3 Packaged Product Quality and Shelf Life

Helen Brown, James Williams and Mark Kirwan

3.1 INTRODUCTION

The intention of this chapter is to illustrate how the product quality and shelf life of packaged foods can be affected by the appropriate selection of packaging materials. Factors that affect product quality and shelf life are considered with examples of how packaging has been used to influence them to extend shelf life. Packaging can become a shelf life limiting factor in its own right. For example, this may be as a result of migration of tainting compounds from the packaging into the food or the migration of food components into the packaging. This chapter, therefore, also discusses the adverse effects that inappropriate packaging materials can have on product quality and shelf life.

Achieving a consensus on the definition of shelf life is never easy. Different groups within the food chain, i.e. consumers, retailers, distributors, manufacturers and growers, proffer subtly different perspectives of shelf life, reflecting the aspect of greatest importance and significance to them. For consumers, it is imperative that products are safe and the quality meets their expectations. Consumers will often actively seek the product on the shelf with the longest remaining shelf life as this is considered to be indicative of freshness. Consumer handling of products in terms of storage and use impacts on shelf life, is perhaps the biggest unknown for manufacturers when designing shelf life trials. For retailers, product quality must meet or exceed consumer expectations for repeat purchases. Product shelf life must be set to ensure that this is the case over the entire product life, allowing sufficient product life for the distribution chain and retail turnover of product and some life for the consumer. Manufacturers, who are responsible for setting product shelf life, must be able to justify the validity of the shelf life assigned. They are also under considerable pressure to produce products that meet the shelf life requirements of retailers, and often this will dictate whether or not a product is stocked. Achieving the desired product shelf life is a powerful driver for product and packaging innovation to extend product life. Many new packaging materials, such as those used in modified atmosphere packaging (MAP) and active packaging, have been developed to complement developments in new preservation techniques. The role of packaging in the maintenance and extension of shelf life cannot be over emphasised.

The Institute of Food Science and Technology (IFST) Guidelines (1993) provides a definition of shelf life: ‘shelf life is the period of time during which the food product will remain safe; be certain to retain desired sensory, chemical, physical and microbiological characteristics; and comply with any label declaration of nutritional data.’ This definition encapsulates most perspectives and leaves some flexibility, i.e. ‘desired ... characteristics’, in assigning product
shelf life. This is essential because once considerations of safety have been met, quality is generally a commercial consideration dependent upon the marketing strategy of the companies.

The shelf life of a product is best determined as a part of the product development cycle. As the packaging may be one of the means by which shelf life limiting processes are controlled, or the packaging per se may limit the product shelf life, it is also important that the packaging requirements for the product are considered early during product development. Shelf life testing is carried out by holding representative samples of the final product under conditions likely to mimic those that the product will encounter from manufacture to consumption. Once the microbiological safety of the product has been determined, quality issues can be considered. This may be based on microbial numbers, chemical specifications or sensory assessment. In most cases, it is likely to be a combination of these. For products with long shelf lives, it is desirable to have indirect or predictive methods for determining shelf life. Increasing temperature is the most common means of accelerating shelf life, but other parameters, such as humidity, shaking or exposure to light, known to affect product stability can be used. Such tests are often product-specific and based on a considerable knowledge of the product and its response under the accelerating conditions. The danger with this approach is that chemical reactions or microbiological growth is initiated, which would not take place under normal storage conditions.

Another approach to accelerated shelf life testing is predictive modelling, where mathematical models are used to predict either the shelf life or the level of a shelf life limiting attribute as a function of the composition of the product. A food’s equilibrium relative humidity (ERH) is the atmospheric humidity condition under which it will neither gain nor lose moisture to the air (value often expressed as $A_w$, the water activity). The relationship between the mould-free shelf life and the ERH has been established for a large number of manufactured bakery products. The ERH of a product can be calculated by using conversion factors to obtain the sucrose equivalents that its ingredients contribute, and this can be used to estimate the mould-free shelf life. Predictive food microbiology is based on mathematical models that describe the growth of microorganisms under the specified conditions, such as temperature, pH or level of preservative. There are a number of predictive food microbiology models available for use, e.g. the Campden & Chorleywood Research Association (now Campden BRI) FORECAST Service and the USDA Pathogen Modelling Program. These models can be used to predict the likely growth of organisms of interest and to quickly assess the effects that changes in product formulation will have on microbial growth and, therefore, shelf life, where microbial number is the shelf life limiting criterion.

In the EU, shelf life is not defined in law, nor is there legislation about how shelf life should be determined. According to Directive 92/59/EEC on general product safety, the manufacturer is responsible only for putting safe products on the market. The EU Directive on food labelling (79/112/EEC and consolidated in 2000/13/EC) requires pre-packaged foods to bear a date of minimum durability (best before or best before end) or, for highly perishable foods from a microbiological point of view, a use by date. The date of minimum durability is defined as ‘the date until which the foodstuff retains its specific properties when properly stored’. This date (and, therefore, the shelf life) is fixed under the producer’s responsibility. The decision as to whether a food requires a use by or best before indication rests with those responsible for labelling the food since they are in the best position to assess its properties. It is an offence to sell any food after the stated use by date and only authorised persons may alter or remove the date. Other specific pieces of legislation impact indirectly on shelf life: for example, if additives are used to achieve the desired shelf life, then legislation relating to the use of additives (those permitted for use and the permitted levels) is relevant. Legislation that prescribes the maximum temperatures for the storage and distribution of chilled and frozen products has a significant
impact, especially on those foods that use temperature as a key factor to control shelf life limiting processes.

Within the European Union (EU), it is the responsibility of the manufacturer, importer or distributor of food contact materials, or those who place them in contact with food prior to sale, to ensure that their products comply with the appropriate legislation. This requirement is unlike the system administered by the Food & Drug Administration in the United States of America that many businesses will be familiar with. There is no harmonised system of prior approval or authorisation of food contact materials within the EU (FSA, 2007).

Legislation regarding food contact materials is intended to ensure that no components of food contact materials likely to endanger health or food quality are transferred into foods. Foods may come into contact with many different materials during preparation, processing, packing and transportation. The definitions of food contact materials are dealt with in European Commission (EC), Regulation No. 1935/2004. EC Regulation 1935/2004 is wide-ranging and replaces Council Directive 89/109/EEC. It includes requirements for good manufacturing practice in the manufacture and use of materials and articles that may come into contact with food so that, under their normal or foreseeable conditions of use, they do not transfer their constituents to foodstuffs in quantities that could:

- endanger human health
- bring about unacceptable changes in the composition of the food or beverage
- deteriorate in the organoleptic characteristics of the food or beverage

Associated with Regulation 1935/2004 is a later EC Regulation, 2023/2006, which gives specific guidance on Good Manufacturing Practice (EC, 2006). This regulation also lays down some specific requirements that apply to processes involving the application of printing inks to the non-contact side of a material or article.


There is a considerable body of legislation relating to plastic materials intended for food contact. This started with Commission Directive 90/128/EEC. Subsequently several amendments were issued, and these were all consolidated in 2002/72/EC. The latter in turn has had additional amendments added, the latest being 2008/39/EC. This legislative material relates to the composition of plastic materials, defined broadly as organic polymers, but does not cover many auxiliary packaging components, such as regenerated cellulose film, elastomers and rubber, paper and board, surface coating containing paraffin or microcrystalline waxes and ion-exchange resins, which have their own Directives. A general overall migration limit of 10 mg/dm² contact area sets a limit on the maximum quantity of constituents allowed to transfer out of plastic materials and articles into food. The plastics Directive 2002/72/EC and its five amendments establish a positive list of approved monomers and starting substances, which are the only such substances permitted for use in food contact plastics. Specific migration limits are included for some monomers and starting substances, which restrict residual levels in the finished material.

A number of other food contact materials have separate EU Directives/Regulations. These include regenerated cellulose film, 2007/42/EC, ceramics, 84/500/EEC plus amendment 2005/31/EC, active and intelligent materials, EC No. 450/2009, recycled plastics, EC

As is the usual practice EU regulations and Directives are passed into the legal framework of member states – in the UK, these comprise Statutory Instruments. Therefore, it is recommended that students refer to the appropriate authorities in member states for up-to-date information on the regulations for materials and articles that may come into contact with food and beverage products. Details of 28 European National Government Authorities are available (EC, 2007). In the UK, the appropriate body is the Foods Standards Agency at www.food.gov.uk.

