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Oxygen, ethylene and other scavengers

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3.1 Introduction

The best known and most widely used active packaging technologies for foods today are those engineered to remove undesirable substances from the headspace of a package through absorption, adsorption or scavenging. To achieve this goal a physical or chemical absorbent or adsorbent is incorporated in the packaging material or added to the package by means of a sachet. In most publications, the term 'absorption' is used loosely to describe any system that removes a substance from the headspace. However, there is a clear difference between absorption and adsorption. Adsorption is a two-dimensional phenomenon while absorption is three-dimensional. According to Mortimer (1993), absorption involves a substance being taken into the bulk of a phase while adsorption involves a substance being taken onto a surface. Both, absorption and adsorption are physical phenomena while scavenging implies a chemical reaction (Brody *et al.*, 2001). This chapter focuses mainly on oxygen and ethylene scavenging and finally also discusses carbon dioxide absorbers and odour removers.

3.2 Oxygen scavenging technology

3.2.1 Introduction

In many cases, food deterioration is caused by the presence of oxygen, as oxygen is responsible for oxidation of food constituents and proliferation of moulds, aerobic bacteria and insects. Modified atmosphere packaging (MAP) and vacuum packaging have been widely adopted to exclude oxygen from the headspace. However, these physical methods of oxygen elimination do not always remove the oxygen completely. Some oxygen (0.1–2%) generally remains in the package and even more when the food is porous. Moreover, the oxygen that permeates through the packaging film during storage cannot be removed by these techniques. In the presence of such amounts of oxygen, many of the oxidation reactions and mould proliferation still proceed. Oxygen scavengers are able to reduce the oxygen concentration to less than 0.01% and can maintain those levels (Rooney, 1995; Hurme and Ahvenainen, 1998; Vermeiren *et al*., 1999). An oxygen scavenger is a substance that scavenges oxygen chemically or enzymatically and therefore, protects the packaged food completely against deterioration and quality changes due to oxygen.

3.2.2 Role of oxygen scavengers

Preventing oxidation

Oxygen scavengers effectively prevent oxidative damage in a wide range of food constituents such as (i) oils and fats to prevent rancidity, (ii) both plant and muscle pigments and flavours to prevent discolouration (e.g. meat) and loss of taste and (iii) nutritive elements, e.g., vitamins to prevent loss of the nutritional value. Berenzon and Saguy (1998) investigated the effect of oxygen scavengers on the shelf-life extension of crackers packaged in hermetically sealed tin cans which were stored at 15, 25 and 35ºC for up to 52 weeks. Oxygen scavengers reduced the hexanol concentration significantly. Peroxide values were markedly reduced by the presence of oxygen scavengers. In the presence of oxygen scavengers, the lag period before the peroxides started to build up was prolonged to, respectively, 17 and 10 weeks at 25 and 35ºC. Sensory evaluations showed that in the presence of oxygen scavengers and independently of storage temperature, no oxidative rancid odours were observed for up to 44 weeks.

Preventing insect damage

Oxygen scavengers are effective for killing insects and worms or their eggs growing in cereals such as rice, wheat and soybeans. Fumigation treatments using gases such as bromides and methyl disulfide kill insects but their residues can remain in the food. Additionally, insects in the egg or pupal stages can be resistant against fumigation treatments. Oxygen scavengers are very effective against insects because they remove the oxygen the insects need to survive.

Prevention of proliferation of moulds and strictly aerobic bacteria

Oxygen scavenging is effective in preventing growth of moulds and aerobic bacteria. Mould spoilage is an important microbial problem limiting the shelf-life of high and intermediate moisture products. Losses due to mould spoilage are a serious economic concern in the bakery industry. Some moulds, such as *Aspergillus flavus* and *Aspergillus parasiticus*, can also produce highly toxic substances called mycotoxins. In gas packaging aerobic growth can still occur depending on the residual oxygen level in the package headspace. It has been demonstrated that moulds can proliferate in headspaces with oxygen concentrations as low as 1–2% (Smith, 1996). Oxygen levels of 0.1% or lower are required to prevent the growth and mycotoxin production of many moulds (Rooney, 1995). The effects of modified atmosphere packaging involving oxygen scavengers, storage temperature and packaging film barrier characteristics on the growth of and aflatoxin production by *Aspergillus parasiticus* in packaged peanuts was investigated (Ellis *et al.*, 1994). A slight mould growth was visible in air-packaged peanuts using a high gas barrier film (Oxygen Transmission Rate (OTR) of 3–6 cc. m^{-2}. day^{-1} at 23ºC and dry conditions) while extensive growth was observed in peanuts packaged under similar air conditions using a low gas barrier film (OTR of 4000 cc m^{-2} day^{-1}). When an oxygen scavenger (Ageless® type S) was incorporated, mould growth was inhibited in peanuts packaged in a high gas barrier film and was reduced when a low barrier film was used. Aflatoxin B_1 production was inhibited in peanuts packaged in a high barrier film with an oxygen scavenger, while a limited amount of aflatoxin less than the regulatory level of 20 ng. g^{-1} was detected in absorbent packaged peanuts using a low barrier film. This study showed that oxygen scavengers are effective for controlling the growth of and aflatoxin production by *Aspergillus parasiticus*. However, the effectiveness of the scavengers will be dependent on the gas barrier properties of the packaging film.

Smith *et al.* (1986) showed that oxygen scavengers are three times more effective than gas packaging for increasing the mould-free shelf-life of crusty rolls. In gas packaged (40% N_2/60% CO_2) crusty rolls with Ageless® the headspace oxygen never increased beyond 0.05% and the product remained mould-free for over 60 days at ambient storage temperature. A similar mould-free shelf-life was obtained in air and N_2 packaged crusty rolls with Ageless®. The mould-free shelf-life of white bread packaged in a polypropylene film could be extended from 4–5 days at room temperature to 45 days by using an Ageless® sachet. Pizza crust, which moulds in 2–3 days at 30ºC was mould-free for over 10 days using an appropriate O_2 scavenger (Nakamura and Hoshino, 1983).

