scans taken from different sheets of paper (although of the same type and manufacturer). The lack of any such spike shows that the two scans are derived from different items.

Similar results have been obtained from a wide range of materials, including metal (aluminium, copper and brass), polycarbonate (as used in laser-engraved identity cards), many different types of coated paperboard, bank note paper, passport back covers and laminated photograph pages, holograms and paper clothing labels. It appears that virtually everything except perfect mirrors and transparent materials possesses a unique fingerprint that can be easily measured through diffuse light scattering.

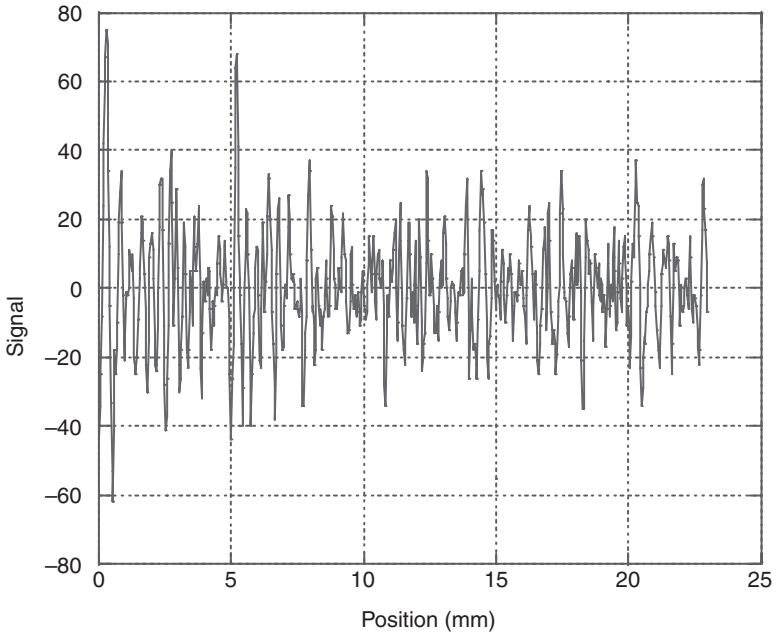
It should be noted that attempts have been made in the past to use naturally occurring randomness from specific material systems as unique identifiers. These include using the randomness in magnetic grain alignment in the magnetic stripe of credit cards and other magnetic media as a unique identifier [3], the randomness of miniature beads in a solid token [4], and direct imaging of paper fibres [5]. What makes LSA distinctive is the fact that it makes very few assumptions about the physical origin of natural randomness. Any form of surface roughness, regardless of whether it comes from fibres, watermarks or any other origin, all lead to diffuse laser scattering.

16.4 The Statistics of LSA

The first step in analysing the statistics of LSA is to convert the analogue sequence into a sequence of binary bits. We do this by applying a simple digitisation rule that if the analogue

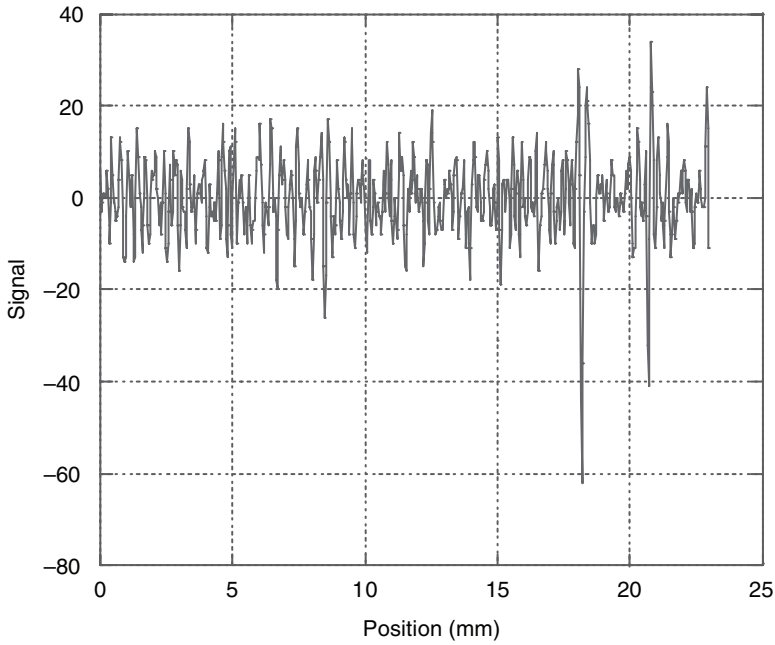


(a)



(b)

Figure 16.3 LSA scans taken from (a) white office paper, (b) coated paper board as used in pharmaceutical and branded product packaging, (c) white PVC as used in credit cards and access control cards. The experimental and signal processing conditions were identical, so the signal amplitudes may be compared.



(c)

Figure 16.3 (Continued)

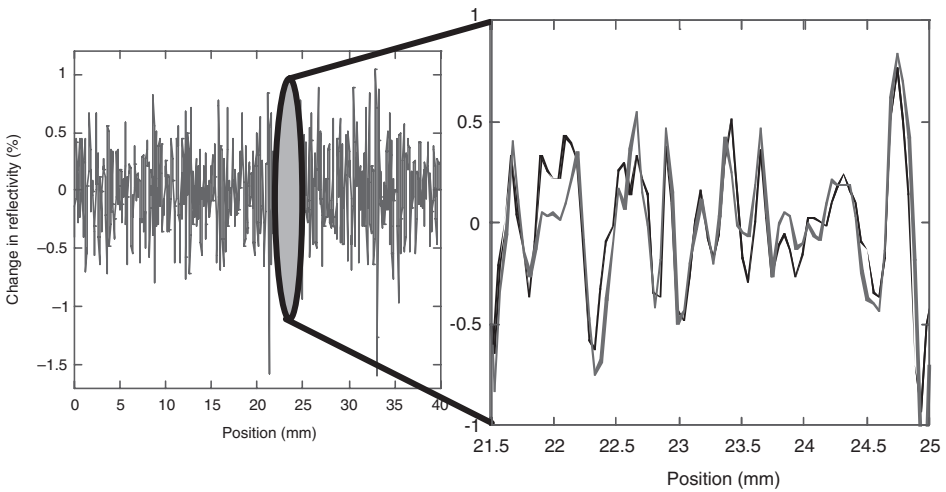


Figure 16.4 A typical LSA scan from office paper. The right hand panel shows a close-up of part of the scan and also shows overlaid a second scan taken from the same item at a later time. Very good agreement between the first and second scans can be seen.

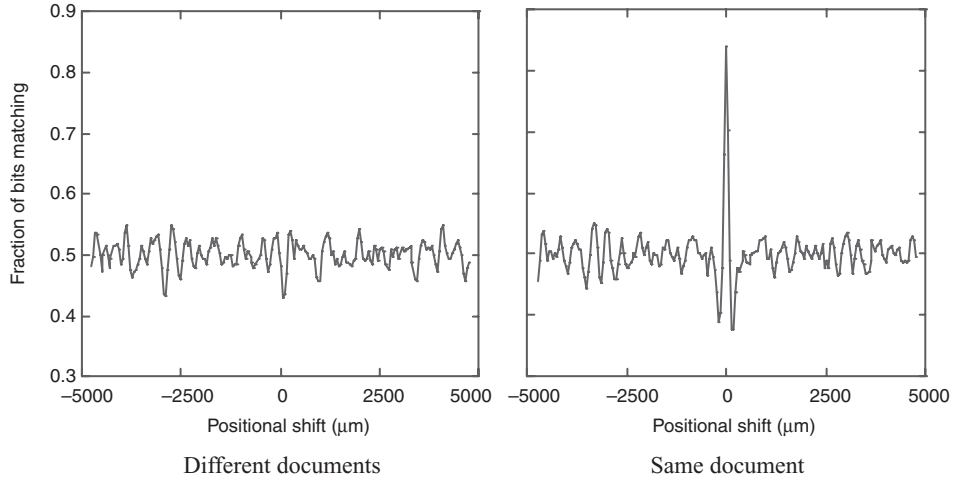


Figure 16.5 Digital cross correlation curves calculated between the LSA fingerprints of two different sheets of office paper (left hand panel) and two scans taken at different times from the same sheet of office paper (right hand panel). The central spike in the cross correlation function indicates recognition of an item.

value is above the mean level (usually zero because of band pass filtering which is applied to the analogue signal – see later in this chapter) then this corresponds to a binary ‘1’ and if it is below the mean then a binary ‘0’, see Figure 16.6. A sequence of binary bits is usually modelled statistically using the binomial distribution. In order to test whether a recorded LSA scan corresponds to the same item as a database target, a digital cross-correlation is performed between the two binary sequences and the maximum value of the digital cross-correlation obtained. The digital cross-correlation value, which we usually refer to as the bit match ratio or BMR can vary between 0 (no bits matched) through to 1 (all bits matched). One would expect that two signatures from different items should have a BMR of a little

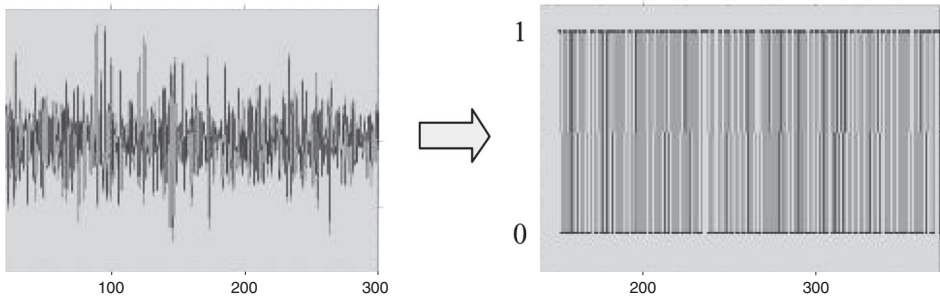


Figure 16.6 Digitising the LSA signature. After bandpass filtering, the LSA signature is uniformly distributed about zero. Analogue values greater than zero then become digital ‘1’ and values lower than zero become digital ‘0’.

above 0.5, while two signatures from the same item should have a BMR close to 1. The BMR for different items does not have an expectation of precisely 0.5 because we search for the maximum value in the digital cross correlation function, i.e. we attempt to move the two sequences with respect to each other in order to improve the match quality as much as possible. This is necessary in case the two items are not in exactly the same physical position during each scan. This has the effect of increasing the expectation of BMR for items which are different from 0.5 to around 0.55 to 0.6.