### 3.2 FACTORS AFFECTING PRODUCT QUALITY AND SHELF LIFE

For many foods, the product shelf life is limited by specific or ‘key’ attributes that can be predicted at the time of product development. This is either on the basis of experience of similar products or observations of them, or from a consideration of:

- the make-up of the product (intrinsic factors)
- the environment that it will encounter during its life (extrinsic factors) and
- the ‘shelf life limiting processes’ that this combination of intrinsic and extrinsic factors is likely to result in

Intrinsic factors are the properties resulting from the make-up of the final product and include the following:

- water activity ($A_w$) (available water)
- pH/total acidity; type of acid
- natural microflora and surviving microbiological counts in final product
- availability of oxygen
- redox potential ($E_h$)
- natural biochemistry/chemistry of the product
- added preservatives, e.g. salt, spices, antioxidants
- product formulation
- packaging interactions, e.g. tin pickup, migration

Selection of raw materials is important for controlling intrinsic factors, since subsequent processing can rarely compensate for poor-quality raw materials.

Extrinsic factors are a result of the environment that the product encounters during life and include the following:

- time–temperature profile during processing
- temperature control during storage and distribution
- relative humidity (RH) during storage and distribution
- exposure to light (UV and IR) during storage and distribution
- composition of gas atmosphere within packaging
- consumer handling
Product packaging can have significant effects on many of these extrinsic factors and many developments in packaging materials have been driven by the need to reduce the impact of these environmental factors and extend shelf life. In some instances, the packaging alone may be effective in extending shelf life, e.g. by providing a complete light and oxygen barrier. In most instances, however, it acts as one of a number of hurdles that, acting together, influence the shelf life.

The interactions of intrinsic and extrinsic factors affect the likelihood of the occurrence of reactions or processes that affect shelf life. For ease of discussion, these shelf life limiting reactions or processes can be classified as: chemical/biochemical, microbiological and physical. The effects of these processes are rarely mutually exclusive but these categories provide a convenient framework for discussion. The effects of these factors are not always detrimental and, in some instances, they are essential for the development of the desired characteristics of a product.

### 3.3 CHEMICAL/BIOCHEMICAL PROCESSES

Many important deteriorative changes can occur from reactions within the food or with its components. Chemical reactions will proceed if reactants are available and if the activation energy threshold of the reaction is exceeded. The rate of reaction is dependent on the concentration of reactants and on the temperature and/or other energy, e.g. light induced reactions. A general assumption is that for every 10°C rise in temperature, the rate of reaction doubles.

Specialised proteins called ‘enzymes’ catalyse biochemical reactions. They can be highly specific catalysts, lowering the activation threshold so that the rate of reaction (of thermodynamically possible reactions) is dramatically increased. The specificity of enzymes for a particular substrate is indicated in the name, usually by attachment of the suffix ‘-ase’ to the name of the substrate on which it acts: for example, lipase acts on lipids and protease on proteins. In this chapter, some examples of chemical and biochemical reactions that affect shelf life and how they can be affected by packaging will be discussed.

#### 3.3.1 Oxidation

A number of chemical components of food react with oxygen affecting the colour, flavour, nutritional status and occasionally the physical characteristics of foods. In some cases, the affects are deleterious and limit shelf life; in others, they are essential to achieve the desired product characteristics. Packaging is used to both exclude, control or contain oxygen at the level most suited for a particular product. Foods differ in their avidity for oxygen, i.e. the amount that they take up; and their sensitivity to oxygen, i.e. the amount that results in quality changes. Estimates of the maximum oxygen tolerance of foods are useful to determine the oxygen permeability of packaging materials required to meet a desired shelf life, see Table 3.1 (Salame, 1986).

Foods containing a high percentage of fats, particularly unsaturated fats, are susceptible to oxidative rancidity and changes in flavour. Saturated fatty acids oxidise slowly compared with unsaturated fatty acids. Antioxidants naturally occurring or added either slow the rate of, or increase the lag time to the onset of, rancidity. Three different chemical routes can initiate the oxidation of fatty acids: the formation of free radicals in the presence of metal ion catalysts, such as iron, or heat, or light – termed the classical free radical route; photo oxidation in which
Table 3.1 The estimated maximum oxygen tolerance of various foods.

<table>
<thead>
<tr>
<th>Food/beverage</th>
<th>Maximum oxygen tolerance (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beer (pasteurised)</td>
<td>1–2</td>
</tr>
<tr>
<td>Typical autoclaved low-acid foods</td>
<td>1–3</td>
</tr>
<tr>
<td>Canned milk</td>
<td>1–3</td>
</tr>
<tr>
<td>Canned meat and vegetables</td>
<td>1–3</td>
</tr>
<tr>
<td>Canned soups</td>
<td>1–3</td>
</tr>
<tr>
<td>Baby foods</td>
<td>1–3</td>
</tr>
<tr>
<td>Coffee (fresh ground)</td>
<td>2–5</td>
</tr>
<tr>
<td>Tomato based products</td>
<td>3–8</td>
</tr>
<tr>
<td>High acid fruit juices</td>
<td>8–20</td>
</tr>
<tr>
<td>Carbonated soft drinks</td>
<td>10–40</td>
</tr>
<tr>
<td>Oils and shortenings</td>
<td>20–50</td>
</tr>
<tr>
<td>Salad dressings, peanut butter</td>
<td>30–100</td>
</tr>
<tr>
<td>Liquor, jams, jellies</td>
<td>50–200+</td>
</tr>
</tbody>
</table>

Source: Salame 1986.

photosensitisers, such as chlorophyll or myoglobin, affect the energetic state of oxygen; or an enzymic route catalysed by lipoxygenase. Once oxygen has been introduced into the unsaturated fatty acids to form hydroperoxides by any of these routes, the subsequent breakdown of these colourless, odourless intermediates, proceeds along similar routes regardless of how oxidation was initiated. It is the breakdown products of the hydroperoxides – the aldehydes, alcohols and ketones that are responsible for the characteristic ‘stale’, ‘rancid’ and ‘cardboard’ odours associated with lipid oxidation.

Lowering the storage temperature does not stop oxidative rancidity because both the first and second steps in the reaction have low activation energies. Reduction of the concentration of oxygen (both dissolved and in the headspace) to below 1%, removal of factors that initiate oxidation and the use of antioxidants are strategies employed to extend shelf life where rancidity is a shelf life limiting factor.

In milk chocolate, the presence of tocopherol (vitamin E), a natural antioxidant in cocoa liquor provides a high degree of protection against rancidity. However, white chocolate does not have the antioxidant protection of cocoa liquor and so is prone to oxidative rancidity, particularly light induced. Even with light barrier packaging its shelf life is shorter than that of milk or plain chocolate. However, the cost of eliminating oxygen from the pack would be prohibitive and not worth the additional cost for the relatively small increase in shelf life that this change would result in.

In snack products, and particularly nuts, the onset of rancidity is the shelf life limiting factor. Such sensitive products are often packed gas flushed to remove oxygen and packed with 100% nitrogen to protect against oxidation, and provide a cushion to protect against physical damage. The packaging material generally used for commodity products with short shelf life is PVdC-coated OPP/LDPE laminates, whilst higher added value products with longer shelf life requirements are often packed in metallised polyester/LDPE laminates.

Investigations of rancidity in potato crisps in relation to the light barrier properties of various films showed that improved light barrier properties of packaging films gave extended shelf life with respect to rancidity. Prolonged storage under fluorescent lights at ambient humidity caused the shelf life of crisps to become limited by rancidity rather than texture changes due to moisture uptake (BCL, 1985).
UV light from either natural or retail display cabinets can cause other changes that limit shelf life. Vitamins A, B2, B6, B12 and folic acid are particularly susceptible to light; beers and lagers are susceptible to light-induced oxidation resulting in flavour and colour changes. Incorporation of chemicals that absorb UV light (Ultra Violet Absorbers) into clear packaging materials, particularly glass beverage bottles and HDPE bottles can help to extend the shelf life of products (Potter et al., 2008).

