9 Active packaging

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9.1 Introduction

Active packaging refers to the incorporation of certain additives into packaging film or within packaging containers with the aim of maintaining and extending product shelf life (Day, 1989). 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; Hotchkiss, 1994). Active packaging includes additives or *freshness enhancers* that are capable of scavenging oxygen; adsorbing carbon dioxide, moisture, ethylene and/or flavour/odour taints; releasing ethanol, sorbates, antioxidants and/or other preservatives; and/or maintaining temperature control. Table 9.1 lists examples of active packaging systems, some of which may offer extended shelf life opportunities for new categories of food products (Day, 1989, 2001; Rooney, 1995).

Active packaging has been used with many food products and is being tested with numerous others. Table 9.1 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. (Chapter 2 discusses biodeterioration of foods and Chapter 3 discusses food quality issues.) The shelf life of packaged food is dependent on numerous factors such as the intrinsic nature of the food, e.g. acidity (pH), water activity (a_w), nutrient content, occurrence of antimicrobial compounds, redox potential, respiration rate and biological structure, and extrinsic factors, e.g. temperature, relative humidity (RH) 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, 1989).

Active packaging is not synonymous with intelligent or smart packaging, which refers to packaging that senses and informs (Summers, 1992; Day, 2001). 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, and are being utilised in applications such as product authenticity, anti-theft and

Table 9.1 Selected examples of active packaging systems

Active packaging system	Mechanisms	Food applications
Oxygen scavengers	1. iron based 2. metal/acid 3. metal (e.g. platinum) catalyst 4. ascorbate/metallic salts 5. 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	1. iron oxide/calcium hydroxide 2. ferrous carbonate/metal halide 3. calcium oxide/activated charcoal 4. ascorbate/sodium bicarbonate	coffee, fresh meats and fish, nuts and other snack food products and sponge cakes
Ethylene scavengers	1. potassium permanganate 2. activated carbon 3. activated clays/zeolites	fruit, vegetables and other horticultural products
Preservative releasers	1. organic acids 2. silver zeolite 3. spice and herb extracts 4. BHA/BHT antioxidants 5. vitamin E antioxidant 6. volatile chlorine dioxide/ sulphur dioxide	cereals, meats, fish, bread, cheese, snack foods, fruit and vegetables
Ethanol emitters	1. alcohol spray 2. encapsulated ethanol	pizza crusts, cakes, bread, biscuits, fish and bakery products
Moisture absorbers	1. PVA blanket 2. activated clays and minerals 3. silica gel	fish, meats, poultry, snack foods, cereals, dried foods, sandwiches, fruit and vegetables
Flavour/odour adsorbers	1. cellulose triacetate 2. acetylated paper 3. citric acid 4. ferrous salt/ascorbate 5. activated carbon/clays/zeolites	fruit juices, fried snack foods, fish, cereals, poultry, dairy products and fruit
Temperature control packaging	1. non-woven plastics 2. double walled containers 3. hydrofluorocarbon gas 4. Lime/water 5. ammonium nitrate/water	ready meals, meats, fish, poultry and beverages

product traceability (Summers, 1992; Day, 2001). Intelligent packaging devices include time-temperature indicators, gas sensing dyes, microbial growth indicators, physical shock indicators, and numerous examples of tamper proof, anti-counterfeiting and anti-theft technologies. Information on intelligent packaging technology can be obtained from other reference sources (Summers, 1992; Day, 1994, 2001).

It is not the intention of this chapter to extensively review all active-packaging technologies but rather to describe the different types of devices, the scientific principles behind them, the principal food applications and 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 also discussed and some recent developments highlighted. More detailed information on active packaging can be obtained from the numerous references listed.

9.2 Oxygen scavengers

Oxygen can have considerable detrimental effects on foods. Oxygen scavengers can therefore help maintain food product quality by decreasing food metabolism, reducing oxidative rancidity, inhibiting undesirable oxidation of labile pigments and vitamins, controlling enzymic discolouration and inhibiting the growth of aerobic microorganisms (Day, 1989, 2001; Rooney, 1995).

Oxygen scavengers are by far the most commercially important sub-category of active packaging. The global market for oxygen scavengers was estimated to exceed 10 billion units in Japan, several hundred million in the USA and tens of millions in Europe in 1996 (Anon, 1996; Rooney, 1998). The global value of this market in 1996 was estimated to exceed $200 million and is predicted to top $1 billion by 2002. The recent commercialisation of oxygen scavenging polyethylene terephthalate (PET) bottles, bottle caps and crowns for beers and other beverages has contributed to this growth (Anon, 1996; Rooney, 1998; Day, 2001).