Figure 16.7 shows a plot known as a Hamming plot. This is similar to the way in which the human biometric research community usually presents data (footnote about axis direction) and is two histograms of the BMRs measured from a large collection of items, each of which has been scanned twice. The first histogram (shown on the left hand side of Figure 16.7) is obtained by comparing the first scan of each item to the second scan of every other item (but not the second scan of itself). Since, by definition, these are always comparisons between different items, one would not expect a high BMR. Indeed, one sees a distribution that is tightly centred around 0.55. This histogram is a measure of the uniqueness of the

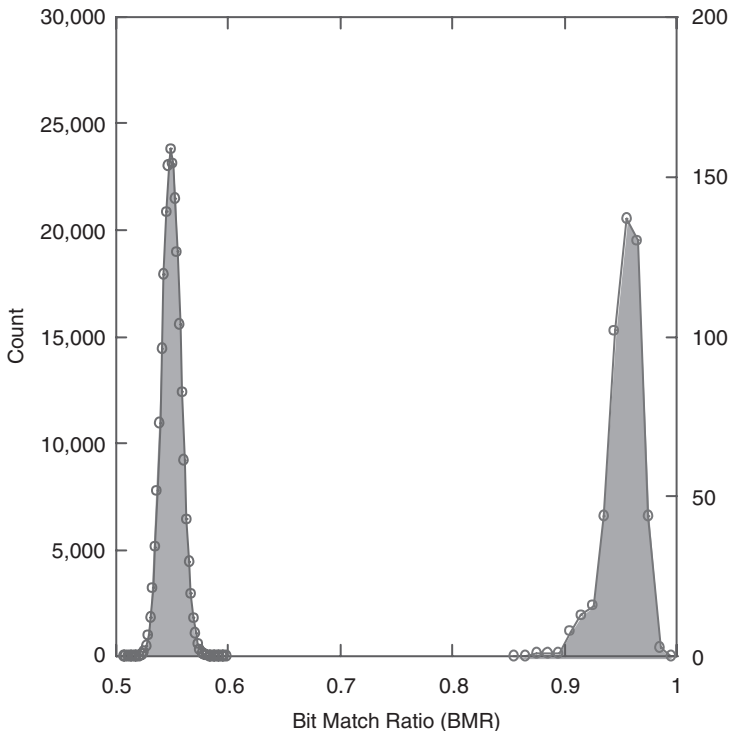


Figure 16.7 A Hamming plot obtained by scanning 500 sheets of office paper twice. The left-hand histogram is obtained by cross correlating scans from different sheets and hence shows the uniqueness of the signatures. The right-hand histogram is obtained by cross correlating two scans from the same sheet and hence shows the quality of recognition. A useful authentication and tracing system will have a finite separation between these two histograms, as indeed is shown here.

signature of each item, as it easily identifies unexpected collisions between the signatures of different items. The second histogram (shown on the right hand side of Figure 16.7) is obtained by comparing the first scan of each item with the second scan of the same item. Since these are always comparisons between different scans of the same item, one would expect a high BMR. In Figure 16.7 one sees a distribution centred on 0.95. This histogram is a measure of the repeatability of a signature.

The simplest test which can be applied to the Hamming plot is to see where an acceptance threshold should be drawn. In the case of Figure 16.7, a threshold could be placed anywhere between 0.65 and 0.8. The acceptance threshold can be used to answer questions of authenticity, since a BMR below the threshold would be expected when comparing an LSA scan of an item with that of a different item and so does not constitute a reliable identification; a BMR above the threshold only occurs when comparing an LSA scan of an item with a scan previously obtained from the same item and so does constitute a reliable identification.

This mode of analysis can be used to implement an authentication technology. A database is constructed of all of the LSA signatures of items manufactured by the brand owner. To authenticate subsequently in the field an item as genuine, its LSA signature is remeasured and then compared to that from every item in the database. If any BMR is greater than the threshold, then the item can be said to be genuine. If no BMR is greater than the threshold, then the item can be said to be counterfeit (or badly scanned).

The next level of analysis is to apply a degree of confidence to the declaration of authenticity. This takes the form of posing the following statistical question: 'The BMR of this rescanned item is high enough to be considered as genuine. Given the known distribution of BMRs from items that are not the same (i.e. the left hand histogram of Figure 16.7), what is the probability that this item could have this BMR if it were *not* genuine?' This probability is usually known as the false positive probability.

This question is answered by finding a statistical model that fits the experimentally observed distribution of the left hand histogram of Figure 16.7 and then extrapolating it to BMR values that were too high to be observed experimentally for that sample size. For a sequence of independent random bits, the binomial distribution is the appropriate model. There are two parameters: p (the probability of a given bit matching) and N (the number of degrees of freedom or effective bits). In order to simplify the statistics, we work now with the cross correlation at zero shift rather than the maximum of the cross correlation across its full range. This is called the native match and excludes any attempt to optimise the match by shifting the two signatures. The advantage of using native match data is that p should become 0.5 and the validity of the binomial model is more self-evident.

Figure 16.8 shows on a logarithmic scale the fitting of a binomial distribution to the experimental data by varying only N and p . One sees that the binomial model fits extremely well, even down to the low occurrence events in the tails of the distribution.

Once N and p are known, a general formula can be written for the false positive probability at a given BMR level. The false positive probability is one minus the cumulative probability up to that BMR level, i.e. it is the probability that a randomly selected item would match this item as well or better. The formula is:

$$\text{Probability that BMR is } k/N \text{ or greater} = \sum_{k=m}^N \frac{N!}{k!(N-k)!} p^k (1-p)^{N-k}$$

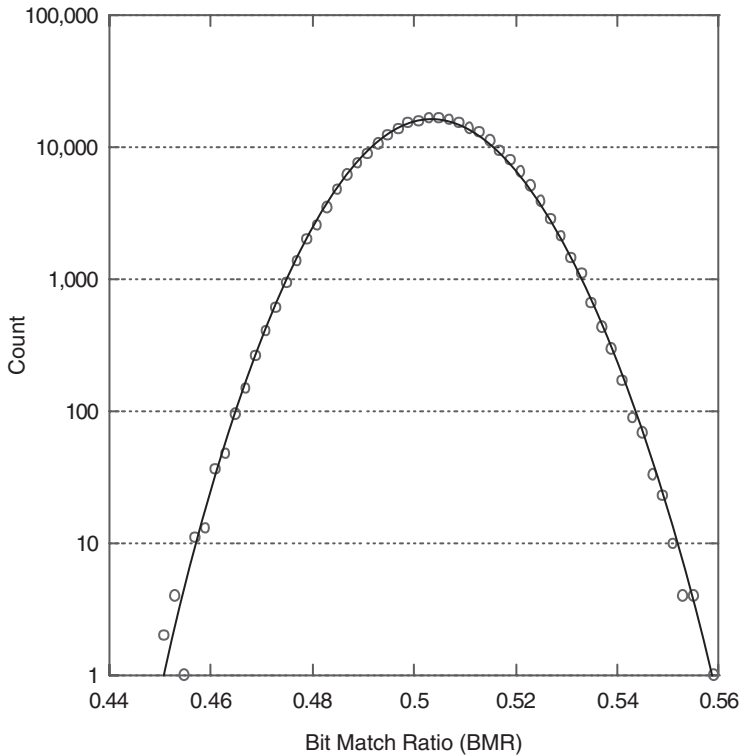


Figure 16.8 The same data shown in the left hand histogram of Figure 16.7 plotted on a logarithmic-linear scale and without any attempt to shift the signatures to optimise the match. The line is a best-fit binomial distribution curve using $p = 0.504$ and $N = 1684$.

The uniqueness is defined as the reciprocal of the false positive probability, and corresponds to the number of items that would need to be sampled on average before one is found that matches the current item as well or better. It is a measure of how many items can be held in a database and still be uniquely and unambiguously identified by their LSA signature. Figure 16.9 shows the same data as Figure 16.7 but with the uniqueness values superimposed above the BMR axis for the values of N and p derived from Figure 16.8. One sees that for the level of BMR usually obtained when an item is correctly identified, the uniqueness is extremely high. This means that the LSA signature can be considered to be absolutely unique and can be used to identify items even in the largest of inventories. This makes it very well suited to consumer goods, where many billions of nominally identical items may be in circulation at a given time. As far as LSA is concerned, each one is different.

In biometric technologies one usually distinguishes between ‘one-to-one matching’ and ‘one-to-many matching’. One-to-one matching is used when the question to be answered is: I believe that I know which item of my inventory this is – am I correct? One-to-many matching is used when the question is: which of all of the items in my inventory is this one? A second identifier is required for one-to-one matching, although this identifier does

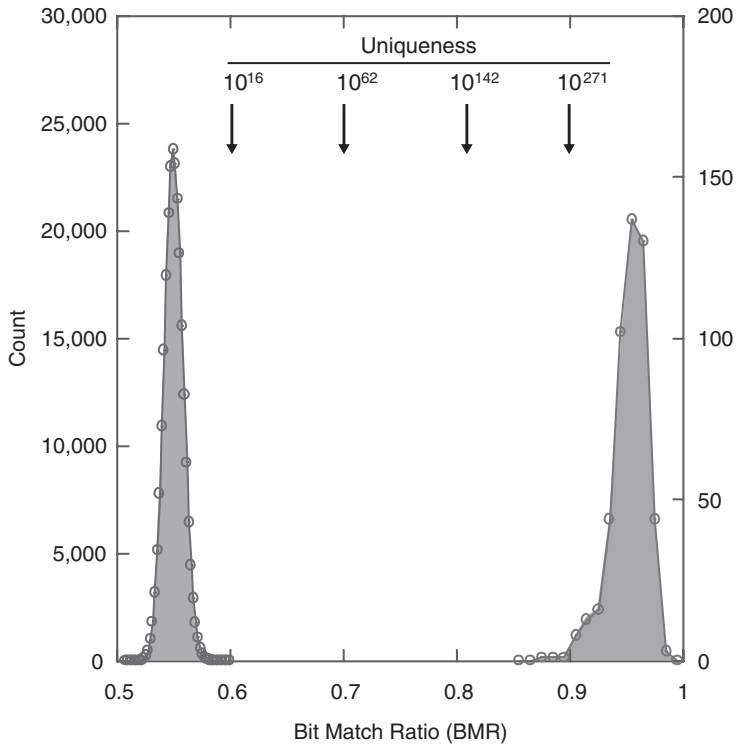


Figure 16.9 The same Hamming plot of Figure 16.7 but with the bit match ratio values converted into equivalent uniquenesses by applying the binomial distribution model using the fitting parameters obtained in Figure 16.8.

not have to be secure. Examples include: a unique serial code printed on the box, in human readable form, a one-dimensional barcode or a two-dimensional barcode; the name of the owner of an identity card or passport; the account number and cheque number on a cheque; a unique identity code carried by an RFID (Radio Frequency Identification) chip or a smart card chip. The advantage of one-to-one matches is that lower uniqueness values can be tolerated. For the data shown in Figure 16.9 this is hardly important since even the very poorest rescans lead to uniqueness in excess of 10^{150} . Suppose, though, the uniqueness were only 10^6 (see later for reasons) and a one-to-one match were being performed. One could then say with a 99.999 % certainty (i.e. a one part in 10^6 uncertainty) that this item is genuine. If, on the other hand, a one-to-many search was being performed across an inventory of 10 million items with the same level of uniqueness, then one could say nothing about whether the item was genuine, since one would expect there to be 10 items in that inventory that match any randomly selected signature, regardless of whether they are genuine. The other advantage of one-to-one matching is that much less computational power is required and so the answer can be obtained more quickly. Figure 16.10 shows the maximum searching speed achievable today using standard computing hardware in a one to many search. One-to-many searches are always divided into two steps. In the first step, a