Vacuum packaging extends the shelf life of chilled fatty fish. Trout stored on ice packaged in PE (high oxygen permeability) can develop a markedly rancid taste after 8 days. For trout vacuum packed in a plastic material with low oxygen permeability the shelf life at 0°C is increased to 20 days. For frozen fish, low storage temperatures combined with good packaging slows down degradation. The packaging must be tight fitting and must have a low water vapour transmission rate (WVTR) as the surface of fish easily suffers freezer burn. For fatty fish it is especially necessary to use a packaging material with low oxygen permeability, and vacuum packaging is preferred.

Oxidation of lycopene, a red/orange carotenoid pigment in tomatoes, causes an adverse colour change from red to brown and affects flavour. In canned tomato products, this can be minimised by using plain unlacquered cans. The purpose of the tin coating is to provide protection of the underlying steel, but it also provides a chemically reducing environment within the can. Residual oxygen is consumed by tin dissolution into the product, minimising product oxidation that would otherwise lead to quality loss. However, the extent of dissolution of tin into the product needs to be taken into account in the assigned shelf life of the product as the maximum permitted level of tin in canned foods in the UK is 200 mg/kg (Tin in Food Regulations 1992, SI 1992 No. 496). Tin dissolution can be avoided by using fully lacquered cans but oxygen-induced quality loss is more likely to occur.

Tomato ketchup used to suffer from ‘black neck’ – the top of the ketchup in contact with oxygen in the headspace turned black. To disguise this a label was placed around the neck of the bottle, hiding the discoulouration. It has since been shown that oxidation depends on the level of iron in the ketchup, and blackening has now been prevented.

Oxygenerated myoglobin, oxymyoglobin, is the pigment in raw meat that is responsible for the bright attractive red colour, which consumers associate with freshness and good eating quality. In conventionally packed fresh beef, meat on a plastic tray is overwrapped with a highly gas permeable plastic material that allows an almost unrestricted supply of oxygen to the myoglobin, favouring the red colour. Secondary packaging is used to facilitate the centralised packing of overwrapped packs or for long-term storage of vacuum-packed primals. Overwrapped packs are packed in a ‘master pack’, a large plastic barrier bag that is evacuated and filled with either carbon dioxide or nitrogen. By vacuum packaging fresh beef, the reduced oxygen level in the pack results in a considerable increase in shelf life; however, the meat colour becomes purple due to myoglobin being converted to the reduced form, which most consumers are not familiar with. By using MAP, where the meat is placed on a tray with a volume about 2–3 times that of the meat and the air is drawn out and replaced with a gas mixture of about 80% oxygen to maintain the bright red colour and 20% carbon dioxide to reduce bacterial growth, life can be extended to approximately 2–3 times that of conventionally packed fresh beef.

Nitrosohemochrome is the pigment responsible for the pink colouration of cooked cured meats. This pigment fades rapidly on exposure to air (oxygen) and light. Therefore, vacuum packaging or MAP is generally used to achieve the desired shelf life of cooked cured meats. The oxygen content must be less than 0.3%, and in MAP, a commonly used mixture is 60% nitrogen and 40% carbon dioxide. Oxygen scavengers are one means of reducing the levels of oxygen to a minimum. Light will often be excluded from such packs by the use of large attractive labels,
protecting the product from retail lighting. In a study on the colour stability of sliced cooked ham exposed to commercial retail lighting conditions (fluorescent light), a residual oxygen level of below 0.15% just after packaging combined with the use of a low oxygen transmission rate film (OTR – 0.04 mL O₂/pack × 24 hours) and low gas to product volume ratio (2.6) were optimal conditions for maintaining the colour of the tested ham slices (Larsen et al., 2006).

For freezing, whole chickens are generally packed after the chilling process but before freezing in thin PE bags. Turkeys and ducks are generally vacuum-packed or shrink-packed in more expensive plastic materials with low WVTR and low oxygen permeability. Turkeys especially demand good packaging because of the tendency for turkey meat to become rancid more quickly than other poultry.

### 3.3.2 Enzyme activity

Fruits and vegetables are living commodities and their rate of respiration affects shelf life – generally, the greater the rate of respiration, the shorter the shelf life. Immature products, such as peas and beans, have much higher respiration rates and shorter shelf life than products that are mature storage organs, such as potatoes and onions. Respiration is the metabolic process whereby sugars and oxygen are converted to more usable sources of energy for living cells. Highly organised and controlled biochemical pathways achieve this metabolic process. Depletion and exhaustion of reserves used for respiration leads to metabolic collapse and an appearance associated with senescence. Disruption of tissues that occurs during the preparation of fruits and vegetables for the fresh cut market leads to leakage of cell contents and encourages invasion by microorganisms. It also leads to an increase in respiration rate (Zhu et al., 2001) that depletes reserves and results in quality loss. In non-storage tissues where there are few reserves, such as lettuce and spinach, or immature flower crops, such as broccoli, this effect is even greater. Use of temperature control reduces the respiration rate (see Table 3.2), extending the life of the product. Temperature control combined with MAP further suppresses the growth of yeasts, moulds and bacteria, extending shelf life further.

Ethylene is a plant hormone that accelerates senescence and the ripening process. It is a colourless gas with a sweet ether-like odour. All plants produce ethylene to differing degrees and some parts of plants produce more than others. The effect of ethylene is commodity dependent but also dependent on temperature, exposure time and concentration. Many commodities if exposed over lengthy periods are sensitive to ethylene concentrations as low as 0.1 ppm. Climacteric fruits, such as apples, avocados, melons and tomatoes, are particularly sensitive to ethylene.

<table>
<thead>
<tr>
<th>Table 3.2</th>
<th>Respiration of intact and fresh-cut honeydew melon stored at chill and ambient temperature.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Respiration rate (arbitrary units) at specified temperature (°C)</strong></td>
<td><strong>Q₁₀ temperature coefficient</strong></td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>----------------------</td>
<td>----</td>
</tr>
<tr>
<td>Intact melon</td>
<td>1.4</td>
</tr>
<tr>
<td>Cut melon</td>
<td>2.3</td>
</tr>
<tr>
<td>Increase in respiration rate [%]</td>
<td>64.3</td>
</tr>
</tbody>
</table>


*Q₁₀ temperature coefficient is a measure of change in a biological system as a consequence of an increase in the temperature of 10 °C.*
Table 3.3 Effect of ethylene on the quality of fruit and vegetables.

<table>
<thead>
<tr>
<th>Commodity group</th>
<th>Effects of ethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leafy vegetables</td>
<td>Turn yellow due to chlorophyll loss. Russet spotting on leaves. Accelerated leaf abscission leading to loss of leaves. Phenolic synthesis leading to browning and bitter flavours.</td>
</tr>
<tr>
<td>Cucumbers</td>
<td>Turn yellow and become soft. Accelerated ripening – tissue softening.</td>
</tr>
<tr>
<td>Unripe fruits</td>
<td>Toughening and thickening of fibres.</td>
</tr>
</tbody>
</table>
| Asparagus       | Ethylene biosynthesis and its regulation is well documented (Adams-Phillips et al., 2004; Martinez-Romero et al., 2007). Physical (cutting) or chill injury induces the production of ethylene particularly in fruiting tissue due to its affect on the rate limiting enzyme (1-aminocyclopropane-1-carboxylic acid synthase) in the biochemical pathway leading to ethylene formation and increases tissue sensitivity to ethylene (Kato et al., 2002). As ethylene induces senescence, it has a significant impact on quality loss, see Table 3.3. Removal of ethylene by absorption using activated carbon or potassium permanganate has been shown to be effective in extending the shelf life of a number of whole and cut fruits and vegetables by extending the time to ripening. The storage life of MAP packaged mangoes was extended from 16 to 21 days by the inclusion of activated carbon and potassium permanganate (Illeperuma & Jayasuriya, 2002). Edible, polysaccharide coatings, such as alginate or pectin, reduced ethylene production of coated fresh-cut pears and increased the water vapour resistance (Oms-Oliu et al., 2008). Addition of anti-browning agents N-acetyl cysteine or glutathione to the edible films prevented enzymic browning of fresh cut pears for 2 weeks.

3.4 MICROBIOLOGICAL PROCESSES

Under suitable conditions, most microorganisms will grow or multiply. Bacteria multiply by dividing to produce two organisms from one, their numbers increasing exponentially. Under ideal conditions, some bacteria may grow and divide every 20 minutes, so one bacterial cell may increase to 16 million cells in 8 hours. Under adverse conditions, this doubling or generation time is prevented or extended – a feature that is exploited when developing food products and processes to achieve the desired shelf life.