It is well known that an oxygen-free atmosphere at a water activity greater than 0.92 can favour the growth of many microbial pathogens including *Clostridium botulinum* (Labuza and Breene, 1989). *Clostridium botulinum* mainly grows under anaerobic conditions but can also have a limited growth under low O_2 conditions. The use of oxygen scavengers could be dangerous if the temperature is not kept close to 0ºC. Daifas *et al.* (1999) investigated the growth and toxin production by *Clostridium botulinum* in English-style crumpets, using an Ageless® FX_{200} oxygen scavenger at room temperature. All inoculated crumpets were toxic within 4 to 6 days and were organoleptically acceptable at the time of toxigenesis. Counts of *C. botulinum* increased to approximately 10^5 CFU/g at the time of toxin production. This study confirms that *C. botulinum* could pose a public health hazard in high a_w – high pH crumpets using an oxygen scavenger when stored at non-chilled conditions. Lyver *et al.* (1998) have done challenge studies on raw surimi nuggets, which were inoculated with 10^4 spores/g of *Clostridium botulinum* type E spores. All

Table 3.1 Effects of oxygen scavengers on foods (Abe, 1994; Smith *et al*., 1990)

Effect	Typical application
Fresh taste and aroma	Various food items, coffee, tea
↔ Mould growth	Bakery products, cheese, processed seafood, pasta
↔ Rancidity	Nuts, fried foods, processed meat, whole milk powder product
↔ Discolouration	Processed meat, green noodle, herbs, tea, dried vegetables
↔ Insect damage	Beans, grain, herbs, spices
Maintaining nutritional value	All kinds of foods

products were packaged in air and air with an Ageless® SS oxygen absorber and stored at 4, 12 and 25ºC. Toxin was not detected in any raw product throughout storage (28 days). The absence of toxigenesis was attributed to the low pH (4.1–4.3) due mainly to the growth of lactic acid bacteria. Whiting and Naftulin (1992) showed that controlling the pH and NaCl concentration of the food product is an important factor in controlling growth of *C. botulinum* under low oxygen concentrations. When oxygen absorbers are used, challenge studies should be done to investigate if *C. botulinum* is able to grow. An overview of the effects of oxygen scavengers and their most important food applications is shown in Table 3.1.

3.3 Selecting the right type of oxygen scavenger

Oxygen scavengers must satisfy several requirements: they must

1. be harmless to the human body. Though the oxygen scavengers themselves are neither food nor food additives, they are placed together with food in a package, and there is therefore the possibility of accidental intake by consumers.
2. absorb oxygen at an appropriate rate. If the reaction is too fast, there will be a loss of oxygen absorption capacity during introduction into the package. If it is too slow, the food will not be adequately protected from oxygen damage.
3. not produce toxic substances or unfavourable gas or odour.
4. be compact in size and are expected to show a constant quality and performance.
5. absorb a large amount of oxygen.
6. be economically priced (Nakamura and Hoshino, 1983; Abe, 1994; Rooney, 1995).

An appropriate oxygen scavenger is chosen depending on the O_2-level in the headspace, how much oxygen is trapped in the food initially and the amount of oxygen that will be transported from the surrounding air into the package during storage. The nature of the food (e.g. size, shape, weight), water activity and desired shelf-life are also important factors influencing the choice of oxygen absorbents. For an oxygen scavenger (sachet) to be effective, some conditions have to be fulfilled (Nakamura and Hoshino, 1983; Abe, 1994; Smith, 1996). First of all, packaging containers or films with a high oxygen barrier must be used, otherwise the scavenger will rapidly become saturated and lose its ability to trap O_2. Films with an oxygen permeability not exceeding 20 ml/m^2.d.atm are recommended for packages in which an oxygen scavenger will be used. Examples of barrier layers used with oxygen scavengers are EVOH (ethylene vinyl alcohol) and PVDC (polyvinylidene chloride) (Nakamura and Hoshino, 1983; Rooney, 1995). If films with high O_2 permeabilities are used (> 100 ml/m^2.d.atm), the O_2 concentration will reach zero within a week but after some days, it will return to ambient air level because the absorbent is saturated. If high-barrier films (e.g. < 10 ml/m^2.d.atm) are used, the headspace O_2 will be reduced to 100 ppm within 1–2 days and remain at this level for the duration of the storage period provided that package integrity is maintained (Rooney, 1995). Secondly, for flexible packaging heat sealing should be complete so that no air invades the package through the sealed part. A rapid, inexpensive and efficient method of monitoring package integrity and ensuring low residual headspace oxygen throughout the storage period is through the incorporation of a redox indicator, e.g. Ageless® Eye®. Ageless® Eye® is a tablet which indicates the presence of oxygen by a colour change. When placed inside the package, the colour changes from blue to pink when the O_2 concentration approaches zero. If the indicator reverts to its blue colour, this is an indication of poor packaging integrity (Smith *et al.*, 1990; Nakamura and Hoshino, 1983; Rooney, 1995). Finally, an oxygen scavenger of the appropriate type and size must be selected. The appropriate size of the scavenger can be calculated using the following formulae (Roussel, 1999; ATCO® technical information, 2002). The volume of oxygen present at the time of packaging (*A*) can be calculated using the formula:

$$A = (V - P) \times [O_2]/100$$

$V =$ volume of the finished pack determined by submersion in water and expressed in ml;

$P =$ weight of the finished pack in g;

$[O_2] =$ initial O_2 concentration in package ($= 21\%$ if air).

In addition, it is necessary to calculate the volume of oxygen likely to permeate through the packaging during the shelf-life of the product (*B*). This quantity in ml may be calculated as follows:

$$B = S \times P \times D$$

S = surface area of the pack in m^2;

P = permeability of the packaging in ml/m^2/24h/atm;

D = the shelf-life of the product in days.

The volume of oxygen to be absorbed is obtained by adding A and B. Based on these calculations, the size of the scavenger and the number of sachets can be determined.

3.3.1 Oxygen scavenging sachets

In general, O_2 scavenging technologies are based on one of the following concepts: iron powder oxidation, ascorbic acid oxidation, catechol oxidation, photosensitive dye oxidation, enzymatic oxidation (e.g. glucose oxidase and alcohol oxidase), unsaturated fatty acids (e.g. oleic acid or linolenic acid) or immobilised yeast on a solid material (Floros *et al*., 1997). A summary of the most important trademarks of oxygen scavenger systems and their manufacturers is shown in Table 3.2.

The majority of presently available oxygen scavengers are based on the principle of iron oxidation (Nakamura and Hoshino, 1983; Rooney, 1995; Vermeiren *et al*., 1999)

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

$$Fe^{2+} + 2OH^- \rightarrow Fe\ (OH)_2$$

$$Fe\ (OH)_2 + \frac{1}{4}O_2 + \frac{1}{2}H_2O \rightarrow Fe\ (OH)_3$$

The principle behind oxygen absorption is iron rust formation. To prevent the iron powder from imparting colour to the food, the iron is contained in a sachet. The sachet material is highly permeable to oxygen and water vapour. A rule of thumb is that 1 g of iron will react with 300 ml of O_2 (Labuza, 1987; Nielsen, 1997; Vermeiren *et al*., 1999). The LD_{50} (lethal dose that kills 50% of the population) for iron is 16 g/kg body weight. The largest commercially available sachet contains 7 grams of iron so this would amount to only 0.1 g/kg for a person of 70 kg, or 160 times less than the lethal dose (Labuza and Breene, 1989). Iron-based oxygen scavengers have one disadvantage: they cannot pass the metal detectors usually installed on the packaging line. This problem can be avoided, e.g. by ascorbic acid or enzyme based O_2 scavengers (Hurme and Ahvenainen, 1998).

Some important iron-based O_2 absorbent sachets are Ageless® (Mitsubishi Gas Chemical Co., Japan), ATCO® O_2 scavenger (Standa Industrie, France), Freshilizer® Series (Toppan Printing Co., Japan), Vitalon (Toagosei Chem.