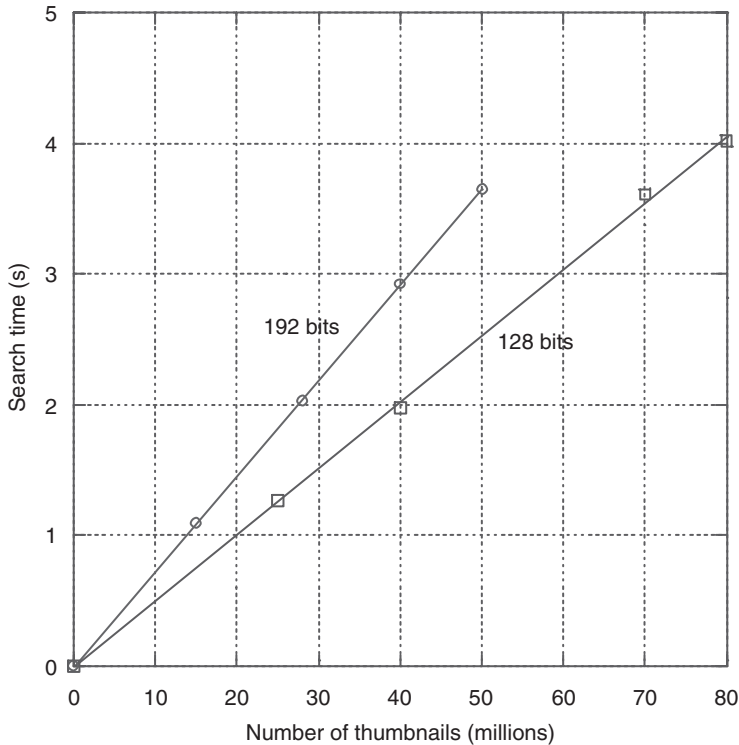


Figure 16.10 The search time of a single Pentium microprocessor using 128- and 192-bit thumbnails. Signatures can be tested at a rate of up to 20 million per second on a single processor.

reduced version of the fingerprint (called a thumbnail) is searched very rapidly. However, since N is low for the thumbnail (recall that N cannot be larger than the number of physical bits in the signature), the uniqueness is poor and so a given search always finds multiple hits. These hits are considered a most likely list and each one is then re-matched using the full length signature. Figure 16.10 shows that up to 20 million thumbnail targets can be tried per second on a single Pentium processor. Figure 16.11 shows the results of a full system implementation of a one-to-many search across 150 million database targets. The query was launched from a remote country using a low quality internet connection, transmitted to a central server, which then used multiple separate PCs to perform the thumbnail search. The correct match was then transmitted back to the overseas issuing machine. The entire query time from original launch to receipt of result (including all Internet transmission delays) took an average of approximately 5 seconds.

What causes the uniqueness to fall from the astronomical values shown in Figure 16.9 down to levels where only one-to-one matching is possible? There are four main sources.

- (i) Materials that offer poorer LSA responses, both in terms of the amplitude of the signal and hence its detectability and also how easy it is to find the correct position for

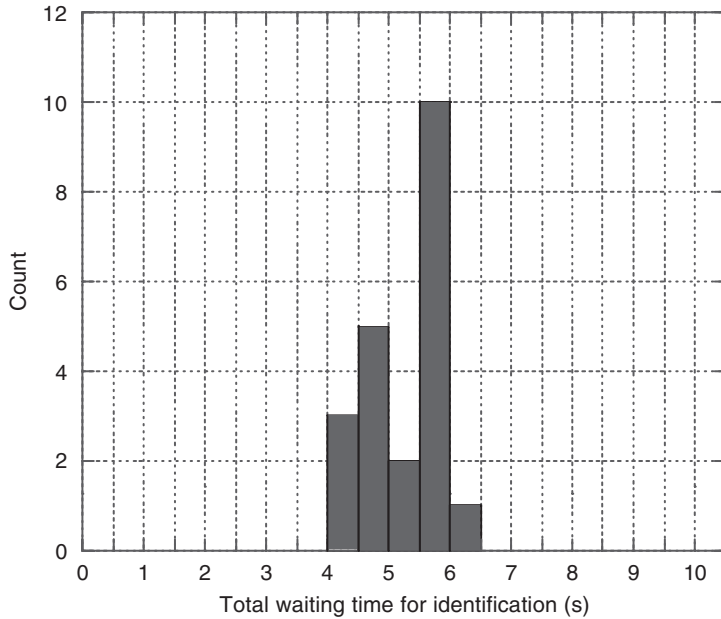


Figure 16.11 A histogram of the total waiting time for a response to a 1 to many LSA search among 150 million items, including all Internet transmission delays. All signatures were stored on one 32-bit server with five Pentium search clients attached to it. No meta-data was used to subdivide the 150 million items.

- scanning. For example, soft, pliable materials can be more difficult than solid, rigid ones. Both of these reduce the BMR of genuine matches, and hence the uniqueness.
- (ii) Items that need to undergo high levels of wear and tear such as chemical attack. This also reduces the BMR of genuine matches and again the uniqueness. In general, LSA has been found to be remarkably robust when items are exposed to damage. Figure 16.12, for example, shows four sheets of paper that underwent an LSA registration scan when pristine, and were then artificially damaged in a number of different ways. In all cases, a good recognition was still possible, although the BMR (and uniqueness) was lower than if no damage had been inflicted.
 - (iii) Small items where the available area for scanning is less than 10 cm². In these cases, the total amount of recorded data is reduced and consequently N in the binomial distribution falls. In this case, even a good BMR level will correspond to a lower level of uniqueness.
 - (iv) Items that have a large amount of high density printing on the surface. If the lengthscale of surface contrast is too small, it is not possible to use signal processing to separate the LSA signal component from the intensity variations due to surface printing. These must be separated since in most applications the surface printing is the same for every item and is not random. Consequently, large areas of the scan must be discarded in the signal processing and the end result is that there is too little data, i.e. N becomes too low again.

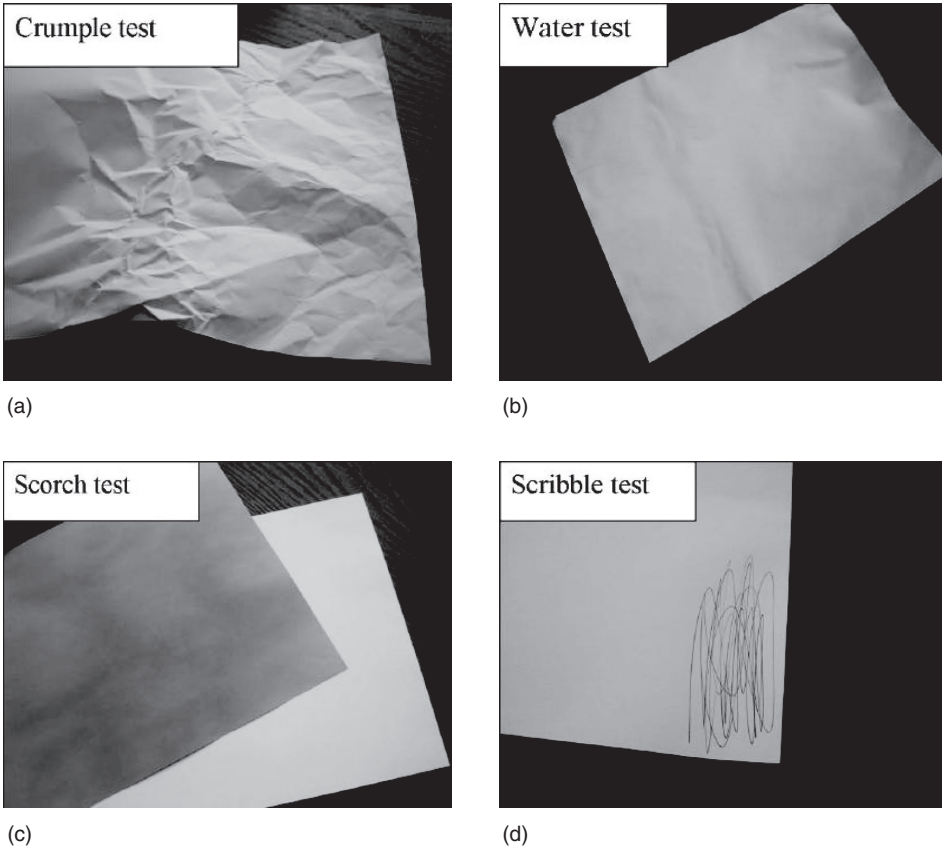


Figure 16.12 Four different types of damage applied to office paper. An LSA signature was recorded from the paper before and after damage. In all cases, a match quality corresponding to a uniqueness of at least 10^{18} was obtained after damage.

In terms of the Hamming plot of Figure 16.7, (i) and (ii) cause the right-hand distribution to move to the left, while (iii) and (iv) cause the left-hand distribution to move to the right. When there is no longer any clear space between these distributions it becomes impossible to select a threshold above which authenticity can be guaranteed; if the distributions overlap, there is no way of knowing if a BMR value in the overlap region is a poor quality match of a genuine item, or a lucky high quality match of a counterfeit item. In these cases, one must limit the use of LSA to one-to-one matching scenarios, or else start to deal with realistic values of both false positive and false negative probability. These situations can sometimes be improved by including additionally considering meta-data about the item, for example its brand, country of origin and date of manufacture.

These limitations apply to all biometric and most sensing technologies. In general terms, LSA has better levels of discrimination than human biometric technologies.

16.5 The Practicalities of Using LSA

LSA is usually a two step process. The first half is known as registration and is used to populate a database of all known items. For most scenarios, especially those involving large inventories of items to be protected (as is the case for consumer goods), this registration phase should be fully automated. This is usually achieved by mounting a static LSA sensor close to a conveyor belt such that the items pass by the sensor as they move along the belt. The advantage of this approach is that the normal production environment is not disturbed. The current generation of LSA sensors is designed to accept a maximum linear speed of 4 metres per second (790 feet per minute) and up to 10 items per second (36 000 items per hour). These two limitations are more than sufficient for most production environments without any modification other than the addition of channelling rails to improve the positional stability of items as they move along the belt. An electronic speed signal is also required to allow the LSA sensor to monitor the instantaneous speed of the item and hence ensure that data points are recorded at a precisely defined spacing. This is usually achieved by adding a rotary encoder to the motor driving the belt. Scans are collected in a local database table on the same computer that drives the LSA sensor. These scans are then uploaded in batch mode on a regular basis (usually between once an hour and once a day) to a central database store. An association is also made in that local database table between each scan and any known meta data. This could include a date–time stamp, a batch number or a customer number (especially if the sensor is placed close to the point where the items go into a final shipping crate) and also some information about the type of product if multiple products are produced on the same line. Meta data has two distinctive roles. The first is to make one-to-many searching easier. For example, many manufactured items carry a batch code stamped onto them. Although this code is rarely unique, a one-to-many search can then be limited only to items with the same batch code. The total search space is then often significantly reduced and, if the uniqueness is low, the false positive/false negative statistics is improved. The second role of meta data is as information to be returned once a successful match has been achieved. This is useful if LSA is not being used only as an authentication technology, but also as a tracing technology, as would be the case for tackling grey market trading. In grey market trading, the item is often known to be genuine but in the wrong country in order to take advantage of differential taxation or pricing. LSA can then be used to retrieve all of the meta data that was stored with the LSA signature at the time of registration, and hence work out who the intended customer was, which shipping route was being used, etc. Although a similar function could be performed by a printed unique identity code, such codes are often defaced by grey market traders to avoid such tracing. In consumer products such as perfume, the aesthetic impact of a printed code may also be undesirable.