The most well known oxygen scavengers take the form of small sachets containing various iron based powders combined with a suitable catalyst. 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*. 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 a common commercial practice 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 (Idol, 1993).

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 (Anon, 1995). 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 (Hurme, 1996).

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 Toppan Printing Co. Ltd and Toyo Seikan Kaisha Ltd have entered the market but Mitsubishi still dominates the oxygen scavenger business in Japan with a market share of 73% (Rooney, 1995). 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. In contrast to the Japanese market, the acceptance of oxygen scavengers in North America and Europe has been slow, although several manufacturers and distributors of oxygen scavengers are now established in both these continents and sales have been estimated to be growing at a rate of 20% annually (Rooney, 1995). Table 9.2 lists selected manufacturers and trade names of oxygen scavengers, including some which are still under development or have been suspended because of regulatory controls (Rooney, 1995, 1998; Castle, 1996; Anon, 1997, 1998; Glaskin, 1997).

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 applied to the inside of packages and the incorporation of oxygen scavenging materials into laminated trays and plastic films have enhanced and will encourage the commercial acceptance of this technology. For example, Marks & Spencer Ltd were 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 now 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 have marketed a laminate containing a ferrous oxygen scavenger which can be thermoformed

Table 9.2 Selected commercial 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
Multisorb Technologies Inc.	USA	FreshMax	iron based	labels
		FreshPax	iron based	labels
		Fresh Pack	iron based	labels
Ciba Speciality Chemicals	USA	Shelf-plus	PET copolyester	plastic film
Chevron Chemicals	USA	N/A	benzyl acrylate	plastic film
W.R. Grace Co. Ltd	USA	PureSeal	ascorbate/ metallic salts	bottle crowns
Food Science Australia/ Visy Industries	Australia	ZERO2	photosensitive dye/organic compound	plastic film
CMB Technologies	France	Oxbar	cobalt catalyst	plastic bottles
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

into an Oxyguard™ tray which has been used commercially for cooked rice (see Fig. 9.1).

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 a_w foods because, when wet, their oxygen scavenging capability is rapidly lost. Instead, various non-metallic reagents and organo-metallic compounds which have an affinity for oxygen have been incorporated into bottle closures, crowns and caps or blended into polymer materials so that oxygen is scavenged from the bottle headspace and any ingressing oxygen is also scavenged. The PureSeal™ oxygen scavenging bottle crowns (marketed by W.R. Grace Co. Ltd and ZapatA Technologies Inc., USA), oxygen scavenging plastic (PET) beer bottles (manufactured by Continental PET Technologies, Toledo, USA) and light