Table 3.2 Some manufacturers and trade names of oxygen scavengers (Ahvenainen and Hurme, 1997; Day, 1998; Vermeiren *et al*., 1999)

Company	Trade name	Type	Principle/Active substances
Mitsubishi Gas Chemical Co., Ltd. (Japan)	Ageless	Sachets and labels	Iron based
Toppan Printing Co., Ltd. (Japan)	Freshilizer	Sachets	Iron based
Toagosei Chem. Ind. Co. (Japan)	Vitalon	Sachets	Iron based
Nippon Soda Co., Ltd. (Japan)	Seaqul	Sachets	Iron based
Finetec Co., Ltd. (Japan)	Sanso-cut	Sachets	Iron based
Toyo Pulp Co. (Japan)	Tamotsu	Sachets	Catechol
Toyo Seikan Kaisha Ltd. (Japan)	Oxyguard	Plastic trays	Iron based
Dessicare Ltd. (US)	O-Buster	Sachets	Iron based
Multisorb technologies Inc. (US)	FreshMax	Labels	Iron based
	FreshPax	Sachets	Iron based
Amoco Chemicals (US)	Amosorb	Plastic film	unknown
Ciba Specialty chemicals (Switzerland)	Shelfplus O_2	Plastic film	Iron based
W.R. Grace and Co. (US)	PureSeal	Bottle crowns	Ascorbate/metallic salts
	Darex	Bottle crowns, bottles	Ascorbate/sulphite
CSIRO/Southcorp Packaging (Australia)	$Zero_2$	Plastic film	Photosensitive dye/ organic compound
Cryovac Sealed Air Co. (US)	OS1000	Plastic film	Light activated scavenger
CMB Technologies (UK)	Oxbar	Plastic bottles	Cobalt catalyst/ nylon polymer
Standa Industrie (France)	ATCO	Sachets	Iron based
	Oxycap	Bottle crowns	Iron based
	ATCO	Labels	Iron based
Bioka Ltd. (Finland)	Bioka	Sachets	Enzyme based

Table 3.3 Types and properties of Ageless oxygen scavenging sachets (Rooney, 1995; Ageless technical information, 2002)

Type	Function	Moisture status	Water activity	Absorption speed[a] (day)
ZP/ZPT	Decreases $[O_2]$	Self-reacting	< 0.95	1–3
SA	Decreases $[O_2]$	Self-reacting	0.65–0.95	0.5–1.0
SS	Decreases $[O_2]$	Self-reacting	0.65–0.95	2–3 (0–4ºC) 10 (−25ºC)
FX	Decreases $[O_2]$	Moisture dependent	> 0.85	0.5–1.0
FM	Decreases $[O_2]$	Moisture dependent also microwaveable products	> 0.80	1.0
E	Decreases $[O_2]$ Decreases $[CO_2]$	Self-reacting	< 0.3	3–8
G	Decreases $[O_2]$ increases $[CO_2]$	Self-reacting	0.3–0.5	1–4
GL	Decreases [O2]	Self-reacting	0.3–0.95	2–4

[a] number of days to reduce the oxygen level to less than 0.01% (measured at room temperature)

Industry Co., Japan), Sanso-cut (Finetec Co., Japan), Seaqul (Nippon Soda Co., Japan), FreshPax® (Multisorb technologies Inc., USA) and O-Buster® (Dessicare Ltd., USA). Some of them will be discussed in detail.

Ageless® can reduce the oxygen in an airtight container down to 0.01% (100 ppm) or less to prolong shelf-life of food products. Several types of Ageless® are commercially available and applicable to many types of foods (Labuza and Breene, 1989; Smith *et al.*, 1990; Abe, 1994; Ageless® technical information, 1994; Rooney, 1995; Smith, 1996). The different types and properties of Ageless® oxygen scavenging sachets are shown in Table 3.3.

A self-reacting type contains moisture in the sachet and as soon as the sachet is exposed to air, the reaction starts. In moisture-dependent types, oxygen scavenging takes place only after moisture has been taken up from the food. These sachets are stable in open air before use because they do not react immediately upon exposure to air therefore they are easy to handle if kept dry.

Toppan Printing Co. developed another type of oxygen scavenging sachet, named Freshilizer®. Two series are commercially available, the F series and C series. Sachets of the F series contain ferrous metal and scavenge oxygen without generating another gas. The C series contain non-ferrous particles and are able to sorb oxygen and generate an equal volume of carbon dioxide to prevent package collapse.

FreshPax™ is a patented oxygen scavenger developed by Multisorb technologies. Four main types of FreshPax are commonly available: type B, D, R and M. Type B is used for moist or semi-moist foods with a water activity above 0.7. Type D is recommended for use with dehydrated and dried foods. To scavenge oxygen at refrigerated or frozen storage temperatures, type R should be used. Type M can be used for moist or semi-moist foods, which are packaged under modified atmospheres containing carbon dioxide.

Another scavenging technology is based on catechol oxidation. As catechol is an organic compound, it passes metal detectors. Tamotsu is the only commercial product in Japan based on this technology (Abe, 1994). Tamotsu type D is used for dry products such as spices, freeze-dried foods, tea. These sachets do not require moisture for their oxygen scavenging reaction.

Another way of controlling the oxygen level in a food package is by using enzyme technology. A combination of two enzymes, glucose oxidase and catalase, has been applied for oxygen removal. In the presence of water, glucose oxidase oxidises glucose, that can be originally present or added to the product, to gluconic acid and hydrogen peroxide (Greenfield and Laurence, 1975; Labuza and Breene, 1989; Nielsen, 1997). The reaction is:

$$2 \text{ glucose} + 2\ O_2 + 2\ H_2O \rightarrow 2 \text{ gluconic acid} + 2\ H_2O_2$$

where glucose is the substrate.

Since H_2O_2 is an objectionable end product, catalase is introduced to break down the peroxide (Rooney, 1995; Vermeiren *et al.*, 1999):

$$2\ H_2O_2 + \text{catalase} \rightarrow 2\ H_2O + O_2 + \text{catalase}$$

Enzymatic systems are usually very sensitive to changes in pH, water activity, temperature and availability of solvents. Most systems require water for their action, and therefore, they cannot be effectively used with low-water content foods (Floros *et al.*, 1997). The enzyme can either be part of the packaging structure or put in an independent sachet. Both polypropylene (PP) and polyethylene (PE) are good substrates for immobilising enzymes (Labuza and Breene, 1989). A commercially available enzyme-based oxygen absorbent sachet is Bioka (Bioka Ltd., Finland). It is claimed that all components of the reactive powder and the generated reaction products are food-grade substances safe for both the user and the environment (Bioka technical information, 1999). The oxygen scavenger eliminates the oxygen in the headspace of a package and in the actual product in 12–48 hours at 20ºC and in 24–96 hours at 2–6ºC. With certain restrictions, the scavenger can also be used in various frozen products. When introducing the sachet into a package, temperature may not exceed 60ºC because of the heat sensitivity of the enzymes (Bioka technical information, 1999). An advantage is that it contains no iron powder, so it presents no problems for microwave applications and for metal detectors in the production line.