If one-to-one matching is to be performed, then the local database table must also contain the association between a second identifier and the LSA signature. The simplest way to achieve this is by having a reader on the production line, as close as possible to the LSA sensor, which reads the existing second identifier at the same time as the LSA signature is being recorded. The two can then be tied together in the same database entry. If this is not possible and the second identifier has to be read either before or after the LSA signature, then a date–time stamp can be used to reconcile the two. This reconciliation does not have to happen in real time, which simplifies much of the integration engineering.

The choice of how large an LSA signature field should be in each database record is a compromise between total database size and uniqueness: N in the binomial distribution

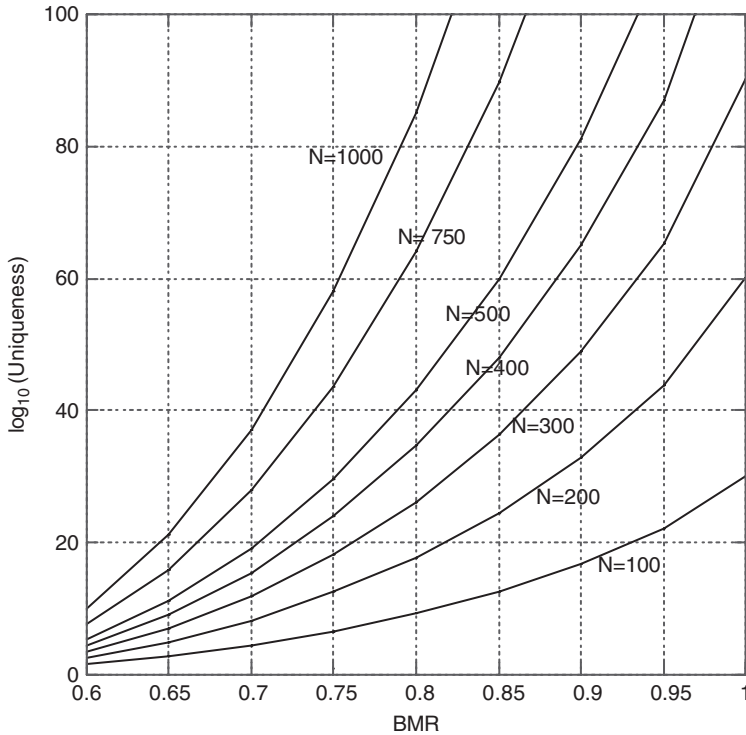


Figure 16.13 A uniqueness table obtained from the binomial distribution model. The uniqueness is calculated for a given bit match ratio and number of effective bits.

cannot be larger than the number of bits physically stored, and is often less. A typical working point is to store 3000 bits (375 bytes) per item, usually made up of 500 bits from each of six photodetectors. Figure 16.13 shows some sample calculations made from the binomial distribution for different values of N and BMR. A BMR of 0.7 can usually be achieved for genuine items unless the items are very heavily damaged or poorly positioned. For one-to-many matching across an inventory of 100 million items it is assumed that a uniqueness of 10^{14} is required. Figure 16.13 shows that in this case, N must be greater than or equal to 400. For one-to-one matching with a 99.99% confidence, a uniqueness of 10^4 is required. Figure 16.13 shows that in this case, N must be greater than or equal to 100. Remember that this is the number of degrees of freedom in the binomial distribution, and not necessarily the database field size, which may be larger. However, with careful system design it is usually possible to arrange for the database field size (in bits) to be no more than twice N , and in many cases it can be much closer. A minimum of 800 bits per item should therefore be allowed for one-to-many searching and 200 bits for one-to-one matching. Extra space must also be allowed for indexing information, etc.

The scenario of one-to-one matching is interesting because this field size is small enough to go directly into a two-dimensional bar code of approximately $8\text{ mm} \times 8\text{ mm}$, which could be printed directly onto the item itself. This is then a variation on the one-to-one matching mode, where the second identifier is not simply a record locator to a database

entry, but rather carries the LSA information itself. In this case, digital encryption must also be added to prevent an attack with access to LSA equipment from printing his or her own codes. The two advantages of this 'without database' mode are firstly that there is no need for the cost of a database infrastructure, and secondly that items can be validated in the field even in extremely remote locations where there is no Internet or mobile phone access. The disadvantage is that there is a considerable technical challenge to printing two-dimensional bar codes in real time on a high speed production line, as the LSA data must be recorded, processed, digitally signed and then formed into a barcode image all within a few tens of milliseconds if the printer is to be close to the LSA sensor. Although more time could be obtained by moving the printer further downstream, there is then a further logistical challenge of ensuring correct synchronisation, especially if items may be removed from the conveyor by quality inspectors, etc.

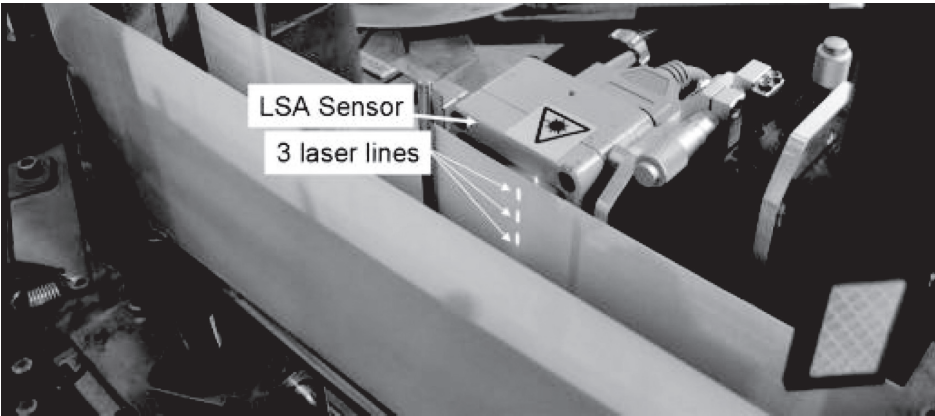
The second half of most LSA implementations is the process of rescanning items in the field for the purpose of authenticating or tracing them. This is usually a manual process, since it is normal for only a small number of items to be authenticated in the field. The portable field scanner therefore incorporates a motor that moves the LSA sensor with respect to the static item. Scanning takes approximately 1 second. The LSA sensor is designed for a working distance of 5 mm between its surface and the surface being scanned. In order to make this distance as easy as possible to find manually, the sensor is sunk into the scanner by 5 mm so that the item to be scanned only needs to be placed in contact with the top of the scanner. Figure 16.14 shows pictures of both the static production line registration sensor and a portable field scanner. The portable field scanner connects to a lap-top computer, which receives the raw scan data from the sensor and applies some initial digital filtering. If no database is being used, then the lap-top must also read the expected LSA signature and then perform the comparison locally. If one is in a one-to-one matching mode but with a database (i.e. the item only carries a record locator) then the lap-top sends the recent scan to the central server, along with the record locator, has been read from the item and the comparison is performed on the server. Alternatively, the lap-top may choose only to transmit the record locator to the central server, retrieve the expected LSA signature and then perform the comparison locally. Which of these modes is used will depend upon the degree of trust that can be assigned to the lap-top and whether security policy allows the proprietary matching algorithms to be placed onto the central server.

The way in which a field scan is processed and matched against one or many database targets can depend upon the item being scanned. In particular, different material types benefit from different digital filter settings and items with a large amount of printed contrast on them will need specially constructed masks to determine which bits should be used. In scenarios where a given field scanner may encounter a wide range of different products (for example a major brand owner may have many products but limited brand protection officers, or customs officials may need to use LSA to verify imports of a wide range of products across multiple brand owners), it is necessary for the user to communicate the product type to the field scanner lap-top before any scans can be processed.

Since different items of a nominally identical type exhibit independent and unique LSA signatures, it also follows that different parts of the surface of an item also have different signatures. It is therefore necessary to perform the field scan in approximately the same area as the registration scan was taken. Achieving this is probably the single greatest challenge to implementing LSA. The problem has been made easier by careful design of the laser



(a)



(b)

Figure 16.14 (a) A portable field scanner and laptop computer; (b) a production line sensor mounted onto a production line.

optics and matching algorithms to engineer the maximum possible tolerance to errors in this positioning. Mispositioning in the direction of scan is relatively easy to correct, since it leads simply to a shift in the position of the maximum value of the cross-correlation function. The cross-correlation function must therefore be evaluated across a wide enough range to be sure to catch the proper peak. The main impact of mispositioning in this direction is therefore an increase in computation time for matching, although if uniqueness is low it can be reduced even further by the number of effective trials inherent with a wider cross-correlation range.

Sensitivity to mispositioning in the direction transverse to the scan direction (but still in the plane of the item being scanned) is achieved by focusing the laser spot to a line rather than a spot, using a cylindrical focusing lens. The short axis of the focused line follows the direction of scan, allowing a short autocorrelation width to the LSA signal and hence a high value for N . The long axis of the focused laser is therefore in the direction for which mispositioning would cause the greatest problem and the recorded LSA signal is derived from a spatial average of the surface structure along the length of the focused laser line. Even if the item is mispositioned much of the same area still ends up being scanned and hence the BMR does not change too much for small misplacements. Figure 16.15 shows a quantitative measure of how BMR depends on transverse mispositioning, along with similar curves for misplacement in the direction of focus of the laser and the yaw rotation axis.

A good LSA implementation will attempt to minimise the uncertainty in the position of the registration scan through the use of guide rails on the conveyor belt. This then allows for the maximum amount of permitted manual misplacement at the field scanner.

Two strategies are in place to minimise misplacements at the field scanner. The first is through mechanical positioning. The field scanners can be fitted with mechanical guide rails that hold the item in the correct place. This works well for rigid rectangular cartons, for plastic cards and for paper documents. It is less suitable where there is a wide range of items to be scanned on a single field scanner, or where the item is a cylindrical bottle or an irregular shape. In these cases, an imaging approach is used. The field scanners contain a small camera that observes the area that is about to be scanned. The camera can be used to identify a location mark on the surface. This may be a brand owner's logo, an explicit 'protected by LSA' logo, an existing bar code or the edge of the item. Software on the laptop uses image recognition to tell the user when the location mark is within a predefined tolerance range of its correct position. In the simplest cases the user then manually moves the item until informed that it is correctly positioned; in more advanced situations a servo moves the item automatically to the correct place.

16.6 Applications and Advantages of LSA

LSA offers many advantages over traditional approaches to brand protection and document security:

- It works across a wide range of materials, including paper, coated paperboard, plastics and metals, allowing the possibility of using a single technology to protect many different types of items. This has advantages for cost of ownership, ease of training and the required amount of supporting infrastructure.