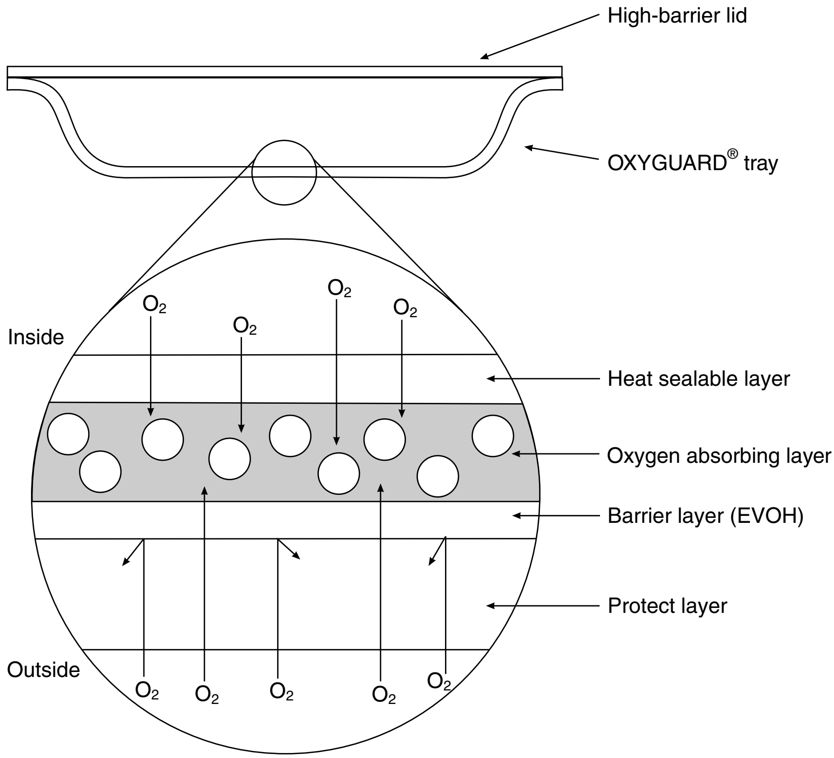

Figure 9.1 Structure of Oxyguard™ tray (courtesy of Toyo Seikan Kaisha Ltd).

activated ZERO2™ oxygen scavenger materials (developed by Food Science Australia, North Ryde, NSW, Australia and now partly owned by Visy Industries, Melbourne, Victoria, Australia) are just three of many oxygen scavenger developments aimed at the beverage market but are also applicable to other food applications (Rooney, 1995, 1998, 2000; Castle, 1996). 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 and necessary packaging criteria) of the different types of oxygen scavengers can be obtained from Labuza and Breene (1989), Idol (1993), Rooney (1995, 1998, 2000) and Hurme and Ahvenainen (1996).

9.2.1 ZERO2™ oxygen scavenging materials

As a case study, brief details of the ZERO2™ oxygen scavenging development are described here (Rooney, 2000). ZERO2™ is the trade name for a range of oxygen scavenging plastic packaging materials under development, in which the reactive components are activated by means of ultraviolet light or related high-energy processes. The plastics' oxygen scavenging properties remain inactive until activated by an appropriate stimulus 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) and is now being developed partly with Visy Industries (Melbourne, Victoria, 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. The headspace and dissolved oxygen is present at the time of closing most packages of foods and beverages. Removal of some or all of this oxygen is required at a rate greater than that of the various food degradation processes that occur in the food. In this case, a headspace scavenger package is required. The oxygen that enters the package by permeation or leakage after closing needs to be removed, preferably before contacting the food. The scavenger required 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 on a pilot scale. 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 barrier for plastics. The conditions found in liquid paperboard cartons, laminate pouches or multilayer barrier bottles were recently studied (Rooney, 2000) in collaboration with TNO Food Science and Nutrition (Zeist, The Netherlands). Experimental conditions were chosen using sachets of a laminate including a layer of ethylene vinyl alcohol (EVOH) 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 one 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 the storage period of one year. Browning was reduced by one third after one year at 25°C. Use of lower surface-to-volume ratios found in commercial packs would be expected to result in more protection against oxidative deterioration.

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 and multilayer PET beer bottles. 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 ZERO2™ layer suggest that the common spoilage moulds can be inhibited completely with little or no carbon dioxide. Sliced smoked ham can be inhibited from discolouring under refrigerated cabinet lighting conditions when the packaging laminate scavenges the initial oxygen concentration of 4% to very low levels. Development of ZERO2™ and competing processes are aimed at inhibiting the widest range of oxygen-mediated food degradation processes. Examples studied so far indicate that some fast degradation reactions can be addressed although there are more challenging cases yet to be investigated (Rooney, 2000).

9.3 Carbon dioxide scavengers/emitters

There are many commercial sachet and label devices that can be used to either scavenge or emit carbon dioxide. The use of carbon dioxide scavengers is particularly applicable for fresh roasted or ground coffees that 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 (Subramaniam, 1998). 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 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, 1989; Anon, 1995; 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 Toppan Printing Co. Ltd (Freshilizer™ type CV).

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 but has a perforated false bottom under which a porous sachet containing sodium bicarbonate/ascorbate is positioned. When exudate from modified atmosphere packed meat or fish contacts the sachet's contents, 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, which 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 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 (Naito *et al.*, 1991; Rooney, 1995).

9.4 Ethylene scavengers

Ethylene (C_2H_4) is a plant growth regulator which 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, colour development in citrus fruits, bananas and tomatoes, stimulation of root production in baby carrots and development of bitter flavour in bulk delivered cucumbers, but in most horticultural situations it is desirable to remove ethylene or to suppress its negative effects. Consequently, much research 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 (Abeles *et al.*, 1992; Rooney, 1995).