During growth in foods, microorganisms will consume nutrients from the food and produce metabolic by-products, such as gases or acids. They may release extracellular enzymes (e.g. amylases, lipases, proteases) that affect the texture, flavour, odour and appearance of the product. Some of these enzymes will persist after the death of the microorganisms that produced them, continuing to cause product spoilage.

When only a few organisms are present, the consequences of growth may not be evident, but when numbers increase the presence of many yeast, bacteria and moulds is evident from the formation of visible colonies, the production of slime or an increase in the turbidity of liquids and from the affects that gas production, acidification and the off-odours caused by secondary metabolites have on the acceptability of the food product. The relationship between microbial numbers and food spoilage is not always clear. Whether or not high numbers of microorganisms result in spoilage is dependent upon the numbers present, the make-up of this number in terms of the type of microorganism and its stage of growth or activity and the intrinsic and extrinsic factors of the food in which it is present. The key to achieving the desired shelf life of a
product is to understand which microorganisms are likely to be the ones that will give rise to product spoilage, and what conditions can be used to either kill or reduce the rate of growth and multiplication. This requires careful selection or manipulation of the intrinsic and extrinsic factors of a food.

The presence of food poisoning organisms (pathogens) is not necessarily evident from changes in the food, and may only be apparent from the effects they produce, ranging from mild sickness to death. With many human pathogens, the greater the number of cells consumed, the greater the chance of infection and the shorter the incubation period before the onset of disease. Therefore, destruction, inhibition or at least control of growth is essential. For some invasive pathogens, e.g. viruses, *Campylobacter*, the infectious dose is low and growth in the food may not be necessary. From the point of view of product shelf life, the first question must always be ‘is the product safe?’ Once this can be achieved, then quality and commercial considerations can be considered.

Using knowledge of the initial levels of microorganisms and the conditions that destroy them or reduce their growth rate, food products are developed and designed by use of the best combination of intrinsic and extrinsic factors. The development and implementation of predictive microbiological growth models, particularly for chilled foods, has assisted in targeted product formulation and definition of packaging requirements to achieve a desired shelf life in terms of microbiological numbers.

3.4.1 Examples where packaging is key to maintaining microbiological shelf life

Heat processing that kills microorganisms is a widely used means of achieving safe products and extending shelf life. The amount of heat treatment required depends on the characteristics of the most harmful microorganism present, the nature of the food in terms of its viscosity, the pH of the food, the shape of the pack and the shelf life required. However, the heat process also changes the texture, taste and appearance of the product. This has prompted the move to minimally processed foods where a number of factors are combined to achieve the desired shelf life, e.g. a mild heat treatment, antioxidant action, and controlled atmosphere packaging each restricting microbial growth, such that their combined effect allows the product to retain their sensory and nutritional properties.

In canning, food is filled into a container that is hermetically sealed and sterilised at 121°C or above to ensure all pathogens, especially *Clostridium botulinum* are destroyed. The critical factor is the time it takes for the coldest part of the product to reach the required temperature. The size and shape of the container is important. Retort pouches are flat in shape so processing time can be reduced compared to a conventional cylindrical can and the reduced processing time generally results in improved taste and texture. Similarly, for sous-vide processing, foods are cooked under vacuum in sealed evacuated heat stable pouches or thermoformed trays. In aseptic processing, the barrier that the packaging poses to heat transfer is removed completely – the product and packaging being sterilised separately and then brought together under clean (aseptic) conditions. Where heat processing has been used to achieve sterility, the use of packaging to maintain sterility throughout subsequent life becomes a key factor to achieving the desired product shelf life – both the packaging and the pack seals must provide a barrier to ingress of microorganisms.

Low temperatures affect whether an organism grows and the rate of growth (Betts *et al.*, 2004). Some microorganisms are adapted to grow at chill temperatures so the composition
of organisms in the natural microflora will change. For example, in fresh milk the dominant microflora are Gram-positive cocci and rods that may spoil the product by souring if stored at warm temperatures. At chill temperatures, the microflora becomes dominated by psychrotrophic Gram-negative rod-shaped bacteria (most commonly *Pseudomonas* spp.). When temperature is used as the key limiting factor to control the rate at which shelf life limiting processes proceed, from a microbiological point of view, the role of packaging is less significant to shelf life because regardless of the packaging, if the temperature is not maintained, spoilage will proceed. Frozen storage temperatures will stop microbial growth and can kill some microorganisms, but is not necessarily a lethal process.

Where vacuum packaging or modified atmospheres are the key shelf life limiting factor controlling microbiological growth, packaging is a critical factor in achieving the desired shelf life. *Pseudomonas* species, the major spoilage group in chilled proteinaceous foods, require the presence of oxygen to grow. The use of vacuum packaging or modified atmospheres excluding oxygen will prevent the growth of this type of bacteria. Whilst other organisms can grow in the absence of oxygen, they generally grow more slowly, and so the time to microbial spoilage is increased. In MAP, the gas mixture must be chosen to meet the needs of the specific product, this is usually some combination of oxygen, nitrogen and carbon dioxide. Carbon dioxide at 20–60% has bacteriostatic and fungistatic properties and will retard the growth of mould and aerobic bacteria by increasing the lag phase and generation time of susceptible microorganisms. Several factors influence the antimicrobial effect of carbon dioxide, specifically the microbial load, gas concentration, temperature and permeability of the packaging film. The antimicrobial effect is enhanced at lower temperatures because carbon dioxide is more soluble in water at lower temperatures forming carbonic acid, so good temperature control is essential to obtain the maximum potential benefits of MAP and vacuum packaging. However, the effect of carbon dioxide is not universal – it has little effect on yeast cells and the growth of lactic acid bacteria is improved in the presence of carbon dioxide and lower oxygen levels. Nitrogen is an inert gas that has no antimicrobial effect per se. It is generally used to prevent package collapse in products that absorb carbon dioxide and is used to replace oxygen in products that are susceptible to the growth of aerobic microorganisms.

Packaging materials designed to have antimicrobial activity provide a hurdle for microbial growth but seldom act alone as the key shelf life limiting factor. Antimicrobial activity can be obtained in two ways. Preservative-releasing or migrating systems contain a preservative intended to migrate into the food and act as a preservative (Luck & Jager, 1997). Natural antimicrobial compounds eugenol, thymol and menthol combined with MAP delayed the ripening process and improved fruit quality by delaying softening and loss of colour in sweet cherries and grapes (Serrano et al., 2008). Allylisothiocyanate, a volatile generated by enzyme activity in Brassica, is reported to slow the growth of microorganisms (Waite, 2003). It has been incorporated into sheets or labels that can be attached on the inside or outside of packs (Wasaouro®, Mitsubishi-kagaku Foods Corporation). For use on the outside of the pack, permeable films, such as polyethylene or oriented polypropylene, are required. Wasaouro® is claimed to be effective against *E. coli*, *Staphylococcus aureus* and *Bacillus subtilis*. It is in use in the Japanese market with rice cakes, bakery products and delicatessen goods (Potter et al., 2008). Non-migrating systems contain or produce a compound that has antimicrobial activity when the target organism comes into contact (Kourai et al., 1994). For both systems, the antimicrobial substance can be incorporated into the packaging material or applied to the surface. Maximum contact is required between food and packaging to ensure adequate protection. Therefore, it is particularly suitable for vacuum-packed foods. A number of antimicrobial packaging materials are commercially available and their activities and effectiveness have been reviewed (Vermeiren
One example of this technology is the use of silver zeolite, an antimicrobial compound manufactured by AgION™, comprising a silver active ingredient with an inert, naturally occurring, inorganic ceramic. The silver ions can be built into food polymer materials and when in contact with food reduce the levels of moulds, yeasts and bacteria. FoodTouch® liners (Microbeguard Corporation), paper with the AgION™ incorporated silver zeolite, can be used with raw and cooked foods to increase shelf life.

Over the last 10 years, nisin has been the most frequently used antimicrobial compound in packaging films, followed by food-grade acids and salts, chitosan, plant extracts, lysozyme and lactoperoxidase (Joerger, 2007). Generally, only about two log10 reductions in microbial numbers are reported for test microorganisms when exposed to control and antimicrobial packaging films, suggesting their use is still best as part of a hurdle technology strategy.