Besides glucose oxidase, other enzymes are able to scavenge oxygen. One such enzyme is alcohol oxidase, which oxidises ethanol to acetaldehyde. It could be used for food products in a wide a_w range since it does not require water to operate. If a lot of oxygen has to be absorbed from the package, a great amount of ethanol would be required, which could cause an off-odour in the package. In addition, considerable aldehyde would be produced which could give the food a yoghurt-like odour (Labuza and Breene, 1989).

The Pillsbury Company holds a 1994 patent that utilises ascorbic acid as reducing agent (Graf, 1994). The product, also referred to as Oxysorb, comprises a combination of a reducing agent, ascorbic acid, and a small amount of a transition metal, such as copper. The oxygen removing system may be added in a small oxygen permeable pouch.

The oxidation of polyunsaturated fatty acids (PUFAs) is another technique to scavenge oxygen. It is an excellent oxygen scavenger for dry foods. Most known oxygen scavengers have a serious disadvantage: when water is absent, their oxygen scavenging reaction does not progress. In the presence of an oxygen scavenging system, the quality of the dry food products may decline rapidly because of the migration of water from the oxygen scavenger into the food. Mitsubishi Gas Chemical Co. holds a patent that uses PUFAs as a reactive agent. The PUFAs, preferably oleic, linoleic or linolenic, are contained in carrier oil such as soybean, sesame or cottonseed oil. The oil and/or PUFA are compounded with a transition metal catalyst and a carrier substance (for example calcium carbonate) to solidify the oxygen scavenger composition. In this way the scavenger can be made into a granule or powder and can be packaged in sachets (Floros *et al.*, 1997).

3.3.2 Oxygen scavenging films

It should be noted that the introduction of oxygen scavenger sachets into the food package suffers from the disadvantage of possible accidental ingestion of the contents by the consumer. Another concern is that the sachet could leak out and contaminate the product. When sachets are used, there also needs to be a free flow of air surrounding the sachet in order to scavenge headspace oxygen (Rooney, 1995). To eliminate this problem, oxygen removing agents can be incorporated into the packaging material such as polymer films, labels, crown corks, liners in closures. These oxygen scavenging materials have the additional advantage that they can be used for all products, including liquid products. The oxygen consuming substrate can be either the polymer itself or some easily oxidisable compound dispersed or dissolved in the packaging material (Nielsen, 1997; Hurme and Ahvenainen, 1998).

A problem related to the use of O_2 scavenging films is that the films should not react with atmospheric oxygen prior to use. This problem has been solved by inclusion of an activation system triggering the O_2 consuming capabilities of the film in the packaging system. Activation by illumination or catalysts or reagents, supplied at the time of filling, may be required to start the reaction.

Illumination of a package that contains a photosensitising dye and a singlet oxygen acceptor results in rapid scavenging of oxygen from the headspace. Australian researchers have reported that reaction of iron with ground state O_2 is too slow for shelf-life extension (Hurme and Ahvenainen, 1998). The singlet-excited state of oxygen, which is obtained by dye sensitisation of ground state oxygen using near infra-red, visible or ultraviolet radiation, is highly reactive and so its chemical reaction with scavengers is rapid (Rooney, 1981). The technique involves sealing of a small coil of ethyl cellulose film, containing a dissolved photosensitising dye and a singlet oxygen acceptor, in the headspace of a transparent package. When the film is illuminated with light of the appropriate wavelength, excited dye molecules sensitise oxygen molecules, which have diffused into the polymer, to the singlet state. These singlet oxygen molecules react with acceptor molecules and are thereby consumed. The photochemical reaction can be presented as follows (Rooney, 1981; Vermeiren *et al.*, 1999):

$$\text{photon} + \text{dye} \rightarrow \text{dye}^*$$
$$\text{dye}^* + O_2 \rightarrow \text{dye} + {O_2}^*$$
$${O_2}^* + \text{acceptor} \rightarrow \text{acceptor oxide}$$
$${O_2}^* \rightarrow O_2$$

This scavenging technique does not require water as an activator, so it is effective for wet and dry products. Its scavenging action is initiated on the processor's packaging line by an illumination-triggering process. Examples of light-activated oxygen scavenger films are OS1000, developed by Cryovac Sealed air corporation and $\text{Zero}_2{}^{\text{TM}}$ developed by CSIRO and marketed by Southcorp Packaging (Australia). Cryovac OS1000 is a multi-layer flexible film with a coextruded sealant. The invisible, oxygen scavenging polymer is a component of the sealant. UV lights are used to trigger the scavenging reaction through a patented activation process. These films are activated on the packaging line just before filling and sealing, so light never comes in contact with the food. The active ingredient in the Southcorp technology, named Zero_2, is integrated into the polymer backbones of such common packaging materials as PET, polyethylene, polypropylene and EVA. The active ingredient is non-metallic and is activated by UV light once it is incorporated into packaging material (Graff, 1998).

Amoco Chemicals has developed Amosorb® oxygen scavenger, a plastic concentrate that sorbs oxygen in food and beverage packages. Amosorb concentrate is a polymer-based oxygen scavenger that can be incorporated as an inner layer within a multi-layer packaging structure during co-extrusion or lamination. The oxygen scavenger is activated by moisture and can reduce headspace oxygen levels to less than 0.01%. It can be incorporated into several packaging structures such as the sidewall or lid of rigid containers, flexible film and closure liners (Edwards, 1998; Amoco Chemicals bulletin AS-1, 1999a; Amoco Chemicals bulletin AS-3, 1999b). In June 2000, the Amosorb 2000 oxygen absorber technology was acquired by Ciba Specialty Chemicals Corporation. The trade name was changed to Ciba Shelfplus O2-2400 (polyethylene application) and Shelfplus O2-2500 (polypropylene application) (Brody *et al.*, 2001).

Oxyguard, from Toyo Seikan Group, is an oxygen scavenger that uses an iron salt-based additive and is available in the form of a flexible or rigid plastic. It is a multi-layer that consists of an outer layer, a barrier layer, an oxygen scavenging layer and an inner layer. The oxygen sorption is initiated by water (Vermeiren *et al.*, 1999; Oxyguard technical information, 2002).

Oxbar™ is a system developed by Carnaud-Metal Box (UK) and is composed of a PET/MXD6/Co film where the PET serves as the structural material and the active ingredients are MXD6 nylon (polymetaxylylene adipamide or polymetaxylylene diamine-hexanoic acid) and cobalt salt. Cobalt catalyses the oxidation of the nylon polymer (Miltz *et al.*, 1995). It can be used for plastic packaging of beer, wine, sauces and other beverages.

3.3.3 Other scavenging devices

Labels

Other layouts for oxygen scavengers are cards and sheets in or labels on the packaging. In 1991, Multisorb technologies introduced the iron-based oxygen scavenging label FreshMax. FreshMax is designed for adhesion within packages and so the risk for ingestion is minimised. The technology has a printed surface and is acceptable for food contact. It is resistant to fat and moisture and can be used for several food products (Anon., 1991; Rooney, 1995; Silgelac technical information, 1998; Caldic technical information, 2002). Standa Industrie has also developed a self-adhesive oxygen scavenging label, named ATCO® and Ageless® also has a label type and a card type.