Table 9.3 lists selected commercial ethylene scavenger systems. Effective systems utilise potassium permanganate ($KMnO_4$) immobilised on an inert

Table 9.3 Selected commercial ethylene scavenger systems

Manufacturer	Country	Trade name	Scavenger mechanism	Packaging form
Air Repair Products Inc.	USA	N/A	$KMnO_4$	sachets/blankets
Ethylene Control Inc.	USA	N/A	$KMnO_4$	sachets/blankets
Extenda Life Systems	USA	N/A	$KMnO_4$	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

mineral substrate such as alumina or silica gel. $KMnO_4$ oxidises ethylene to acetate and ethanol and in the process changes colour from purple to brown and hence indicates its remaining ethylene scavenging capacity. $KMnO_4$-based ethylene scavengers are available in sachets to be placed inside produce packages, or inside blankets or tubes that can be placed in produce storage warehouses (Labuza & Breene, 1989; Abeles *et al.*, 1992; Rooney, 1995).

Activated carbon-based scavengers with various metal catalysts can also effectively remove ethylene. They have been used to scavenge ethylene from produce warehouses or incorporated into sachets for inclusion into produce packs or 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 (Abeles *et al.*, 1992; Rooney, 1995).

In recent years, numerous produce packaging films and bags have appeared in the market place which are based on the putative ability of certain finely ground minerals to adsorb ethylene and to emit antimicrobial far-infrared radiation. However, little direct evidence for these effects have 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 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 adsorption. In fact, almost any powdered mineral can confer such effects without relying on expensive Oya stone or other speciality minerals (Abeles *et al.*, 1992; Rooney, 1995).

9.5 Ethanol emitters

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. Ethanol can be sprayed directly onto food products just prior to packaging. 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 films and sachets (Rooney, 1995).

Many applications of ethanol emitting films and 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) and Ageless™ type SE (Mitsubishi Gas Chemical Co. Ltd). All of these films and sachets contain absorbed or encapsulated ethanol in a carrier material which 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%) adsorbed 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 contents* and include a diagram illustrating this warning. Other ethanol emitters such as Negamould™ and Ageless™ type SE are dual-action sachets which scavenge oxygen as well as emit ethanol vapour (Rooney, 1995).

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; Hebeda & Zobel, 1996). 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).

9.6 Preservative releasers

Recently, there has been great interest in the potential use of antimicrobial and antioxidant packaging films which 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, economic factors and/or regulatory constraints (Rooney, 1995).

Some commercial antimicrobial films and materials have been introduced, primarily in Japan. For example, one widely reported product is a synthetic silver zeolite which 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 (Anon, 1994; Rooney, 1995; Weng *et al.*, 1997; Gray, 2000). These include organic acids, e.g. propionate, benzoate and sorbate, bacteriocins, e.g. nisin, spice and herb extracts, e.g. from rosemary, cloves, horseradish, mustard, cinnamon and thyme, enzymes, e.g. peroxidase, lysozyme and glucose oxidase, chelating agents, e.g. EDTA, 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. Figure 9.2 illustrates the controlled release of volatile chlorine dioxide that has received GRAS status for food use in the USA (Gray, 2000).

An interesting commercial development in the UK is the recent exclusive marketing of food contact approved Microban™ (Microban International, Huntersville, USA) kitchen products such as chopping boards, dish cloths and bin bags by J. Sainsbury Plc. These Microban™ products contain triclosan, an antibacterial aromatic chloro-organic compound, which is also used in soaps, shampoos, lotions, toothpaste and mouth washes (Goddard, 1995a; Jamieson,

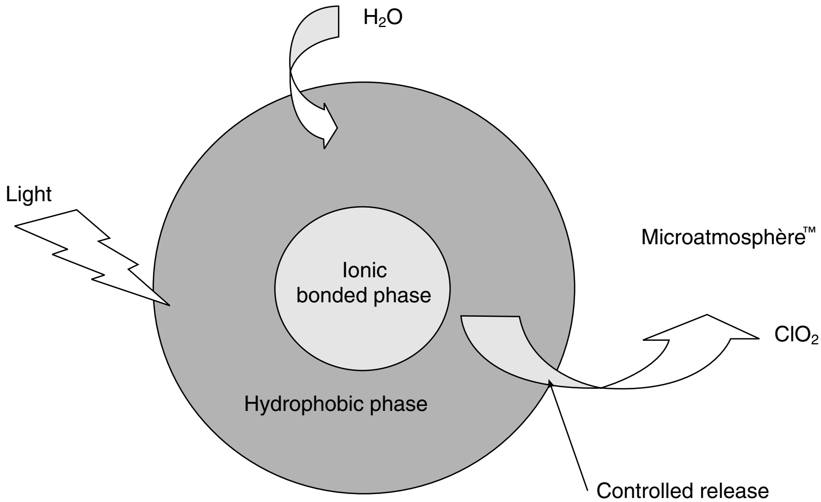

Figure 9.2 Microatmosphère™ chlorine dioxide releasing antimicrobial labels (courtesy of Bernàrd Technologies Inc., USA).