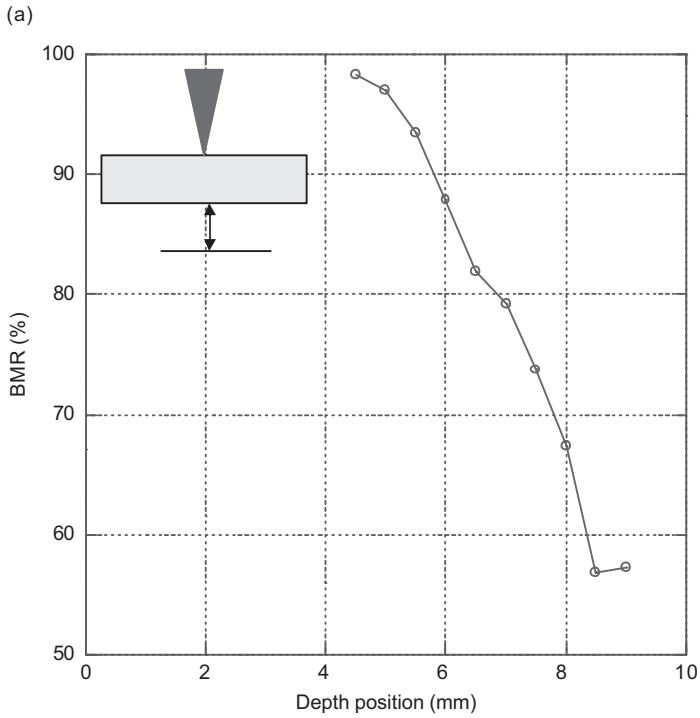
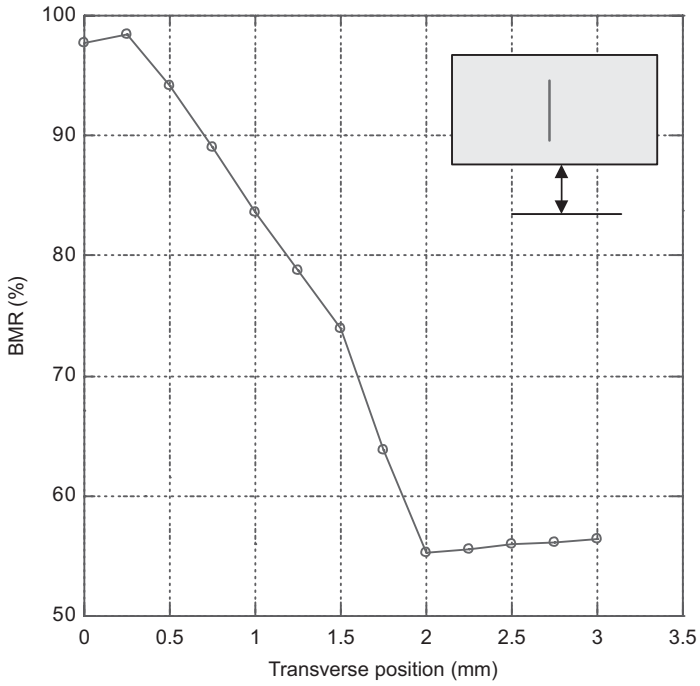


Figure 16.15 Variation in the bit match ratio as an item is misplaced in (a) the direction transverse to the scan, (b) the direction along the laser beam and (c) yaw.

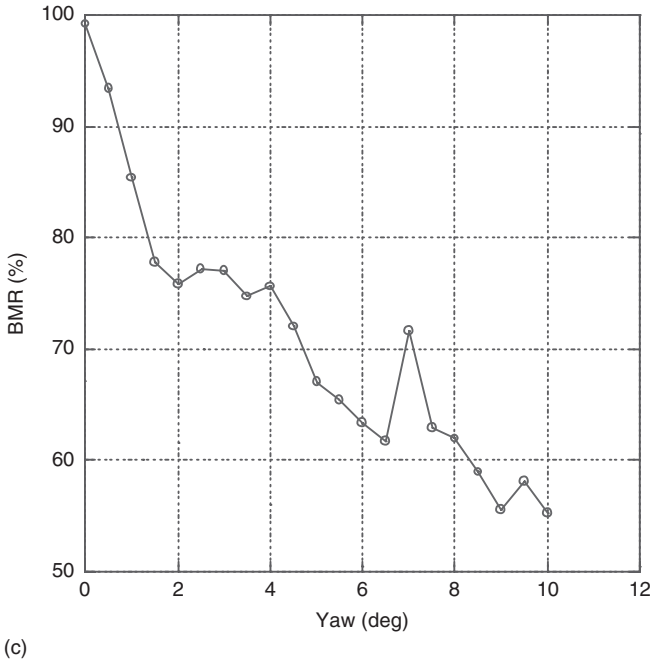


Figure 16.15 (Continued)

- It does not require any modification to the item being protected such as the embedding of chips, the attachment of tags or the incorporation of special inks, fibres or particles into the material of the item. This has significant cost implications in high volume manufacture, as well as preserving the aesthetic appeal of items.
- In most cases, the database registration can be achieved without slowing the production line. This is important for keeping the marginal cost added to the product to a minimum.
- It is intrinsically very robust. Items can be exposed to normal levels of wear and tear (and in some cases heightened levels) without loss of recognition of the signature.
- It can be entirely covert. This is essential for grey market tracing, where it is important that the grey market trader does not realise that items are traceable.
- It is privacy neutral. Concern has been expressed at the possibility of remotely read technologies such as RFID being compromised by attackers with sensitive radio equipment. This can range from having person details remotely extracted from a passport or identity card to criminals filtering crowds of people to see who is carrying high value items. The physics of LSA means that it can only ever be read by proximity, i.e. it is a line of sight only technology.

Five distinct areas of application of LSA have been identified so far:

- (i) Use as an authentication technology for documents, pharmaceuticals and high-value branded products. Preventing counterfeiting, with its associated loss of market, loss of brand integrity and increased liability is the main benefit to the customer.

- (ii) Use as a tracing technology for items that might be grey market traded.
- (iii) Use as a privacy technology, where the LSA signature is involved in an encryption/decryption system.
- (iv) Preventing the copying of unique identifiers. An increasingly popular trend is to use online digital printing to apply a unique identity code to items such as pharmaceuticals. The code can be used to implement tracing and providing codes are allocated sparsely, it offers a degree of prevention of counterfeiting since the probability of a counterfeiter hitting upon a valid code by chance is small. A very attractive feature of digitally printed unique identity codes is that they can be checked by the consumer from home using an Internet web site. The main disadvantage to digitally printed unique identifiers is that they can be copied. A fraudster only has to buy one genuine item and then make multiple copies of that valid code. The database containing all known genuine codes also has to be very carefully protected. However, by combining unique identifiers with LSA, this final weakness can be overcome, as the unique identifier can be tied to a particular physical product.
- (v) Adding functionality to overt security features. Many brand owners like to use an overt security feature, such as a hologram or security label, which can be checked without special equipment. We find that most holograms and security labels have a good LSA signature that can then be used as an additional covert feature. There is a useful synergy between the two technologies since the image of the hologram or security label can be used as the location mark for the LSA field scanner, and the registration LSA scan of the hologram or security label can be read before it is applied to the item. This means that it is not necessary to implement LSA reading technology onto the production line, thus making the solution more ubiquitous and lower cost.

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17

Legislative Issues Relating to Smart Packaging

Rinus Rijk

17.1 Introduction

Every day large quantities of food have to be discarded because they are no longer fit for consumption. This may emanate from production failures but an important part is found in the elapse of the 'best before' date [1]. Particular perishable foods like fresh meat and meat products have to be taken from the shelves. In some cases a supermarket may successfully sell the products that have reached their shelf life by significant reduction in price. From an economic point of view this is an undesirable situation, while disposal of food is considered more and more to be an unacceptable environmental burden. Failures in production may be incidental and difficult to avoid, but many cases of deterioration of food due to microbiological contamination, enzymatic or chemical reactions are occurring. Proper hygiene, and good quality control systems and suitable packaging may contribute to avoiding the ultimate decay of the food, but also the use of smart packaging may contribute to a decrease in food disposal.

Today, consumers show a preference for fresh and mildly preserved foods with good quality and taste. Quality, price and appearance are important but food safety is the major issue in consumer perception. Safe food with good taste and quality starts with the selection of the food itself. As the saying goes 'garbage in, garbage out' is certainly applicable to perishable foods. Processing of the food should be subject to good manufacturing practice in which high standards of hygiene and proper preservation are leading issues. Consumers, and also retailers and producers, are often very interested in relevant information on the quality of the packaged food. Information on the composition is obligatory for most packaged

foodstuffs [1,2] as well as information on the shelf-life of the food. The composition of the food is mainly of nutritional interest, whereas the best-before data gives guidance on the maximum storage period. The best-before data is usually established based on experience but is no guarantee that the food is still fit for consumption. When the food is contaminated before packing, not stored at the prescribed temperature or when the packaging has failed, then the food may be spoiled before the best-before date. New developments in smart packaging provide the consumer tools to obtain information on the quality of the food and allows food producers to pack the food in packaging material that releases or absorbs substances that influence positively the quality and shelf-life of the packaged food.

This chapter is focused on the current status of legislative requirements for active and intelligent materials and articles, which are in place at the European level or which will become valid within a reasonable time frame. In this chapter ‘active and intelligent packaging’ or ‘smart packaging’ refers to any form, shape or size of active and intelligent, materials and articles. Where ‘packaging’ is used this is not restricted to packaging materials used only to wrap the food.

In this chapter the expression ‘smart packaging’ covers both ‘active packaging’ and ‘intelligent packaging’. Active packaging is designed to absorb or release substances from or to the packaged food. Intelligent packaging does not influence the food but is capable of providing information on the conditions of the packaged food.

It is evident that smart packaging offers a number of benefits in the food production, retail and distribution chain, but the consumer may also profit from this smart packaging. Unacceptable migration, misleading the consumer or providing incorrect information are only a few drawbacks that may occur with smart packaging. In the European Community, individual member states have not drafted any regulations to guarantee food safety in respect of smart packaging. The European directives require that packaging materials are as inert as possible, which is a contradiction to smart packaging that may be designed to release substances to the food. Therefore, in 2004 the EU commission has amended the general requirements for food contact materials and has drafted a specific regulation taking into account the results of a European Commission funded project (FAIR-project CT-98-4170) known by the acronym of ‘ACTIPAK’ [3]. The aim is to have safe materials with harmonised requirements all over the European Community. The Actipak project included an inventory of existing active and intelligent packaging, classification of active and intelligent systems in respect of:

- legislation on food contact materials;
- an evaluation of microbiological safety;
- shelf-life-extending capacity, efficacy of active and intelligent systems;
- toxicological, economic and environmental evaluation of active and intelligent systems and recommendations for legislative amendments.

The results of the investigation contributed to the revision of the old framework Directive 89/109/EEC [4] on food contact materials. In the new Framework Regulation (EC) No. 1935/2004 [5] the provisions for the use of active and intelligent packaging systems is specified.

A project group under the Nordic Council of Ministers published, in 2000 [6], a comprehensive report on legislative aspects of active and intelligent food packaging, which also contributed to proposals for new legislation.

17.2 Smart Packaging

Smart packaging may be divided into three different groups, i.e. (i) intelligent materials that provide information to the user; (ii) active absorbing materials that remove substances from the food or the environment of the packaged food, and (iii) active releasing materials that are designed to release substances to the food or its environment. Smart packaging is today considered a new development but actually the principles are very old. As an example, the use of oak barrels for storage and maturation of wine, whisky and other alcoholic drinks has been used for centuries. The release of oak aroma is an appreciated additional effect besides the storage of the drinks.