Bottle closures

Removal of oxygen from a bottle by a closure requires that a component reacts with gaseous oxygen in the headspace of the bottle. Darex oxygen scavenging technology utilises a material that can be incorporated into barrier packaging such as crowns, cans and a broad variety of plastic and metal closures. The basic reaction of their oxygen scavenging technique is ascorbate oxidising to dehydroascorbic acid and sulphite to sulphate. Darex DarExtend is designed to be incorporated as an integral part of traditional barrier packaging such as the aluminium roll-on closures as well as in plastic closures and crowns. Darex DarEval is an EVOH-based oxygen scavenging barrier resin used as an inner layer in multi-layer PET. DarEval enables multi-layer PET bottles to have a glass-like performance (Rooney, 1995; Vermeiren *et al.*, 1999; Darex Technical Information, 2002). The major use is in crown caps to protect beer from oxidation. Other examples of oxygen scavenging crowns caps are Pure Seal caps (W.R. Grace Co., USA) and Oxycap (Standa Industrie, France).

3.3.4 Economic aspects

Oxygen scavengers have several economic advantages for the food processor (Nakamura and Hoshino, 1983; Rooney, 1995; Smith, 1996):

- increased product shelf-life and distribution radius
- a longer time between deliveries enabling larger deliveries

- increased length of time product can stay in the distribution pipeline
- reduced distribution losses
- reduced evacuation/gas flushing times in gas packaged products thereby increasing product throughput
- reduced costs required for gas flushing equipments.

To save time and labour, oxygen scavenging sachets can be inserted automatically (Ageless® technical information, 1994). Also labels can be applied automatically at conventional line speeds. An iron-based sachet with a capacity of 100 ml O_2 would cost 5.03 euro for 3000 pieces. The same sachet with a capacity of 1000 ml O_2 would cost 20.4 euro for 500 pieces. The price of another iron-based sachet of another trademark, which absorbs 100 ml O_2, is about 40 euro for 300 pieces.

3.4 Ethylene scavenging technology

3.4.1 Introduction

Ethylene acts as a plant hormone that has different physiological effects on fresh fruit and vegetables. It accelerates respiration, leading to maturity and senescence, and also softening and ripening of many kinds of fruit. Furthermore, ethylene accumulation can cause yellowing of green vegetables and may be responsible for a number of specific post-harvest disorders in fresh fruits and vegetables. Although some effects of ethylene are positive, such as degreening of citrus fruit, ethylene is often detrimental to the quality and shelf-life of fruits and vegetables. To prolong shelf-life and maintain an acceptable visual and organoleptical quality, accumulation of ethylene in the packaging of fruits and vegetables should be avoided. A number of ethylene sorbing substances are described. Most of these are supplied as sachets or integrated into films. Many of the claims for ethylene adsorbing or absorbing capacity have been poorly documented so the efficacy of these materials is difficult to substantiate (Vermeiren *et al*., 1999; Zagory, 1995).

3.4.2 The role of ethylene scavengers

Ethylene is a naturally occurring, chemically simple molecule of the alkene type that regulates numerous aspects of growth, development and senescence of many fruits and vegetables. As it is effective at part-per-million to part-per-billion concentrations and its effects are very dose-dependent, it is considered as a plant hormone (Saltveit, 1999). Environmental ethylene can be produced both biologically and non-biologically. Non-biological sources of ethylene are incomplete combustion of fossil fuels, burning of agricultural wastes and leakage from industrial polyethylene plants (Sawada and Totsuka, 1986). Ethylene is thus a common air pollutant and ambient atmospheric levels are normally in the range of 0,001–0,005 ppm (Abeles *et al*., 1992). Biological sources of ethylene include higher plant tissues, several species of bacteria and fungi, some algae and mosses (Zagory, 1995).

In higher vascular plants, a relatively simple biosynthetic pathway produces ethylene:

$$\text{Methionine} \rightarrow \underset{\text{(SAM)}}{\text{S-adenosylmethionine}} \xrightarrow[\substack{\uparrow \\ \text{fruit ripening, wounding}}]{\text{ACC synthase}} \underset{\text{carboxylic acid (ACC)}}{\text{1-amino-cyclopropane-}} \xrightarrow[\substack{\uparrow \\ \text{ripening, ethylene}}]{\text{ACC oxidase } (O_2, CO_2)} CH_2{=}CH_2$$

The amino acid methionine (MET) is converted to S-adenosyl methionine (SAM) which is then converted in the next step to 1-amino-cyclopropane carboxylic acid (ACC) by the enzyme ACC synthase. The production of ACC is often the controlling step for ethylene synthesis. A number of intrinsic (e.g. developmental stage) and extrinsic (e.g. wounding) factors influence this pathway. In the final step, ACC is oxidised by the enzyme ACC oxidase to form ethylene. This last step requires the presence of oxygen and low levels of CO_2 to activate ACC oxidase. The ACC oxidase activity can show a dramatic increase in ripening of fruit in response to ethylene exposure (Saltveit, 1999). As in the case of other hormones, ethylene is thought to bind to a receptor, forming an activated complex that in turn triggers a primary reaction. This primary reaction then initiates a chain of reactions leading to a wide variety of physiological responses (Yang, 1985).

Ethylene has since long been recognised as a problem in post-harvest handling of horticultural products (fruits, vegetables and flowers). The diverse physiological effects of ethylene have been extensively reviewed by many authors (Abeles *et al*., 1992; Hopkins, 1995 and Saltveit, 1999). Some of the effects of ethylene are beneficial and economically useful, such as flowering of pineapples, de-greening of citrus fruits and ripening of tomatoes. However, ethylene is often involved in the decline of the quality and shelf-life of many fruits and vegetables. Only those effects that are deleterious to packaged plant produce will be discussed here.

First of all, ethylene accelerates the respiration of fruits and vegetables. Respiration rate generally is well correlated with perishability of produce. Commodities such as asparagus, broccoli, mushrooms, and raspberries with high respiration rates have short shelf-lives. At the end of growth, climacteric fruit (e.g. banana, avocado) undergoes a large increase in respiration accompanied by marked changes in composition and texture. The ripening of climacteric fruit is associated with a large increase in ethylene production. The increases in respiration and ethylene production can be induced prematurely in climacteric fruit by treating them with a suitable concentration of ethylene. The ripening process is irreversible once endogenous ethylene production increases to a certain level (McGlasson, 1985). As climacteric fruit starts to ripen, this negative feedback inhibition of ethylene on ethylene synthesis changes into a positive feedback promotion in which ethylene stimulates its own synthesis (i.e. autocatalytic ethylene production) and copious amounts of ethylene are produced. Reducing the external concentration of ethylene around bulky ripening climacteric fruit (e.g. apples, bananas, melons, tomatoes) has almost no effect on reducing the internal concentration in these fruit. Internal concentrations of ethylene can exceed 100μ l/l, even when the external concentration is zero. Therefore, reducing the external ethylene concentration generally has no effect on the ripening of fruit that has progressed a few days into its climacteric stage. However, at the initial stages of ripening, when the internal levels are still low, inhibiting the synthesis of ethylene and removal of ethylene can significantly retard ripening (Saltveit, 1999). Non-climacteric fruit show no increase in respiration and ethylene production during ripening. In contrast, an unnaturally climacteric-like respiratory increase can be induced in non-climacteric fruit by treating them with ethylene. Yet this increased respiration is not accompanied by an increase in endogenous ethylene production and is still reversible upon removal of the exogenous ethylene (McGlasson, 1985). In most cases, exposure to a few parts per million of ethylene leads to increased respiration and consequently increased perishability (Zagory, 1995).