1997; Rubinstein, 2000). Another interesting development is the incorporation of methyl salicylate (a synthetic version of wintergreen oil) into RepelKote™ paperboard boxes by Tenneco Packaging (Lake Forest, Illinois, USA). Methyl salicylate has antimicrobial properties, but RepelKote™ is primarily being marketed as an insect repellent and its main food applications are dried foods which are very susceptible to insect infestations (Barlas, 1998).

Two influences have stimulated interest in the use of antioxidant packaging films. The first of these is the consumer demand for reduced antioxidants and other additives in foods. The second is the interest of plastic manufacturers in using natural 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 & Breene, 1989). Recently there has been much interest in the use of α-tocopherol (vitamin E) as a viable alternative to BHT/BHA-impregnated packaging films (Newcorn, 1997). The use of packaging films incorporating natural vitamin E can confer benefits to both film manufacturers and the food industry. There have been questions raised regarding BHT and BHA's safety, and hence using vitamin E is a safer alternative. 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 limited spoilage mechanism (Labuza & Breene, 1989; Rooney, 1995; Newcorn, 1997).

9.7 Moisture absorbers

Excess moisture is a major cause of food spoilage. Soaking up moisture by using various absorbers or desiccants is very effective in 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 (Rice, 1994; Rooney, 1995). The use of moisture absorber sachets is common in Japan, where popular foods feature a number of dried products which need to be protected from 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 have used silica gel-based moisture absorber sachets for maintaining the crispness of filled ciabatta bread rolls.

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 which 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. 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) 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 RH. 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 a Pichit™ film which consists of a layer of humectant carbohydrate and propylene glycol sandwiched between two layers of polyvinyl alcohol (PVOH) plastic film. Pichit™ 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 (Labuza & Breene, 1989; Rooney, 1995). Another example of this approach has been applied in the distribution of horticultural produce. In recent years, 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 which 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 multi-layered box is able to take up water in the vapour state when the temperature drops and the RH rises. Conversely, when the temperature rises, the multi-layered box can release water vapour back in response to a lowering of the RH (Patterson & Joyce, 1993).

9.8 Flavour/odour adsorbers

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 to selectively 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, a tetraterpenoid which 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 (Rooney, 1995). A possible active-packaging solution would be to include limonin adsorbers (e.g. cellulose triacetate or acetylated paper) into orange juice packaging material.

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 auto-oxidation 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 (Franzetti *et al.*, 2001). In Japan, Anico Co. Ltd have 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 adsorbed 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 (Anon, 1996). This technology is based upon a molecular sieve with pore sizes of around five nanometres, and Dupont claim that their OTC removes or neutralises aldehydes although evidence for this is lacking. The claimed food applications for this technology are snack foods, cereals, dairy products, poultry and fish (Anon, 1996). A similar claim of aldehyde removal has been reported (Goddard, 1995b). Swedish company EKA Noble in co-operation with Dutch company Akzo, have developed a range of synthetic aluminosilicate zeolites which, they claim, adsorb 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 adsorbed in the pore interstices of the powder (Goddard, 1995b).

9.9 Temperature control packaging

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 & Breene, 1989).

Self-heating cans and containers have been commercially available for decades and are particularly popular in Japan. Self-heating aluminium and steel cans and containers for sake, coffee, tea and ready meals are heated by an exothermic reaction which occurs when lime and water positioned in the base are mixed. In the UK, Nestlé has recently introduced a range of Nescafé coffees in self-heating insulated cans that use the lime and water exothermic reaction. 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 has recently been introduced is the Chill Can™ (The Joseph Company, USA) which relies on a hydrofluorocarbon (HFC) gas refrigerant. The release of HRC gas is triggered by a button set into the can's base and can cool a drink by 10°C in two minutes. However, concerns about the environmental impact of HFC's are likely to curtail the commercial success of the Chill Can™ (Anon, 1997).