In Tables 17.1 and 17.2 below a non-exhaustive overview is given of different smart packaging and its intended function.

Table 17.1 *Examples of typical active packaging materials*

Active function	
Oxygen absorbers	Based on iron or iron oxide, enzymatic oxidation, ascorbic acid oxidation, light activated quinone containing film or photo initiated polymers and applied to remove oxygen to avoid bacterial growth and oxidation.
Oxygen scavenger plus carbon dioxide generator	Based on the dye-sensitised oxidation of furoic acid, which consumes oxygen and generates a similar volume of carbon dioxide [7]. Also enzymatic systems based on the enzymatic oxidation of glucose to gluconic acid will absorb oxygen and release carbon dioxide at the same time.
Moisture absorbers	Based on cellulose fibres or a cross-linked polymer to remove the drip from fresh meat. Some times mixtures of herbs are added to avoid microbiological growth in the drip juice to assure a longer shelf life. For dry foods, e.g. biscuits, moisture regulators based on silica gel or molecular sieves may be employed.
Moisture regulators	Based on sugar solution contained in a water permeable plastic bag. The regulator is used for fresh meat or fish to obtain better backing properties.
Ethylene scavenger	Based on potassium permanganate on an inorganic substrate. Other systems include plastic films with finely dispersed minerals, e.g. silica gel, zeolite or active carbon. Reaction of the coloured tetrazine with ethylene. As the reaction product of ethylene with tetrazine is colourless, the packaging serves as intelligent packaging at the same time [7].
Aldehyde scavenger	Based on the reaction of amines, incorporated in the packaging, with aldehydes (Schiff bases).
Amine scavenging film	Based on ionomeric polymer. Depending on the degree of free acid groups in the polymer, a film made of ionomer has a capacity to absorb and remove amines from fresh fish [8].

(Continued)

Table 17.1 *Examples of typical active packaging materials (Continued)*

Active function	
Sulphite scavenger	Based on absorption of sulfite by zeolite-containing polymers [8].
Bitter taste remover	Based on an immobilised enzyme, naringinase, in a cellulose acetate film to remove the bitter taste (naringin and limonin from grapefruit juice [9]).
Carbon dioxide absorber	Carbon dioxide is scavenged by calcium hydroxide provided the water content is sufficiently high. This is an irreversible system. Reversible systems are based on absorption on zeolite or active carbon [10].
Antimicrobial systems	More efficient systems are based on the release of an antimicrobial agent by transmission through the gas phase. Known releasers are ethanol, SO ₂ or CO ₂ . Many other systems are being tested. Application of non-volatile substances requires an intimate contact with the food to allow transfer from the packaging onto the food. Tests have been performed with organic acids, nisin, lysozyme [11], chitosan, herb extracts, allyl isothiocyanate, but none of the systems were found to be generally applicable.
Heat releaser	Microwave susceptors.
Other releasers	Packaging that can release antioxidants, flavours, and colours is of great interest.

Table 17.2 *Examples of intelligent packaging materials*

Active Function	
Time/temperature indicators	Many time-temperature indicators (TTIs) are available today. Most of the indicators are based on the diffusion rate of one layer into a second layer of the TTI, leading to colour change. Some indicators only register the time or the temperature. A system using enzymatic reaction is commercially available. In general all these indicators are readable by the consumer. An example of an indicator only intended for the retailer is a printed bar code label. The bar code will change in time and that package will be recognised as not suitable for sale.
Oxygen indicators	Based on a colour change when oxygen is present. In this way they may be applied to indicate leakage of, e.g., modified atmosphere packaging.
Carbon dioxide indicator	Generally used to detect the microbiological activity by means of a colour change.
Microbial growth indicator	Indicators to detect metabolites are of great interest, but reliable systems are not yet commercially available.
Ripening indicator	The indicator shows the best time of consumption by means of colour indicator.

17.3 Legislation Relevant to Smart Packaging

Smart packaging may have a complex composition. In principle a smart packaging may be composed of different parts. There is the active or intelligent ingredient, which may be 'absorbed' on carrier materials and the active or intelligent ingredient together with the carrier may be packaged in a sachet composed of different materials. The substances released or absorbed to the food may be subject to specific regulations related to food quality, whereas the packaging material may be subject to EU or national regulations. However, the use of smart packaging may also be subject to other legal requirements. In the following sections the relevance of the various legal requirements is discussed.

17.3.1 Framework Regulation (EC) No 1935/2004 on Food Contact Materials

Framework regulation (EC) No 1935/2004 [5] applies to all materials and articles intended to come into contact with foodstuffs. It sets general requirements and provisions are formulated that specific directives or regulations may be published that set detailed requirements. If such detailed requirements are not established then national regulations may be valid, or it should be demonstrated that the material or article does not pose a threat to human health. Particular Article 3 of the Framework Regulation requires that food contact materials shall not transfer their constituents to foods in quantities that could: 'endanger human health, or bring about an unacceptable change in the composition of the food, or bring about a deterioration in the organoleptic characteristics'. In addition, there is a requirement that the consumer shall not be misled by labelling, advertising or presentation. Also in the former framework directive 89/109/EEC [4] these requirements were included. However, smart packaging, like releasing materials, cannot meet these requirements as they are designed to change intentionally the composition or the organoleptic properties of the food. Absorbing materials may also change intentionally the composition or organoleptic properties of the food. The amended framework was transposed into a regulation, which has legal power whereas a directive has to be implemented in the national laws of the member states.

Active and intelligent packaging are described by the following definitions:

“active food contact materials and articles” (hereinafter referred to as “active materials and articles”) means materials and articles that are intended to extend the shelf-life or to maintain or improve the condition of packaged food. They are designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food;

“intelligent food contact materials and articles” (hereinafter referred to as “intelligent materials and articles”) means materials and articles which monitor the condition of packaged food or the environment surrounding the food’.

The definition of active packaging refers to 'deliberately incorporated components' with the intention of releasing or absorbing substances to or from packaged food. This distinguishes active materials from passive packaging materials, which in a few cases may have an effect on the food, but which are added for other reasons, e.g. a monomer. The definition also excludes all packaging materials from natural sources. For instance, wooden barrels are therefore not subject to the provisions on active materials. The substances released from such barrels are not deliberately added to the FCM, but, if a wood extract were to be incorporated into

an active packaging system then this would fall under the general and specific measures on active materials and articles. The definition on intelligent materials is restrictive as it refers to packaged foods only. This means that an ordinary thermometer or recording equipment used in food production or storage are not considered 'intelligent' articles.

A special article 4 has been inserted, which sets specific requirements for active and intelligent packaging. Changes in the composition or organoleptic characteristics of the food due to the use of active packaging is allowed, on condition that the final food complies with the provisions of Directive 89/107/EEC [12] on food additives and its related implementing measures. In the absence of Community measures, national provisions shall be applicable. Actually this means that only substances recognised as food additives or food ingredients may be released to the food. As they intentionally become part of the food, the final food product should be labelled properly in accordance with Directive 2000/13/EC [1] as last amended by Directive 2003/89 [2]. Insert of Article 4 in Regulation 1935/2004 took away the major hurdle, in the old framework Directive 89/109/EEC, for the introduction of active packaging with a releasing function. Additional requirements on active and intelligent materials are related to misleading the consumer and to labelling. Active packaging used to change the composition of food or its organoleptic properties, in order to mask spoilage of that food, is not acceptable, whilst information provided by intelligent packaging shall be reliable and not mislead the consumer. It is required to label non-edible parts of a smart packaging when brought into contact with food. In practice this may be restricted to that smart packaging that is packed together with the food in the form of, for instance, a sachet. Smart packaging integrated in the primary packaging itself will not need any labelling because it cannot be distinguished from the packaging material itself. Finally the consumer should be informed about the presence of smart packaging by adequate labelling.

A provision is made to allow the introduction of a specific measure for active and intelligent materials and articles. The specific measure may include a list of authorised substances incorporated into active and intelligent packaging and, where applicable, the conditions of use of these substances.

The regulation introduces the European Food Safety Authority (EFSA) and its role, including procedures and time frames. These are in accordance with 'general food law' [13]. EFSA has to be consulted on issues affecting public health. This means also that the authorisation of active and intelligent components will be subject to an EFSA evaluation.

If required in a specific measure, then relevant food contact materials (FCM) shall be accompanied by a declaration of compliance, while appropriate documents shall be provided to the relevant authorities to demonstrate such compliance. As most of the requirements in the framework regulation are applicable to all FCM, active and intelligent materials are subject to these rules as they can be considered FCM. In some cases there may be no direct contact with the food, e.g. intelligent packaging positioned on the outside of the primary package, but they are subject to the framework regulation for the reliability of the information provided to the consumer.

17.3.2 Specific Regulation on Active and Intelligent Materials and Articles

A specific regulation [14] on active and intelligent packaging is under preparation and approaching its final stage. In spite of the fact that this is still a draft regulation, the final regulation most likely will not significantly differ in the principles laid down in that

document. Therefore the document can be taken as a starting point for requirements on active and intelligent packaging.

The draft regulation deals in particular with the authorisation procedure for active and intelligent 'components'. Active and intelligent packaging shall comply with the requirements of Regulation (EC) No 1935/2004 [5] and they should be 'suitable and effective for the intended purpose' and the active and intelligent components shall be included in the Community list. Only if these requirements are fulfilled is an active and intelligent packaging considered to comply with the requirements of this draft regulation.

Active and intelligent components are defined as 'individual substances or a combination of substances which cause the active function or provide the intelligent information'. As mentioned already, most active and intelligent packaging has a complex structure. In general, active and intelligent packaging can be split into two parts. One part includes the active or intelligent components, while the second part concerns the so-called carriers or passive parts that contain the component. Carriers may be interpreted as including a material on which a releasing component is adsorbed, but also the packaging of the components. In the example of an ethanol releaser, the ethanol is absorbed onto a silica gel, which in turn is packaged in a paper or plastic sachet. The ethanol is defined as the active component, which is subject to authorisation. The silica gel and the sachet form the passive part and should comply with safety requirements as defined in the framework regulation and implemented EU or national measures, but they are not subject to this draft regulation.

Migration of food contact materials (FCM) is subject to EU or national regulations. Overall migration and specific migration limits are established in the various regulations [15,16]. These limits are set to assure inertness and safety of the FCM. Active releasing packaging is not designed to be inert. It will in many cases exceed the overall migration limit and in some cases the specific migration limits set for FCM. Thus a substance released on purpose from an active packaging material should not be included in the overall migration. So special protocols may be needed for the determination of the overall migration. CEN methods EN 1186, Parts 1–15 [17] may not be suitable. Specific migration limits mentioned in the regulations on packaging materials may be exceeded provided the final food complies with the rules and restrictions applicable to processed foods.

Authorisation of the active or intelligent components will be granted after a positive opinion from EFSA and will only be valid to the applicant for an authorisation. The authorisation will be valid for a period of 10 years and may be renewed for another period of 10 years. The authorisation will be published in a Decision to the applicant. In addition the active and intelligent components will be inserted into a list of authorised components. In the Community list, issues like name and address of the applicant, name of the component, description of the active or intelligent system and the conditions of use, maximum amount of released components and any other relevant restriction will be inserted and made public.