Ethylene is often referred to as the ripening hormone because it can accelerate softening and ripening of many kinds of fruit by the direct or indirect stimulation of the synthesis and activity of many enzymes such as pectinases, cellulases, esterases and polygalacturonase. Examples are a reduced firmness of watermelons through ethylene exposure and an increased toughness of asparagus spears after exposure to 100 ppm ethylene for 1 hour, which was associated with increased activity of peroxidases and accelerated lignin biosynthesis. In most cases, for packaged fruits it would be desirable to prevent exposure to ethylene and thereby preventing rapid ripening (Zagory, 1995; Kader, 1985). Ethylene accelerates chlorophyll degradation and induces yellowing of green tissues, thus reducing market quality of leafy green vegetables such as spinach, floral vegetables such as broccoli and immature fruits such as cucumbers (Kader, 1985) and promotes changes that are important to flavour such as starch to sugar conversion, loss of acidity and formation of aroma volatiles in climacteric fruit. Furthermore, ethylene can be responsible for a number of specific post-harvest disorders of fruits and vegetables such as russet spotting of lettuce, sprouting of potatoes and formation of bitter-tasting isocoumarins in carrots (Zagory, 1995; Kader, 1985).

One of the major problems in the post-harvest storage of fruits and vegetables is the proliferation of opportunistic microorganisms that thrive on injured or senescent tissues. By stimulating ripening and senescence, ethylene also enhances the opportunities for pathogenesis. Fruits and vegetables have an epidermal layer that provides a protective barrier against infections but plant pathogenic moulds and bacteria possess mechanisms to penetrate into external tissues (Jacxsens, 2000). The growth of a number of post-harvest pathogens e.g. the development and sporulation of the decay-causing fungi *Penicillium* and *Botrytis cinerea* is directly stimulated by ethylene. In addition, several post-harvest plant pathogens produce ethylene and this ethylene may compromise the natural defences of the plant tissues (Barkai-Golan, 1990; Saltveit, 1999).

Plant organs like stems, roots and leafy parts that are consumed as vegetables are less sensitive to ethylene exposure compared to fruits, but some vegetables such as tomato, cucumber and broccoli are from a morphological point of view 'fruits' and responsive to ethylene (Jacxsens, 2000). These vegetables can benefit from the removal of ethylene as ethylene detrimentally affects their colour by yellowing and texture by promoting unwanted softening in cucumbers and peppers or toughening in asparagus and sweet potatoes (Saltveit, 1999).

Strategies for protecting harvested horticultural products from the detrimental effects of ethylene can be placed into three major categories: avoidance, e.g., through temperature control, removal and inhibition. In the category 'removal', adsorption of ethylene will be discussed below.

3.4.3 Principle of ethylene adsorption

The double bond of ethylene makes it a very reactive compound that can be altered or degraded in many ways. This creates a diversity of opportunities for commercial methodologies for the removal of ethylene. Ethylene can be absorbed or adsorbed by a number of substances, reviewed by Zagory (1995), including activated charcoal, molecular sieves of crystalline aluminosilicates, Kieselguhr, bentonite, Fuller's earth, brick dust, silica gel and aluminium oxide. A number of clay materials such as cristobalite, Oya stone and zeolite have been reported to have ethylene sorbing capacity. Some regenerable sorbents have been shown to have ethylene adsorbing capacity and have the benefit of being reusable after purging. Examples are propylene glycol, hexylene glycol, squalene, phenylmethylsilicone, polyethylene and polystyrene. Some sorbents have been combined with catalysts or chemical agents that modify or destroy the ethylene after adsorption. For example, activated charcoal, used to adsorb ethylene, has been impregnated with bromine or with 15% $KBrO_3$ and 0,5 M H_2SO_4 to eliminate the activity of ethylene. A number of catalytic oxidisers have been combined with adsorbents to remove the adsorbed ethylene such as potassium dichromate, potassium permanganate (KMnO4), iodine pentoxide and silver nitrate, each respectively embedded on silica gel. Electron-deficient dienes or trienes such as benzenes, pyridines, diazines, triazines and tetrazines, having electron-withdrawing substitutes such as fluorinated alkyl groups, sulphones and esters, will react rapidly and irreversibly with ethylene. Such compounds can be embedded in permeable plastic bags or printing inks to remove ethylene from packages of plant produce (Holland, 1992). Metal catalysts immobilised on absorbents such as powdered cupric oxide, will effectively oxidise ethylene, but in many cases the reactions require high temperatures (>180ºC). Clearly such systems would be inappropriate for food packaging applications (Zagory, 1995).

Most suppliers offer ethylene adsorbers based on KMnO4. To be effective, KMnO4 must be adsorbed on a suitable inert carrier with a large surface area such as celite, vermiculite, silica gel, alumina pellets, activated carbon, perlite or glass. Typically, such products contain about 4–6% KMnO4. The oxidation of ethylene with potassium permanganate can be thought of as a two-step process. Ethylene (CH_2CH_2) is initially oxidised to acetaldehyde (CH_3CHO), which in turn is oxidised to acetic acid (CH_3COOH). Acetic acid can be further oxidised to carbon dioxide and water:

$$3CH_2CH_2 + 2KMnO_4 + H_2O \rightarrow 2MnO_2 + 3CH_3CHO + 2KOH \tag{1}$$

$$3CH_3CHO + 2KMnO_4 + H_2O \rightarrow 3CH_3COOH + 2MnO_2 + 2KOH \tag{2}$$

$$3CH_3COOH + 8KMnO_4 \rightarrow 6CO_2 + 8MnO_2 + 8KOH + 2H_2O \tag{3}$$

Combining eq. 1–3, we get:

$$3CH_2CH_2 + 12KMnO_4 \rightarrow 12MnO_2 + 12KOH + 6CO_2$$

Potassium permanganate adsorbers change from purple to brown as the MnO_4^- is reduced to MnO_2, indicating the remaining adsorbing capacity. Adsorbent materials containing $KMnO_4$ cannot be integrated into food-contact packaging but are supplied only as sachets because of their toxicity and purple colour (Sherman, 1985; Zagory, 1995). Different studies have shown that these sachets effectively remove ethylene from packages of pears (Scott and Wills, 1974), bananas (Liu, 1970; Jayaraman and Raju, 1992; Chamara *et al.*, 2000), kiwifruit (Ben-arie and Sonego, 1980), diced onions (Howard *et al.*, 1994), apples (Shorter *et al.*, 1992), grapes (Don and Koo, 1996), mango, tomato and other fruits (Jayaraman and Raju, 1992). Examples of suppliers of potassium permanganate based ethylene scavengers are given in Table 3.4. Not only sachets are commercialised but the technique has been transferred to household refrigerators e.g. Mrs. Green's Extra Life cartridges from Dennis Green Ltd. and Fridge Friend box. A special case is the paper Frisspack (Dunapack, Hungary), for manufacture into corrugated fibreboard cases. This paper contains a chemosorbent to bond with ethylene, which is then oxidised by $KMnO_4$ (Brody *et al.*, 2001).