3.5 PHYSICAL AND PHYSICO-CHEMICAL PROCESSES

Physical changes affecting shelf life can be brought about directly by physical damage or by physico-chemical processes resulting from the underlying food chemistry. Many packaging functions, such as protection of the product from environmental factors and contamination, such as dust and dirt, dehydration and rehydration, insect and rodent infestation, containment of the product to avoid leakage and spillage, and physical protection action against hazards during storage and distribution, are taken for granted by the consumer. However, careful consideration of the extent of protection required for the product in the context of the rigours of the storage and distribution chain through which it is to pass, is required if the product is to meet its shelf life. Packaging is very often the key factor to limiting the effects of physical damage on product shelf life. Whilst the threat of careless or deliberate tampering cannot be accounted for when assigning product shelf life, the use of tamper evident packaging provides a means of signalling whether packaging and, potentially, a preservative system has been breached.

3.5.1 Physical damage

During product life, particularly in storage, distribution and consumer handling, products are subjected to vibration on vehicles, compressive loads during stacking in warehouses and sudden jolts and knocks. The formulation of the product must be sufficient to tolerate such shocks or extended periods of vibration, e.g. emulsions must be stable enough to withstand vibration, and the packaging must be able to withstand and protect against such forces. Vulnerable areas on packs are heat seals and screw caps, where damage resulting in leakage may result in loss of the preservation effect provided by the packaging. For fragile products that are susceptible to crushing, such as breakfast cereals and biscuits, the outer carton provides protection from physical damage and from potential tampering. Whey protein films as coatings enhance the integrity of foods that disintegrate on handling, e.g. freeze dried foods, have been investigated (Brody, 2009). Fruit and vegetables that are susceptible to bruising require protection from rough handling and the outer packaging used for distribution purposes needs to withstand stacking to considerable heights and withstand high and variable humidity. The design of packaging for this purpose should be based on the properties of the commodity in terms of the humidity level it can withstand, the airflow allowed, the rate of respiration of the product and its susceptibility to bruising.
3.5.2 Insect damage

Infestation of foods can be extremely unpleasant for the consumer because it is often not detected until the package is opened. Insect infestation can occur at any point after manufacture, but is most likely during extended storage periods or during shipment. Although the problem may arise without being the fault of the food manufacturer, loss of materials can be expensive and cases can severely damage the reputation of brands. Package pests are classified in two groups—penetrators and invaders (Highland, 1984, 1991). Penetrators are capable of boring through one or more layers of flexible packaging materials. It is possible to reduce infestation with penetrators by preventing the escape of odours from the package through the use of barrier materials (Mullen, 1997). A rapid method to evaluate the usefulness of odour barriers has been developed (Mullen, 1994). Invaders are more common and enter packages through existing openings, usually created from poor seals, openings made by other insects or mechanical damage. It is, therefore, important that seals are not vulnerable to attack from insects. The corners of square packages can also be potential points of entry for insects. Various new packaging systems have been devised to minimise potential infestation (Hennlich, 2000).

3.5.3 Moisture migration

Moisture migration leading to loss or gain of moisture is a significant physical cause of the loss of shelf life of foods. Hygroscopic foods require protection from moisture take-up, which in dry products such as breakfast cereals and biscuits causes loss of texture, particularly crispness. For breakfast cereals, the inner liner provides most protection to the food. Its main purpose is to protect from moisture transfer so as to preserve the product characteristics. The most effective type of liner will be determined during shelf life testing or by combining information from break point testing (holding at increasing humidities) and knowledge about the characteristics of the moisture permeability of the packaging material.

Protection or prevention of moisture loss is best achieved by maintaining the correct temperature and humidity in storage. In chilled and frozen foods, water loss (desiccation, dehydration or evaporation) can result in quality loss; however, it is often the resulting weight loss that is of greater importance due to the high monetary value of the products sold on a weight basis. The impact that packaging can have is illustrated by the losses that occur in chilled foods sold unwrapped from delicatessen counters, particularly cooked fresh meat, fish, pâtés and cheese. The shelf life of such products differs markedly from the wrapped equivalent—6 hours versus a few days to weeks. Evaporative losses result in a change in appearance (Table 3.4), to such an extent that the consumer will select products that have been loaded into the cabinet most recently in preference to those that have been held in the display cabinet. The direct cost of

<table>
<thead>
<tr>
<th>Evaporative loss (g/cm²)</th>
<th>Change in appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Up to 0.01</td>
<td>Red, attractive and still wet; may lose some brightness</td>
</tr>
<tr>
<td>0.015–0.025</td>
<td>Surface becoming drier; still attractive but darker</td>
</tr>
<tr>
<td>0.025–0.035</td>
<td>Distinct obvious darkening; becoming dry and leathery</td>
</tr>
<tr>
<td>0.05</td>
<td>Dry, blackening</td>
</tr>
<tr>
<td>0.05–0.10</td>
<td>Black</td>
</tr>
</tbody>
</table>

evaporative loss from unwrapped foods in chilled display cabinets was estimated to be in excess of £5 million per annum in 1986 (Swaine & James, 1986). In stores where the rate of turnover of product is high, the average weight loss will be greater because of the continual exposure of freshly wetted surfaces to the air stream.

Weight loss during storage of fruit and vegetables is mainly due to transpiration. Most have an equilibrium humidity of 97–98% and will lose water if kept at humidities less than this. For practical reasons, the recommended range for storage humidity is 80–100% (Sharp, 1986). The rate of water loss is dependent on the difference between the water vapour pressure exerted by the produce and the water vapour pressure in the air, and air speed over the product. Loss of as little as 5% moisture by weight causes fruit and vegetables to shrivel or wilt. Films used in MAP packaging should have low water vapour transmission rates (WVTRs) to minimise changes in moisture content inside the pack. As the temperature of air increases, the amount of water required to saturate it increases (approximately doubling for each 10°C rise in temperature). If placed in a sealed container, foods will lose or gain water until the humidity inside the container reaches a value characteristic of that food at that temperature. If the temperature is increased and the water vapour in the atmosphere remains constant, then the humidity of the air will fall. Minimising temperature fluctuations is crucial for the prevention of moisture loss in this situation.

Severe dehydration in frozen foods leads to freezer burn – the formation of greyish zones at the surface due to cavities forming in the surface layer of the food. Freezer burn causes the lean surfaces of meat to become rancid, discoloured and physically changed. Packaging in low water vapour permeability materials protects against water loss during storage and distribution. However, as temperatures tend to fluctuate rather than remaining constant, dehydration will still occur if the package used does not fit tightly round the product. As water is removed from the food, it will remain inside the package as frost. Frost in packages can amount to 20% or more of product weight and the concomitant desiccation of the product results in an increased surface area and thus greater access to oxygen, increasing the rate of quality loss at the food surface. The problem can be reduced by removing as much air from the pack as possible but for retail packed frozen foods, such as vegetables, this is difficult to achieve and such products are very susceptible to internal frost formation, particularly if they are allowed to spend a long time in the outer layers of display cabinets. By using laminates that include a layer of aluminium foil, internal frost formation can be reduced considerably.

One of the most widely experienced quality changes involving the migration of water is sogginess in sandwiches. Moisture migration from the filling to the bread can be reduced by the use of fat-based spreads to provide a moisture barrier at the interface (McCarthy & Kauten, 1990). In pastry and crust-based products, such as pies and pizzas, migration of moisture from fillings and toppings to the pastry and crust causes similar problems. The migration of moisture or oils may be accompanied by soluble colours; for example, in pizza toppings where cheese and salami come into contact red streaking of the cheese is seen, and in multilayered trifles migration of colour between layers can detract from the visual appearance unless an appropriate strategy for colouring is used. Migration of enzymes from one component to another, for example when sliced unblanched vegetables are placed in contact with dairy products, can lead to flavour, colour or texture problems depending on the enzymes and substrates available (Labuza, 1985). Packaging sensitive components in separate compartments for the consumer to mix them at the point of consumption has been one means of using packaging to overcome such problems. Edible films, some as obvious as enrobing a wafer biscuit with chocolate to prevent moisture uptake, or as simple as an oil layer or a gelatin film over pâté are alternative solutions to such problems.
3.5.4 Barrier to odour pick-up
In practice, several commodities are sometimes stored or distributed in the same container or trailer. Dairy products, eggs and fresh meat are highly susceptible to picking up strong odours. Chocolate products because of the high fat content and sometimes bland flavour, if inadequately wrapped and stored next to strong smelling chemicals, such as cleaning fluids, or in shops close to strongly flavoured sweets, such as poorly wrapped mints, can result in unacceptable flavour pick-up. Packaging reduces the problem but most plastic materials allow quite a significant volatile penetration – the plastic materials used for vacuum packs and MAP have low permeability, and this reduces, but does not prevent, the uptake of foreign odours, i.e. taints.