Besides the requirements for labelling of FCM there is an addition requirement for active and intelligent packaging. Materials that may be mistaken as a part of the food such as loose sachets must be labelled using the words 'DO NOT EAT' and where possible the symbol for a non-edible part (Figure 17.1).

A requirement, in line with Regulation (EC) No 1935/2004 [5], concerning a declaration of compliance and the availability of appropriate documentation, has been confirmed in the draft regulation. It means that for any active and intelligent material a statement shall be provided that certifies that the material is safe to be used in contact with food under specified conditions of contact. To support such a statement the certifier shall have documentation



Figure 17.1 *Symbol proposed for labelling active and intelligent materials.*

that can prove the validity of the certificate. These documents shall be available to relevant authorities for inspection. In many cases this will include analytical data on, say, migration, total release, and effectivity of the active and intelligent active components. Although this draft regulation requires a declaration of compliance related to the active and intelligent components only, it may be necessary to include also the passive parts in the declaration as well. For plastic materials such a declaration is obligatory.

17.3.3 Authorisation Procedure and EFSA Guidelines

The European Food Safety Authority (EFSA) has been appointed to advise the European Commission on the safety of substances to come into contact with foods or to become part of that food. Opinions of EFSA are based on a risk assessment. In general the conclusions given in an opinion will be adopted by the Commission. There is an intense discussion about the final risk evaluation and the management of the evaluations. It is clear that active and intelligent components should appear in a community list of authorised components. The initial intention has been to set an authorisation to the petitioner only. However, more member-state representatives would like to see a general authorisation in order to avoid a repeated evaluation of the same components. The final outcome will be unsure. In the flow scheme in Figure 17.2 the principles of authorisation procedure is depicted. Final authorisation may appear in a different way in the final regulation

The Scientific Committee of Food (SCF), the predecessor of the European Food Safety Authority (EFSA), established guidelines for food contact materials [18] and in particular for plastics. EFSA's working group on food contact materials provided detailed explanatory guidance [19] in the Note for guidance. The guidelines are not generally applicable to active and intelligent packaging, and EFSA will publish additional guidelines and explanatory guidance that may support applicants when drafting an application and developing a testing protocol. This guidance should be available as soon as the regulation on active and intelligent packaging is ready for implementation.

Only a rough and predictive overview of the guidelines is feasible at this stage. EFSA will require all data needed to make a proper safety assessment, and in spite of any guidelines they will always be authorised to ask for additional information.

It is likely that an application should contain:

- general information on the identity of the applicant;
- summary document that summarises all the information provided;

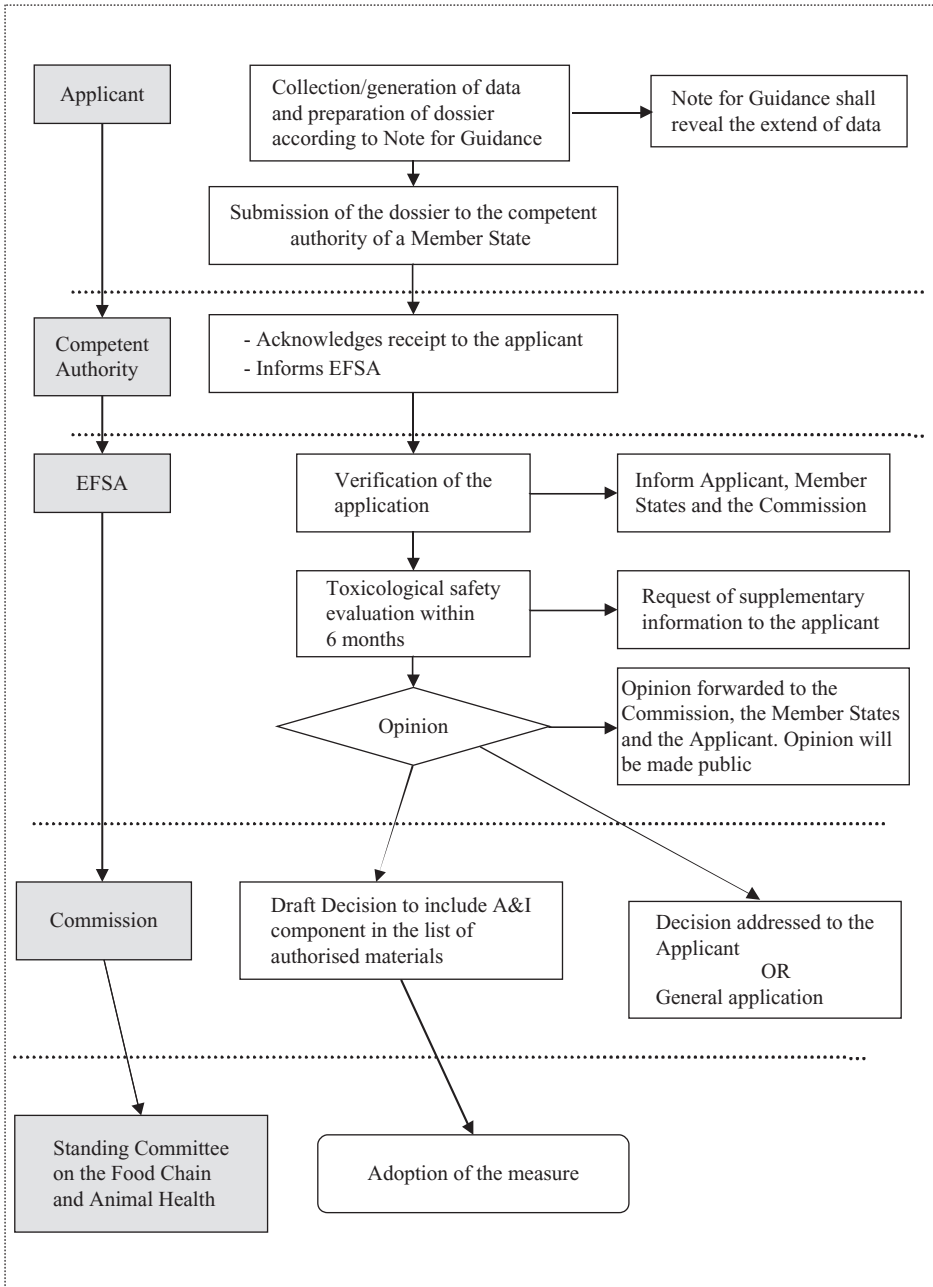


Figure 17.2 Procedure for application, evaluation and authorisation of active and intelligent components.

- technical dossier containing a description of the active or intelligent material, its function and the active or intelligent components. Additional information may be required but this could depend on the type of active or intelligent packaging.

For releasing materials there will likely be a focus on the releasing component and its authorisation as a food additive, including any quantitative restriction or a restriction on the types of food. The information on efficacy may be important, e.g. in the case of a released preservative the final efficacy in the food should be demonstrated. A general rule to be considered is that if the released component shows insufficient or no technical effect on the food, then the food additive does not comply with the requirements on food additives [12,20] or any other relevant regulation on the composition of food and its additives, e.g. the requirements on food flavours [21,22]. As a consequence, such a material may not obtain a favourable opinion. However, in real life it is difficult to demonstrate the technical effect of any food additive added during the production process. The requirement to demonstrate efficacy would be more restrictive than the authorisation of the actual food additives. Because efficacy is difficult to prove and very expensive because many foodstuffs may require testing, it should be taken into account that this requirement will not appear in the final regulation or only as a general statement, as in the food additive Directive 89/107/EEC. Some information may be requested on the carrier of the releasing substance, but as this will not be part of an authorisation, the safety of the carrier is the responsibility of the producer and the final user. In many cases the carrier may be subject to other provision on food contact materials. In principle the carrier should be inert and should not migrate to the food at an unacceptable concentration.

For absorbing materials the focus will be on the toxicological properties and quantities of components that (unintentionally) migrate into the food. If the absorber consists of plastic only then the plastics Directive 2002/72/EC, last amended by Directive 2007/19/EC [23], will be applied. Many active materials are composed of various types of materials in addition to the active component, e.g. plastic, paper, metal and adhesive. No harmonised EU regulation may exist on these materials and therefore they are subject to the framework regulation [5] and relevant national provisions of the EU member states. The efficiency or capacity of the absorber may be part of the final evaluation but probably this will depend on the function of the absorber and the introduction of any safety concern. If there is no safety concern then efficiency will be considered as a marketing tool and self regulating when the absorber is either not or insufficiently efficient. As an example, the use of an oxygen absorber that has insufficient capacity to decrease and maintain the oxygen content to a low concentration may at least mislead the consumer or create in the worst case an even more dangerous situation due to the overgrowth of specific microbes. Also the possible growth of anaerobic bacteria present on some foodstuffs may be a reason not to apply an oxygen scavenger.

Intelligent materials may need a demonstration of the reliability of the information provided, to comply with the respective requirement in the draft regulation. In respect of unintended migration a distinction may be feasible for materials that are positioned inside or outside the primary packaging. In the latter case the actual migration of any intelligent component may be negligible and it would be logical to adapt the need for toxicological information to the 'no migration' or 'functional barrier' principle [23]. This would mean that unauthorised substances can be used behind a barrier layer, provided the substances are

not mutagenic, carcinogenic or toxic to reproduction according to Annex IV of Directive 67/548/EEC [24]. If the intelligent material is, or may come, into contact with the food then the intelligent ingredients will need an evaluation based on migration level and toxicological properties as outlined in the Note for guidance [18,19].

17.3.4 General Safety

It is important that food is fit for consumption and many EU directives and regulations related to food and food safety have been published. In addition, there is a concern about the general safety of articles, e.g. an active package in the form of a sachet should not be confused with edible parts but it should also not be of a size that can easily be swallowed by consumers, and in particular by children. Many regulations have been extensively discussed before [25]. Without being exhaustive, the following subjects could be subject to relevant European or member states' regulations and might be taken into account in a safety evaluation or risk assessment either performed by EFSA, national authorities or the manufacturer:

- food contact materials;
- food additives;
- flavourings;
- hygiene;
- biocides;
- labelling;
- general product safety;
- misleading claims.

Fit for use may relate to the chemical composition or to microbiological condition of the food. Chemical composition may refer to food additives [12], flavouring substances [21,22] or sweeteners [26] (incidental contamination is not relevant in these considerations). When substances are added via active packaging then the final food must still comply with the relevant requirements for food production and composition. The regulation on hygiene [27] requires that all measures shall be taken to assure the wholesomeness of the food. Active packaging may be a useful tool to comply with this requirement as it is usually applied to extend the shelf-life of the food, or at least to maintain the quality of food during its shelf-life. The regulation on biocides [28] is actually not applicable as biocides are not allowed in processed food. Only substances that are authorised as preservatives in food may be applied. Food contact materials with antimicrobial surfaces (e.g. after incorporation of silver ions in food contact materials) are frequently, but incorrectly, referred to as active packaging. The antimicrobial surface has or should have no effect on the food itself and therefore it is excluded by the definition of active packaging.