Another type of ethylene scavenger is based on the adsorption of ethylene on activated carbon and subsequent breakdown by a metal catalyst. Use of charcoal with palladium chloride prevented the accumulation of ethylene and was effective in reducing the rate of softening in kiwifruits and bananas and chlorophyll loss in spinach leaves, but not in broccoli (Abe and Watada, 1991). Some Japanese concepts such as Neupalon, Hatofresh System and Sendomate (Table 3.4) are also based on the adsorption of ethylene by activated carbon that is impregnated with different types of substances (palladium catalyst or bromine-type inorganic chemicals) to help the breakdown of ethylene (Zagory, 1995).

Other ethylene absorbing technologies are based on the inclusion of finely dispersed minerals. Typically these minerals are zeolites or local kinds of clays that are embedded in polyethylene (PE) bags that are then used to package fresh produce (Zagory, 1995). The fine pores of these minerals serve to absorb gases such as ethylene. Most of these films are opaque and not

Table 3.4 Some commercialised ethylene scavengers

Company	Trade name	Type	Principle/active substances
Purafil (Georgia, US)	Purafil	Pellets to be used in e.g. sachets	Potassium permanganate-impregnated alumina pellet
DeltaTRAK (US)	Air Repair	Sachets for shipments	Potassium permanganate
Ethylene Control (US)	Fridge Friend	Sachets, box for consumer's refrigerator	Potassium permanganate
International Ripening Company (US)	No specific name	Sachets for shipping boxes	Potassium permanganate
Dennis Green Ltd. (US)	Mrs. Green's Extra Life	Cartridges for consumer's refrigerator	Potassium permanganate
Grofit plastics (Israel)	Biofresh	Zipper bags, bags and films	-
Nippon Container Corporation (Japan)	FAIN	Films for inner surface of cardboard	-
Sekisui Jushi (Japan)	Neupalon	Sachet	Activated carbon
Mitsubishi Chemical Co. (Japan)	Sendomate	Sachet	Activated carbon + Pd-catalyst
Honshu Paper (Japan)	Hatofresh System	Paper bag or corrugated box	Activated carbon + bromine type inorganic chemical
E-I-A Warenhandels GmbH (Austria)	Profresh	Film	Minerals
Evert-fresh Co. (US)	Evert-Fresh Green-Bags	Bags for consumer use	Minerals
Peakfresh products (Australia)	Peakfresh	Film	Minerals
Odja Shoji C. (Japan)	BO film	Film	Crysburite ceramics
Cho Yang Heung San Co. (Korea)	Orega bag	Bags for consumer use	Minerals
OhE Chemicals (Japan)	Crisper SL	Film	-
Marathon products (US)	Ethylene Filter products	Sachet	-
Dessicare (US)	Ethylene EliminatorPak	Sachet	Zeolites
Pacific Agriscience (Singapore)	BI-ON	-	-

capable of sufficiently absorbing ethylene (Suslow, 1997). Although the incorporated minerals may absorb ethylene, they also alter the permeability of the films, both ethylene and CO_2 diffuse more rapidly and oxygen will enter more rapidly than through pure PE. These changes in permeability can reduce headspace ethylene concentrations and consequently improve shelf-life independently of any ethylene absorption. In fact, any powdered material can be used to reach these effects. However, even if the minerals do absorb ethylene, this capacity is often lost when incorporating these minerals into a polymer matrix (Zagory, 1995). Japanese or Korean companies marketed many of these bags for their internal markets and some of them are now also sold in the USA and Australia but fewer in Europe. The Orega bag based on the US patent of Dr Matsui (Matsui, 1989) contains fine porous material consisting of pumice-tuff, zeolite, active carbon, cristobalite and clinoptilolite mixed with a metal oxide. A similar concept is a sheet, described in the US patent assigned to Nissho and Co. (Japan) (Someyo and Nobuo, 1992), consisting of a synthetic resin film or a fibrous material and containing crushed coral, a stony substance formed from the massed skeletons of marine organisms that has calcium carbonate as the main ingredient. Others are Evert-Fresh Green-Bags, Peakresh™, BO film and Profresh®. An overview of some commercially available ethylene scavengers is given in Table 3.4.

3.4.4 Measuring ethylene sorption

There are many bags and films being sold offering improved post-harvest life of fresh produce due to the sorption of ethylene by minerals finely dispersed into polyethylene bags. The evidence offered in support of this claim is generally based on shelf-life experiments comparing common polyethylene bags with the so-called ethylene sorbing films. Such studies generally show an extension of the shelf-life and/or reduction of the headspace ethylene. However, such data do not support claims of ethylene sorbing capacity as the improved shelf-life and reduced ethylene level could also result from the increased gas permeabilities of these types of films. To evaluate the ethylene sorbing capacity of any ethylene sorbing substance, a direct measurement of ethylene depletion in closed systems containing samples of the bags without any produce is necessary. Furthermore, such studies should be done at low temperature and high relative humidity to mimic the conditions of performance (Zagory, 1995).

A possible method to determine the ethylene sorbing capacity uses closed recipients which include the film in their screw top. These recipients are flushed with ethylene and stored at a low temperature. At regular times the ethylene concentration in the recipients is measured by using a gas chromatograph. As the permeability is influenced by the relative humidity, water is brought in each recipient to reach a high relative humidity.

3.4.5 Economic aspects

It is extremely difficult to assess the economic importance of protecting harvested horticultural products from ethylene. Detrimental effects of ethylene during the normal short-term marketing of fruit and vegetables are not well defined and certainly are secondary to considerations regarding the maintenance of optimum temperature and humidity. However, costs to the individual shippers involved can easily run into tens of thousands of dollars when losses do occur from problems like russet sprouting of lettuce. Losses caused by ethylene are known to occur, but they are usually quantitatively undefined. A conservative estimate for the US would be in the tens of millions of dollars annually (Sherman, 1985). The ethylene sorbing packaging concepts could possibly contribute to an increase in the export of fresh produce.