3.5.5 Flavour scalping
If a chemical compound present in the food has a high affinity for the packaging material, it will tend to be absorbed into or adsorbed onto the packaging until equilibrium concentrations have been established in food and packaging. This loss of food constituents to packaging is known as scalping. Scalping does not result in a direct risk to the safety of the food, or in the introduction of unpleasant odours or flavour. However, the loss of volatile compounds that contribute to its characteristic flavour affects sensory quality. It is common for unpleasant flavours naturally present in a food to be masked by other flavours, the high notes. If the high notes are scalped by the packaging material, the product is either bland or unpleasant flavours are more perceptible. The degree of scalping is dependent partly on the nature of the polymer and partly on the size, polarity and solubility properties of the aroma compound. A comparison of the loss of apple aroma compounds through scalping by low density polyethylene (LDPE), linear low density polyethylene (LLDPE), polypropylene (PP), nylon 6 (a polyamide, PA) and polyethylene terephthalate (PET) showed polypropylene absorbed the highest quantities of volatiles (Nielsen et al., 1992).

Where particular food-packaging combinations are susceptible to scalping, introducing an effective barrier layer may reduce the problem. Such systems must be carefully designed and tested to high levels of sensitivity to ensure that permeation through the barrier is minimised (Franz, 1993).

3.6 MIGRATION FROM PACKAGING TO FOODS
The direct contact between food and packaging materials provides the potential for migration. Additive migration describes the physico-chemical migration of molecular species and ions from the packaging into food. Such interactions can be used to the advantage of the manufacturer and consumer in active and intelligent packaging, but they also have the potential to reduce the safety and quality of the product, thereby limiting product shelf life. Much work has been carried out into the migration of substances from packaging into food. This has included the development of methods for the identification and diagnosis of problems, using chemical and sensory assessment. The kinetics of migration have been modelled to allow prediction of the extent of migration over the shelf life of the product. In the UK, a number of surveillance exercises have been undertaken into the levels of particular migrants in foods (Table 3.5). The history of these surveillance exercises provides a useful summary of the concerns surrounding food contact materials over recent years.
### Table 3.5 Examples of Food Surveillance Information Sheets (FSIS) on food contact materials published by MAFF.

<table>
<thead>
<tr>
<th>FSIS</th>
<th>Date</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/00</td>
<td>Oct 00</td>
<td>Benzophenone from cartonboard</td>
</tr>
<tr>
<td>7/00</td>
<td>Oct 00</td>
<td>Chemical migration from can coatings into food – terephthalic and isophthalic acids</td>
</tr>
<tr>
<td>9/00</td>
<td>Nov 00</td>
<td>BADGE and related substances in canned foods</td>
</tr>
<tr>
<td>10</td>
<td>Jan 01</td>
<td>2-mercaptobenzothiazole and benzothiazole from rubber</td>
</tr>
<tr>
<td>13/01</td>
<td>Apr 01</td>
<td>Survey of bisphenols in canned foods</td>
</tr>
<tr>
<td>27/02</td>
<td>July 02</td>
<td>Paper and board packaging: not likely to be a source of acrylamide in food</td>
</tr>
<tr>
<td>29/02</td>
<td>Aug 02</td>
<td>Tin in canned fruit and vegetables</td>
</tr>
<tr>
<td>43/03</td>
<td>Oct 03</td>
<td>Chemicals used in plastic materials and articles in contact with food (year 1)</td>
</tr>
<tr>
<td>55/04</td>
<td>May 04</td>
<td>Chemicals used in plastic materials and articles in contact with food (year 2)</td>
</tr>
<tr>
<td>76/05</td>
<td>Oct 05</td>
<td>Benzophenone and 4-hydroxybenzophenone migration from food packaging into foodstuffs (year 3)</td>
</tr>
<tr>
<td>18/06</td>
<td>Nov 06</td>
<td>Benzophenone and 4-hydroxybenzophenone migration from food packaging into foodstuffs</td>
</tr>
<tr>
<td>A03029</td>
<td>Sept 02</td>
<td>See also in the FAS Report Repository ‘Investigation of the significant factors in elemental migration from glass in contact with food’.</td>
</tr>
</tbody>
</table>

### 3.6.1 Migration from plastic packaging

The popularisation of polymeric packaging materials has resulted in increased concerns over the migration of undesirable components into foods. This has the potential to affect product quality (Tice, 1996) as well as safety (Carter, 1977). These concerns are generally focused on the levels of residual monomers and plastics additives, such as plasticisers and solvents, present in polymers intended for direct or close contact with food. It is, therefore, important that the formulation of plastic packaging materials is designed so that the polymerisation process is as complete as possible. A typical modern plastic packaging material may comprise many different constituents, which all have the potential to result in safety and/or quality problems if the material is poorly designed or there are errors in the manufacturing procedure. The material itself is a polymer or copolymer manufactured from one or more types of monomers, such as styrene, vinyl acetate, ethylene, propylene or acrylonitrile. All polymers contain small quantities of residual monomers left unreacted from the polymerisation reaction. These constituents are potentially available to migrate into foods. A food surveillance exercise undertaken in the UK measured the levels of styrene monomer in a total of 248 samples of food from a wide variety of manufacturers and in a wide variety of pack types and sizes (MAFF, 1994). Samples of milk and cream products, sold as individual portions (~10 g), contained the highest levels of styrene, ranging from 23 to 223 μg/kg, with a mean value of 134 μg/kg. Two samples of low fat table spread product contained styrene at an average concentration of 9 μg/kg. Styrene was detected at levels between 1 and 60 μg/kg in the majority of remaining samples, with an average of less than 3 μg/kg. A total diet study estimated that the average daily intake of styrene is between 0.03 and 0.05 μg/kg body weight for a 60 kg person (MAFF, 1999b), with part of this coming from styrene naturally formed in food. This compares favourably with a provisional maximum tolerable daily intake of 40 μg/kg body weight set by the Joint FAO/WHO Committee on Food Additives (WHO, 1984). The presence of styrene in food, however, also has the potential to affect flavour. Taste recognition threshold concentrations for styrene in a number of different
food types are below the level detected in foods (Table 3.6) and customer complaints due to tainting with styrene do still occur.

Additives are used to aid the production of polymers and to modify the physical properties of the finished material. For instance, plasticisers, added to give a plastic the desired flexibility, have been identified as a potential threat to health. The World Health Organization (WHO) has published opinions on a number of commonly used plasticisers with comments on toxicity.

The use of plasticised PVC as cling film has been targeted as a potential problem in terms of migration. Studies have been conducted on the migration of the plasticiser di-(2-ethylhexyl)adipate from PVC films into food during home-use and microwave cooking (Startin et al., 1987) and in retail food packaging (Castle et al., 1987). The level of migration increased with both the length of contact time and temperature of exposure, with the highest levels observed where there was a direct contact between the film and food, and where the latter had a high fat content on the contact surface. Use of a thinner PVC film was suggested as means of reducing the migration of this plasticiser (Castle et al., 1988).

Mineral hydrocarbons, including liquid paraffin, white oil, petroleum jelly, hard paraffin and microcrystalline wax, may be used in certain polymers as processing aids. They have been detected in polystyrene containers at levels between 0.3 and 3% (Castle et al., 1991), in polystyrene and ABS pots and tubs at between 0.3 and 5.5% (Castle et al., 1993a), and cheese coatings at up to 150 mg/kg (Castle et al., 1993b). The same studies also detected migration of these compounds into various foods, with the extent of migration broadly dependent on temperature and fat content.

The high performance of plastic packaging materials means that often only one layer of packaging is necessary to protect the product throughout shelf life. This means that the material used to protect the product is also required to promote it as a brand and provide the consumer with information on ingredients and nutritional information. Consequently, the food must be stored in contact with or in close proximity to printing inks, which can often pose a greater threat to product safety and quality than the base packaging material itself.

Table 3.6  Taste recognition threshold concentrations for styrene in different food types.