Products shall be safe as established in Directive 2001/95/EC [29]. 'Safe products' means that under normal or reasonably foreseeable conditions of use the product does not present any risk or only the minimal risks compatible with the product's use. In making a risk assessment, the characteristics of the product, presentation, labelling instructions and the category of consumers, especially children, have to be taken into account. Issues such as shape and size of active or intelligent packaging may give reasons for concern. A sachet filled with active compounds may be misunderstood by consumers and pose a

health risk. In some cases a visually attractive object may be packed together with the food. In such instances extreme care should be taken to avoid confusing non-edible objects with foodstuffs. Appropriate labelling will be essential. In such cases it might be more appropriate to incorporate the active or intelligent packaging into the primary packaging or at least to adhere it to the primary packaging.

Where an absorber is the reason for a change of the consumable amount of food, then this should be taken into account in accordance to Directives 75/106/EEC [30] and 76/211/EEC [31], include labelling of weight and tolerances.

Independent of the active and intelligent components the support or carrier of the components should comply with existing rules and not release unacceptable amounts of substances. Besides the framework Regulation 1935/2004 [5] and the specific Directive 2002/72/EC on food contact materials, other directives on food contact materials have been adopted and may be relevant in assuring the safety of active or intelligent packaging. This concerns directives on regenerated plastics [32–34], ceramics [35] and a regulation on certain epoxy compounds [36]. In the absence of harmonised EU regulations, existing national regulations may be applicable and may be useful to demonstrate safety of active or intelligent packaging.

17.3.5 Labelling

Consumers have the right to be informed about the composition of the food and so protect their interests, which may be very diverse. Labelling appears to be a complex issue as there are many EU directives and regulations that include requirements on labelling. Food labelling may concern the food, food additives or food contact materials as well as active and intelligent packaging.

Framework regulation 1935/2004 [5] requires labelling of food contact materials that are not yet in contact with food. This labelling could be done by 'for food contact', or indicating use (e.g. 'soup spoon'), or by using the symbol in Figure 17.3. Exceptions to this rule are articles that from their shape are clearly designed for food contact. In addition food contact materials should be labelled with instructions for safe use. Identification should be added to allow food contact materials to be traced. Labelling of food contact materials should not mislead the ultimate consumer.

For active packaging, information on the permitted use and the identity and quantity of the released substance has to be provided in order to allow a food packer to comply with any restriction. Materials that may be mistaken for a part of the food, such as loose sachets, must be labelled using the symbol for a non-edible part (Figure 17.1).



Figure 17.3 *Symbol for food contact materials.*

Directive 2000/13/EC [37], last amended by Directive 2003/89/EC [38] deals with labelling, presentation and advertising of foodstuffs and is applicable to all foodstuffs intended for sale to consumers or caterers. Also Directive 89/107/EEC sets requirements for labelling of food additives. In principle all substances used in the manufacture or preparation of foodstuffs and still present in the finished product should be declared on the label, in order to inform the consumer about the substances present. It is of no interest how or when the substances are added to the food and therefore substances released from an active packaging system should be declared.

A minimum durability date should be provided and for highly perishable foodstuffs a 'use by' date should be given. This latter requirement is a hindrance to the use of a time temperature indicator (TTI). A 'use by' date should also cover foreseeable incorrect storage conditions, e.g. during transport. Therefore 'use by' dates are set on a very safe (short) period. By use of appropriate TTIs the total safe consumption period could be used for the benefit of both consumer and manufacturer or retailer. It is assumed that further effort by TTI manufacturers may result in a legal recognition of TTI as a replacement for the 'use by' date.

Modified atmosphere gases are regulated as food additives (Directive 95/2/EEC [39]). Gases that may be added are listed. When modified gas packaging is applied this should be labelled; however, there are no provisions for the removal of gases from the packed food. This means that a CO₂-releasing system falls within the definition of food additive, but an oxygen scavenger does not comply with the definition as the oxygen is removed. The final gas composition in a modified atmosphere may be comparable to that in packaged food using an oxygen absorber, but it is not yet clear if there is any regulation that would prevent the use of oxygen absorbers. On the other hand there is no prohibition on the removal of the oxygen from packaged food and no labelling requirement for the modified atmosphere. Only Regulation 1935/2004 requires that when an active device, extending the shelf life of the food is present, then the packaged food should be labelled for the presence of such a device.

17.4 Demonstration of Compliance of Active and Intelligent Packaging

17.4.1 Basic Rules for Migration Testing

Since active and intelligent packaging are considered to be food contact materials, the migration of packaging substances should be examined according to the existing EU directives or national provisions. At the EU level the framework Regulation 1935/2004 sets the general requirements for all food contact materials and particular Article 3, stating that the packaging material should not endanger human health, is the most important. Specific Directives on plastics (2002/72/EC) [5], regenerated cellulose (93/10/EEC) [32] and ceramics (84/500/EEC) have been published and implemented in national legislation in the EU. The plastics directive contains a positive list of monomers and an incomplete list of additives for the use in plastics. To support testing of plastic materials for compliance with the plastic directive two additional directives are available. Directive 82/711/EEC [40], as last amended by Directive 97/48/EC [41], sets requirements (time temperature conditions, selection of simulants) for testing of plastic materials and articles with food simulants. Directive 85/572/EEC [42] indicates the simulants that shall be used for specified foods or groups of foods.

To support the analyst in applying such controls, CEN (the European Standardisation Commission) has in TC 194 adopted and validated analytical methods for the determination of the overall migration and the migration of some specific substances [43]. These methods are intended to be applied for testing plastic materials and articles. At national level, e.g. in The Netherlands [44], the methods and simulants may also be used to demonstrate compliance with national regulation of non-plastic or multilayer materials composed of plastics and non-plastics (e.g. plastic on paper, coating on metal).

In principle a food contact material is brought into contact with the selected simulant(s) under selected conditions of time and temperature. Homogeneous materials are contacted by submersion while multilayers or thin films often have single-sided contact with the food simulant. After the contact period the simulant is separated from the food contact material and the overall migration is determined gravimetrically [17], while specific migration is determined using a suitable analytical method like gas or liquid chromatography with spectroscopic detection. The determination of the overall migration in olive oil is more complex and sensitive to analytical and systematic errors.

17.4.2 Active and Intelligent Packaging

Some active and intelligent materials function as primary packaging by wrapping or holding the food, but many active and intelligent packaging has varying shape, size and composition. In many cases conventional migration tests use single-sided contact and cannot be applied for technical reasons related to, for instance, the size of the packaging. Within the Actipak project migration experiments were performed by total immersion of active and intelligent packaging into the various simulants. It appeared that in many cases overall migration was exceeded [45]. In addition the amount of released components shall not be included in the overall migration value. Therefore, it was concluded that determination of the overall migration from active and intelligent packaging using conventional methods is not applicable in many cases. There is a need for dedicated tests that simulate better the conditions of contact for some types of active and intelligent packaging [46]. The development of dedicated methods is required in order to allow a proper judgement of the suitability of active and intelligent packaging. However this requires a closer look at the origin of the problems in determining migration.

Although this is a complex problem, almost requiring a different approach for each type of packaging, a number of starting points can be distinguished:

- (a) active or intelligent packaging being at the same time primary food packaging;
- (b) active packaging is a releasing material;
- (c) active material is an absorber;
- (d) intelligent material is inside the primary packaging; or
- (e) intelligent material is outside the primary packaging.

Another variable is the type of food in contact with the active or intelligent packaging. Here there may be liquid contact (e.g. for an oxygen-scavenging crown cork for beer), dry contact (e.g. a preservative releaser for buns) or semi-solid contact (e.g. an oxygen scavenger for processed ham).

As the framework regulation and the draft specific regulation for active and intelligent materials are asking for a declaration of compliance it will be very important that relevant and reliable methods will become available. Suitability of packaging material can be established before it is transferred into a active or intelligent material, whereas the safety of the active or intelligent components can be assessed separately. As a starting point, it will then be clear whether or not the packaging and active components can be used for food contact. However, the determination of the actual migration of the various substances is very problematic. The surface-to-volume ratio should be taken into account, but at this moment the various directives only use a surface-to-volume ratio of $6 \text{ dm}^2/\text{kg}$ food. As a simple example the determination of the migration of iron from an iron-based oxygen absorber is more complex than usually considered. In the case of such an absorber being used in contact with meat, a simple determination of iron is not realistic as the food itself already contains a high amount of iron, and realistic migration data will not be obtained. Using a simulant like 3 % acetic acid is not realistic either because the iron will dissolve and turn the simulant brown, showing an excessive migration of iron. So one should develop a method that simulate better the food product and the conditions of contact. Although some preliminary experiments have been carried out there is still a lot of work to do to find proper methods. In addition the EU regulations should be amended to accept the deviating dedicated migration conditions. At the TNO Institute in Zeist, The Netherlands, some successful experiments were performed using the so-called sandwich method. In principle the article is placed in a sandwich structure between simulant moistured filter paper as depicted in Figure 17.4.

After a proper storage period the overall migration is determined by extracting the filter paper with the simulant and subsequent gravimetric determination of the residue after evaporation of the simulant. Specific migration of iron can be determined by combustion of the filter paper and determination of the iron by means of atomic adsorption spectroscopy. Organic substances might be determined after extraction with an organic solvent and subsequent analysis of the substance of interest.

Much intelligent packaging (e.g. time/temperature indicators, TTI) is placed *in situ* on the outside of the packaging. Taking into account the construction of most TTIs and the barrier of the primary food packaging, it is assumed that a functional barrier prevents the migration of any of the intelligent components. Migration testing should then not be necessary while substances that are not listed may be used in accordance with Directive 2007/19/EC [23].

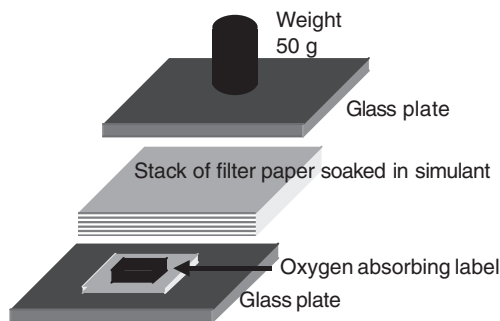


Figure 17.4 Exploded view of dedicated testing of active packaging labels or sachets.

Many forms of active and intelligent packaging, not used as primary packaging, are designed to have little or no contact with food. For instance, an oxygen absorber label has a contact area of only a couple of square centimetres. The conventional surface to volume ratio of 6 dm²/kg food will never be achieved. Similar arguments are valid for many types of intelligent packaging. Plastics Directive 2002/72/EC [15] allows the use of the real ratio of surface to volume. Therefore migration should be expressed in mg/subject and divided by the quantity (kg) of food in contact with the subject. This calculation should be done before checking compliance with overall or specific migration limits listed in relevant regulations.

17.5 Conclusions

In Europe the use of active and intelligent packaging materials is still limited. Hard evidence for why this is so compared with countries like Japan and the USA, is difficult to identify. Costs and consumer interest may be part of the reasons. As the consumer is more and more interested in safe and convenient food the introduction of active and intelligent packaging will progress with time. Anyway the legislative hurdle has been removed by the publication of Framework Regulation 1935/2004 [5], which allows the release of components to the food even if the overall migration limit is exceeded.

With the publication of a specific Regulation on active and intelligent materials, a system of authorisation becomes available. This may be a reason for increased use of active and intelligent materials. Apart from specific regulations, directives and regulations related to food and food safety may also be relevant for active and intelligent packaging. Further development of dedicated test methods to demonstrate compliance with the requirements is needed.

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