9.10 Food safety, consumer acceptability and regulatory issues

At least four types of food safety and regulatory issues related to active packaging of foods need to be addressed. First, any need for food contact approval must be established before any form of active packaging is used. Second, it is important to consider environmental regulations covering active-packaging materials. Third, there may be a need for labelling in cases where active packaging may give rise to consumer confusion. Fourth, it is pertinent to consider the effects of active packaging on the microbial ecology and safety of foods (Rooney, 1995). All of these issues are addressed in an EC funded *Actipack* project which aims to evaluate the safety, effectiveness, economic and environmental impact and consumer acceptance of active and intelligent packaging (De Kruijf, 2000).

Food contact approval will often be required because active packaging may affect foods in two ways. Active packaging substances may migrate into the food or may be removed from it. Migrants may be intended or unintended. Intended migrants include antioxidants, ethanol and antimicrobial preservatives which would require regulatory approval in terms of their identity, concentration and possible toxicology effects. Unintended migrants include various metal compounds which achieve their active purpose inside packaging materials but do not need to, or should not, enter foods. Food additive regulations require identification and quantification of any such unintended migration.

Environmental regulations covering reuse, recycling, identification to assist in recycling or the recovery of energy from active packaging materials need to be addressed on a case-by-case basis. European Union companies using active packaging as well as other packaging need to meet the requirements of the

Packaging Waste Directive (1994) and consider the environmental impact of their packaging operations.

Food labelling is currently required to reduce the risk of consumers ingesting the contents of oxygen scavenger sachets or other in-pack active-packaging devices. Some active packages may look different from their passive counterparts. Therefore it may be advisable to use appropriate labelling to explain this difference to the consumer even in the absence of regulations.

Finally, it is very important for food manufacturers using certain type of active packaging to consider the effects this will have on the microbial ecology and safety of foods. For example, removing all the oxygen from within the packs of high a_w chilled perishable food products may stimulate the growth of anaerobic pathogenic bacteria such as *Clostridium botulinum*. Specific guidance is available to minimise the microbial safety risks of foods packed under reduced oxygen atmospheres (Betts, 1996). Regarding the use of antimicrobial films, it is important to consider what spectrum of microorganisms will be inhibited. Antimicrobial films which only inhibit spoilage microorganisms without affecting the growth of pathogenic bacteria will raise food safety concerns.

In the USA, Japan and Australia, active packaging concepts are already being successfully applied. In Europe, the development and application of active packaging is limited because of legislative restrictions, fear of consumer resistance, lack of knowledge about effectiveness and economic and environmental impact of concepts (Vermeiren *et al.*, 1999). No specific regulations exist on the use of active packaging in Europe. Active packaging is subjected to traditional packaging legislation, which requires that compounds are registered on positive lists and that the overall and specific migration limits are respected. This is more or less contradictory to the concept of some active packaging systems in which packaging releases substances to extend shelf life or improve quality (De Kruijf, 2000). The food industry's main concern about introducing active components to packaging seems to be that consumers may consider the components harmful and may not accept them. In Finland, a consumer survey conducted in order to determine consumer attitudes towards oxygen scavengers revealed that the new concepts would be accepted if consumers are well informed by using reliable information channels (Ahvenainen & Hurme, 1997). More information is needed on the chemical, microbiological and physiological effects of various active concepts on the packaged food, i.e. in regard to its quality and safety. So far, research has mainly concentrated on the development of various methods and their testing in a model system, but not so much on functioning in food preservation with real food products. Furthermore, the benefits of active packaging need to be considered in a holistic approach to environmental impact assessment. The environmental effect of plastics-based active packaging will vary with the nature of the product/package combination, and additional additives need to be evaluated for their environmental impact (Vermeiren *et al.*, 1999).

9.11 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. 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.

Oxygen scavengers are by far the most commercially important sub-category of active packaging and the market has been growing steadily for the last ten years. It is predicted that the recent introduction of oxygen scavenging films and bottle caps will further help to stimulate the market in future years and the unit costs of oxygen scavenging technology will drop. Other active packaging technologies are also predicted to be us+ed more in the future, particularly carbon dioxide scavengers and emitters, moisture absorbers and temperature control packaging. Food safety and regulatory issues in the EU are likely to restrict the use of certain preservative releasers and flavour/odour adsorber active packaging technologies. 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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