<table>
<thead>
<tr>
<th>Food type</th>
<th>Fat content (%)</th>
<th>Taste recognition threshold concentration (μg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td>Emulsions</td>
<td>3</td>
<td>196</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>654</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1181</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1396</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1558</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>2078</td>
</tr>
<tr>
<td>Yoghurts</td>
<td>0.1</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>171</td>
</tr>
<tr>
<td>Yoghurt drinks</td>
<td>Natural</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>Strawberry</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>Peach</td>
<td>94</td>
</tr>
</tbody>
</table>

Source: Linssen et al. 1995.
One of the most common types of ink and varnish formulations to be used is UV curable ink. This is made up of monomers, initiators and pigments. Following application to the packaging, the ink is exposed to a source of ultraviolet radiation, converting the photoinitiator to a free radical that reacts with a monomer, thus initiating the polymerisation. During polymerisation, or curing, polymers are formed that irreversibly bind to the base packaging and trap the colourant into the polymer matrix, leaving a high quality, fast and safe printed surface. Other ink and varnish systems comprise pigment resin and a vehicle that may be either an organic solvent or water. Adequate drying with these inks requires removal of this solvent or water.

However, the quality of the print can be highly dependent on a number of factors. In the case of UV cured inks, excessive residual quantities of monomer or photo-initiator can result if the ink formulation is unbalanced, or through the incorrect function of the UV source. The migration of these constituents into a food may pose a risk to health and affect sensory quality. In addition to the inherent odour of these constituents, it is known that interactions between migrants and food components can lead to the formation of more potent tainting compounds. For example, the migration of benzophenone, a commonly used odourless photoinitiator, has been found to result in the generation of alkyl benzoates, which contribute undesirable flavours (Holman & Oldring, 1988).

A survey of printing inks on a selection of packaging materials for products, including confectionery, snacks, chips, potatoes, chocolate bars and biscuits, in England and Spain found plasticisers above detectable levels (Nerin et al., 1993). Plasticisers are commonly used in printing inks to contribute to adhesion to packaging, imparting improved flexibility and wrinkle resistance. Phthalates were identified as the major plasticisers in printing inks, although some samples contained N-ethyl- and N-methyl-toluene sulphonamide and tris(2-ethylhexyl) trimellitate. Although the printing inks were generally applied to the outer surface of the packaging, and, consequently, were not in direct contact with the food, it has been shown that plasticisers can migrate through the plastic layer to the food (Castle et al., 1988).

Adhesives used to seal packaging can also be a source of migrating constituents. Common types of adhesive for use in food packaging are hot melt, pressure sensitive, cold seal, water-based, solvent-based, solvent-free, acrylics and polyurethanes. An adhesive should be chosen for an application on the basis of the nature of the product (e.g. it would be inappropriate to use a hot melt adhesive on a milk chocolate bar pack), the type of packaging used and special requirements, such as the inclusion of desirable odour volatiles into a cold seal to enhance product perception on opening.

A list of substances used in the manufacture of adhesives for food was compiled from a survey of adhesive manufacturers (Bonell & Lawson, 1999). More than 360 substances were listed as being used in one or more of the commonly used adhesives. A subsequent study into the chemical composition and migration levels focused on polyurethane adhesives (Lawson & Barkby, 2000). Major migrants (10–100 g/dm) were identified to be residual polyether polyols, cyclic reaction products formed during the preparation of polyester polyols, and low levels of additives used in the preparation of the adhesive. It was also suggested that constituents in the printed surface of packaging could migrate into the adhesive layer, when stored in direct contact, and then migrate into food after the packaging was formed.

The potential for interactions between different components of a packaging material is increased in multilayer laminate systems. These complex packaging materials are manufactured by combining different polymeric and non-polymeric, e.g. metals, constituents to fulfil property requirements. The presence of numerous components, and adhesives used to bind them, can increase the probability of problems occurring and the difficulty associated with identifying the cause.
3.6.2 Migration from other packaging materials

Although the majority of research into interactions between food and packaging is concentrated on plastics, more traditional materials, such as paper, board and cans, also present problems.

Paper and board has been used to package food products for many years. Their composition is generally less complex than plastics, presenting less scope for migration. However, a number of taint problems in foods have been attributed to paper and board packaging.

Chlorophenols can be responsible for antiseptic taints. An investigation into a particularly disagreeable odour and taste in a shipment of cocoa powder found that the paper sacks used to package the product contained a number of chlorophenols in the paper itself at levels up to 520 µg/kg, and in the glued side seams at up to 40 000 µg/kg (Whitfield & Last, 1985). It was concluded that 2,4-dichlorophenol, 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol had been formed during the bleaching of wood pulp for paper manufacture, while pentachlorophenol had been used as a biocide in adhesives. It is important that the wood used in pallet construction is also free from such biocide treatment.

Chloroanisoles can be formed from chlorophenols through fungal methylation (Crosby, 1981). These compounds have lower sensory thresholds than the equivalent chlorophenol, and can be responsible for strong musty taints. It has been known for chloroanisoles to be formed from chlorophenols in damp paper and board materials (Whitfield & Last, 1985).

Health concerns have been raised over the use of recycled paper and board for food contact because of the possible migration of diisopropyl naphthalenes (DIPNs). These constituents, usually present in a number of isomeric forms, are commonly used in the preparation of special papers, such as carbonless and thermal copy paper. Research has shown that DIPNs are not eliminated during the recycling of paper (Sturaro et al., 1995) and have the potential to migrate into dry foods, such as husked rice, wheat semolina pasta, egg pasta and cornflour (Mariani et al., 1999). A UK survey confirmed that the use of recycled paper and board packaging materials can result in the migration of DIPNs into food (MAFF, 1999a). It was proposed that migration may be reduced if a film or laminate was placed between the food and the board. However, there was no simple relationship between the presence of an intervening film wrap and reduced levels of DIPNs in foods. Ironically, there may also be an argument for the use of DIPNs in functional packaging, as they have been identified as potential suppressants of sprouting in potatoes (Lewis et al., 1997).

Migration from can lacquers into canned foods has been another area of concern over recent years. The migrants considered to pose the greatest health concern are the monomers bisphenol-A and bisphenol-F, and their diglycidyl ethers, known as BADGE and BFDGE, respectively. A study into the mechanisms involved in the migration of bisphenol-A from cans into drinks found that it was necessary to heat the can to a temperature above the glass transition temperature of the epoxy resin (105°C) in order for the compound to be mobilised (Kawamura et al., 2001).

It has been proposed that BADGE can react with food components following migration (Richard et al., 1999). After addition to homogenates of tuna in water, 97% of BADGE could not be detected either as BADGE or as its hydrolysate or HCl derivative. Following addition to some foods, a small percentage of added BADGE was converted to methyl thiol derivatives but no other products could be identified, possibly because BADGE reacted with such a large number of components that the resulting chromatographic peaks were not detectable. A consequence of these results is the possibility that migration of BADGE into foods may have been grossly underestimated.

Another example of interactions between food and migrants from packaging material is catty taint, studied extensively in the 1960s. An initial study (Neely, 1960) reported on the formation
of a substance having an objectionable odour similar to that of cat urine. Subsequent work suggested that the cause was a sulphur derivative of a compound related to acetone.

It was later found that the catty odour was formed from mesityl oxide, which is readily formed from acetone (migrating from the packaging) in the presence of dehydrating reagents (Pearce et al., 1967). The mesityl oxide formed reacts rapidly with hydrogen disulphide at room temperature to generate the taint, but the catty odour is only evident at extreme dilutions. Higher concentrations of the tainting compound are perceived as having a mercaptan-like odour.

A study into the structure–odour relationship for catty smelling mercapto compounds confirmed 4-methyl-4-mercaptopen-2-one to be the volatile principally responsible for catty taint (Polak et al., 1988) and that it has a sensory threshold as low as 0.1 μg/kg (ppb) in bland foods (Reineccius, 1991). The most recent published study on an occurrence of a catty food taint, concerned separate complaints of an obtrusive off-odour in cook-in-the-bag ham products produced by two different manufacturers (Franz et al., 1990). The laminate packaging used in both products contained acetone, a precursor of mesityl oxide, although at concentrations considered too low to induce the formation of catty taint (0.4 and 1 mg/m², respectively). Subsequent work found the source to be diacetone alcohol (DAA), present at a concentration of 3 g/m² and 9 mg/m², respectively. The DAA was converted to mesityl oxide within the laminate packaging material through dehydration by an ethylene ionomer. The authors concluded that avoiding the use of mesityl oxide precursors, such as DAA, in packaging materials, could prevent the occurrence of catty taint in sulphur-rich foods.

3.6.3 Factors affecting migration from food contact materials

The extent of migration from food contact materials into food is dependent on a number of factors. Most obviously, the quantity of available potential migrants in the packaging material itself is of paramount importance. These levels must be minimised by careful design and production of the packaging.

The degree of contact between food and packaging also has a direct influence on migration, and in cases where particular problems have been encountered, it may be necessary to protect a food from direct contact with, for example, a printed surface.

As migration is a process that usually occurs gradually, the period of time for which the food and packaging are in contact should also be considered when trying to anticipate potential migration issues. Thus, there may be less concern over migration for a chilled dairy product with a short shelf life than over a box of shortbread biscuits with a shelf life of 6 months.

The intrinsic factors of a food are of great significance to the degree of migration likely to occur. A potential migrating constituent of the packaging is gradually transferred to the food causing the concentration of that constituent to gradually decrease in the packaging and increase in the food. Eventually, a point of equilibrium is reached when the concentration of the constituent stays constant in food and packaging. The quantity of the constituent in the food at the point of equilibrium is dependent on the physical affinity of the constituent for the packaging and food; for example, the degree of migration of a hydrophobic monomer, such as styrene, is partially dependent on the lipid content of the food. This was demonstrated in a study of migration from polystyrene into cocoa powder and chocolate flakes (Linssen et al., 1991). Residual styrene in the packaging material was quantified at around 320 mg/kg, and the amounts of styrene ranged from 7 to 132 μg/kg in cocoa drinks and from 414 to 1447 μg/kg in the higher fat chocolate flakes. Sensory assessment detected a styrene taint only in the chocolate flakes. Therefore, by considering the composition of the foodstuff, it may be possible
to minimise the level of migration into foods from food contact materials. The same process of partitioning constituents between food and packaging to a point of equilibrium occurs in flavour scalping, discussed earlier in this chapter.

An investigation into the migration of paramagnetic additives from rigid PVC into a food simulant of pure or mixed fatty esters found that there was a tendency for the fatty esters to migrate into and plasticise the PVC matrix (Riquet et al., 1994). This had the effect of increasing the mobility of the additive and accelerated its migration into the food simulant.

### 3.6.4 Packaging selection to avoid migration and packaging taints

For general selection of packaging, it is of paramount importance to ensure that the material complies with relevant legislation. This may entail specific and global migration measurements to check that the packaging is safe. When selecting a packaging material for a defined purpose, it is important to consider all components of the end product, how they are likely to interact, and the effect that the interaction will have on the food. The potential for taints can be evaluated by considering three questions: firstly, the composition of the packaging material – is it optimised to minimise the quantity of potential migrating components that are available to migrate into food? Secondly, what is the probability that any available migrating components might migrate into the food – this will depend on the composition of the food, which determines the affinity of migrants for the food matrix. The majority of migrating constituents likely to result in taints are hydrophobic and so are more likely to present problems in high fat foods. Thirdly, what impact is the migrating compound likely to have on the product? This is influenced by how strongly flavoured the product is. For example, similar levels of migration into a white chocolate product and a meat pie may make the chocolate unpalatable, but may not be detectable in the pie. Thus, the levels of migration that can be tolerated (within legislative limits) are dependent on the flavour characteristics of the food.

### 3.6.5 Methods for monitoring migration

There are two commonly used approaches to monitoring the occurrence and impact of migration from packaging into food. The first, and most standardised approach, is sensory assessment, in which a panel assesses a product to determine whether contact with the packaging has affected sensory properties. The advantage of this approach is the relative ease with which a panel can be assembled and trained. Data obtained from a properly designed assessment is of great relevance to a packaging or food manufacturer because the panel are using the same means of analysis that a consumer will use upon opening a product, namely the olfactory senses. Therefore, the panel should detect any problems that would be apparent to a consumer.

The disadvantage of a sensory approach is the inability to diagnose identified problems. Where problems have been identified, either through a quality assurance sensory panel or a consumer complaint, or are anticipated; for example, when developing a new packaging material or when starting to use a new supplier for a constituent of the packaging, it is appropriate to use instrumental chemical analysis. Chromatographic methods can be used to identify differences between a suspect packaging sample and a reference sample. This can provide detailed information on problems, such as residual solvents or monomers, high levels of plasticisers and the presence of impurities.
A typical sensory method, based on British Standard BS3755:1964 (BSI, 1971) ‘The Assessment of Odour from Packaging Material used for Foodstuffs’, can be applied either to food simulants or specific food products. If performing a potential taint test on a packaging to be used on a range of foods, it is typical to use fairly bland foods, such as cream or butter (high fat), icing sugar or plain biscuits (high carbohydrate and dry), cooked chicken breasts (high protein) and melon pieces (high water).

The samples of food are stored in two glass tanks, one containing the material under test, the other the food alone. Usually, the food is not placed in direct contact with the material under investigation. This is to restrict the types of constituents that can migrate into the food, and is for the safety of the sensory panel. The volatile nature of odour compounds allows odours to transfer indirectly through the air inside the chamber to the food. In one of the tanks, a known area of the packaging material is placed so that it surrounds the bowl into which the food is placed. The tank is sealed with lid and held at ambient temperature for a set time, usually 24 hours. The other tank is set up and stored in exactly the same way omitting the packaging material.

The most suitable method to test for differences between control and test food samples is usually a triangle test, based on British Standard BS5929: 3:1984 (BSI, 1984) ‘Sensory Evaluation on Sensory Analysis of Food, Part 3, Triangular Test’. Aliquots of food samples from the tanks are placed into identical containers for presentation to assessors, who are given three samples, two of which are identical. The assessor is then requested to identify which of the samples is different to the other two, and should give a response even if he/she believes there is no perceivable difference. It is important that sufficient assessors are used to allow distinction between significantly perceived differences and random responses. Care should also be taken to avoid distractions such as external odours or noise, and to ensure that the presentation and appearance of all samples is equivalent, using controlled lighting if necessary.

Instrumental chemical analysis can be used both to identify the cause of observed tainting problems and to routinely screen for targeted analytes known to be potential migrants. Following the report of a packaging related taint, a typical chemical investigation would begin with headspace analysis of the suspect packaging material and food contained within, using a gas chromatogram/mass spectrometer (GC/MS), and similar, untainted reference samples for comparison. A comparison of the GC/MS chromatograms of the two packaging samples can often reveal clear differences that may explain the cause of the taint, such as a large peak for benzophenone, a photoinitiator, indicating that a UV curable ink may have been insufficiently cured. Reliable sensory data can be helpful in identifying analytes to be targeted in the analysis. Once differences have been identified between the two packaging samples, the chromatograms of the food samples can be compared with respect to those analytes to confirm whether the suggested compound could have been responsible for the taint.

In cases where this approach is unsuccessful or reference samples are not available, the technique of GC sniffing can be invaluable. For this technique, the GC outlet is split so that some of the flow is directed to a detector (e.g. an MS) and the remainder passes through a sniffer port where the odour is assessed. It is common for tainting compounds to have very low sensory thresholds, meaning that a very low concentration may generate an easily detected odour but only give a very small chromatographic peak. Using GC-sniffing, the chromatographic retention time of the tainting compound can be determined by the response of the sensory assessor, and the identity of that compound confirmed, using mass spectrometry.

If specific problems have caused a taint, it may be considered necessary to regularly screen samples of packaging material for indicators that the problem may be returning. This is possible by establishing a routine chromatographic method or electronic nose sensors may be used in-line to continually monitor for potential problems (Squibb, 2001).
3.7 CONCLUSION

The objective of this chapter has been to illustrate by way of examples, factors that affect the quality and safety of packaged food products. The desire to extend product shelf life will continue to stimulate the development of new processing and packaging innovations. Selection of the most appropriate product packaging requires a knowledge and understanding of the food chemistry and microbiology of the product, the environmental conditions that it will encounter from production to consumption and how this affects interactions between the packaging and the food.

REFERENCES


James, S.J. (1985) *Display Conditions from the Products Point of View*. Institute of Food Research, Bristol Laboratory, Teach-in on retail display cabinets.