In the US, ethylene control within packages of fresh and minimally processed fruit and vegetable products remains almost exclusively a reaction of $KMnO_4$ on a porous mineral structure (Brody *et al*., 2001). The major disadvantage of permanganate scavengers seems to be their expense e.g. 0.33 euro for a 27g sachet, 0.39 euro for a 28g sachet, 0.26 euro for an 8g sachet, 6.25 euro for a Mrs. Green's Extra Life cartridge and 2.2 euro for a Fridge friend box. Prices of mineral-containing bags for consumer use range, e.g., from 1.96 euro to 4.26 euro depending of the size of the sachets. Despite the many Asian claims for the effectiveness of activated carbon and minerals, little proof has been offered to convince packagers to use them. For this reason, there are no strong commercial applications of ethylene-removing films in the US. On the other hand, sachets based on $KMnO_4$ are in widespread commercial use.

3.5 Carbon dioxide and other scavengers

3.5.1 Carbon dioxide scavengers

Role

Carbon dioxide is formed in some foods due to deterioration and respiration reactions. The produced CO_2 has to be removed from the package to avoid food deterioration and/or package destruction. Fresh roasted coffee can release considerable amounts of CO_2 due to the Strecker degradation reaction between sugars and amines (Labuza and Breene, 1989). Unless removed, the generated CO_2 can cause the packaging to burst due to the increasing internal pressure. Another CO_2-producing food product is kimchi, a general term for fermented vegetables such as oriental cabbage, radish, green onion and leaf mustard mixed with salt and spices. Because kimchi cannot be pasteurised for its sensory quality, the fermentation process still continues with the concomitant production of CO_2. The accumulation of CO_2 in the packages causes ballooning or even bursting. Scavengers might therefore be useful.

Principle

The reactant commonly used to scavenge CO_2 is calcium hydroxide, which, at a high enough water activity, reacts with CO_2 to form calcium carbonate:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

A disadvantage of this CO_2 scavenging substance is that it scavenges carbon dioxide from the package headspace irreversibly and results in depletion of CO_2, which is not always desired. In the case of packaged kimchi, depletion of CO_2 in the kimchi juices causes loss of the product's characteristic fresh carbonic taste. Therefore reversible absorption or adsorption by physical sorbents such as zeolites and active carbon may be an alternative (Lee *et al*., 2001).

Commercially available technologies

Carbon dioxide scavengers are often commercialised as a sachet with a dual function, both O_2 and CO_2 scavenging. The O_2 and CO_2 scavenging sachet FreshLock or Ageless® E (Mitsubishi Gas Chemical Company, Japan), containing $Ca(OH)_2$ (Natawa *et al*., 1982) is used for storing coffee. A similar sachet is Frehilizer type CV of Toppan printing Co. (Japan) (Smith *et al*., 1995). Multiform Desiccants patented (US 5322701) a CO_2-absorbent sachet including a porous envelope containing CaO and a hydrating agent such as silica gel on which water is adsorbed. The water given off by the supersaturated silica gel combines with the calcium oxide to form calcium hydroxide (Cullen and Vaylen, 1994). Furthermore, a whole range of freshness-retaining mineral-based ethylene scavengers, mentioned in Table 3.4 also claim to scavenge carbon dioxide.

3.5.2 Odour scavengers

Role

As far as food aromas are concerned, plastics are usually considered to have a negative impact on food quality. Flavour scalping, i.e., sorption of food flavours by polymeric packaging materials, may result in loss of flavour and taste intensities and changes in the organoleptic profile of foods. However, flavour sorption could be used in a positive way to selectively absorb unwanted odours or flavours. Odour removers have the potential to scavenge the malodorous constituents of both oxidative and nonoxidative biochemical deterioration. Many foods such as fresh poultry and cereal products develop during product distribution very slight but nevertheless detectable deterioration odours such as sulphurous compounds and amines from protein/amino acid breakdown or aldehydes and ketons from lipid oxidation or anaerobic glycolysis. These odours are trapped within gas-barrier packaging so that, when the package is opened, they are released and detected by consumers. Another reason for incorporating odour removers into packages is to obviate the effect of odours developed in the package materials themselves (Vermeiren *et al*., 1999; Brody *et al*., 2001). Although removal of these undesired odours may be attractive from a commercial point of view, care must be taken as in some cases these odours may be a signal indicating that the products are exceeding the microbial or chemical limits.

Principle and commercial applications

An active packaging to reduce bitterness in grapefruit juices has been described. The causes of the bitter taste are glycosidic flavanone naringin and triterpenoid lactone limonin. Naringin is the bitter component found in most fresh citrus fruits and therefore in freshly processed citrus juices. Limonin is formed as a result of heat treatment of the juice during processing and a chemical reaction in the acidic juice medium. To counteract this, an active thin cellulose acetate (CA) layer for application on the inside of the packaging has been developed. This layer contains the fungal-derived enzyme naringinase, consisting of α-rhamnosidase and β-glucosidase, which hydrolyses naringin to naringenin and prunin, both non-bitter compounds. Food-contact approved CA films, which contained immobilised naringinase showed a 60% naringin hydrolysis in grapefruit juice in 15 days at 7ºC and a reduction in the limonin content due to adsorption on the CA film (Soares and Hotchkiss, 1998a,b, Vermeiren *et al.*, 1999).

Malodorous amines, resulting from protein breakdown in fish muscle, include strongly alkaline compounds (Rooney, 1995). A Japanese patent based on the interactions between acidic compounds, e.g., citric acid, incorporated in polymers and the alkaline off-odours, claims amine-removing capabilities. Hence the earliest work involved incorporation of such acids in heat-seal polymers such as polyethylene and extruding them as layers in packaging (Rooney, 1995; Hoshino and Osanai, 1986). Another approach to remove amine odours has been provided by the Anico Co. (Japan). The Anico bags made from a film containing ferrous salt and an organic acid such as citric or ascorbic acid are claimed to oxidise the amine or other oxidisable odour-causing compounds as they are absorbed by the polymer (Rooney, 1995).

Aldehydes, formed from the breakdown of peroxides produced during the initial stages of auto-oxidation of fats and oils, can make a wide variety of fat-containing foods, such as potato crisps, biscuits and cereal products, organoleptically unacceptable. Removal of aldehydes such as hexanal and heptanal from package headspaces by means of the layer Bynel IXP101, a HDPE master batch, is claimed by Dupont Polymers (Rooney, 1995). Brody *et al.* (2001) described laboratory tests on peanut butter, coffee and a snack product demonstrating the effectiveness of the aldehyde scavenger. DuPont's materials are compositions of polyalkylene imine (PAI), particularly polyethylene imine and polyolefin polymer. The invention comprises a discontinuous PAI phase and an olefinic polymer continuous phase in a weight ratio of PAI to olefinic polymer of about 0.001 to 30:100 (Brody *et al.*, 2001). DuPont also developed a scavenger for the removal of hydrogen sulphide that could be incorporated into the lid of packaged processed cured poultry (Brody *et al.*, 2001).

Some commercialised odour-absorbing sachets, e.g., MINIPAX® and STRIPPAX® (Multisorb technologies, USA) absorb the odours mercaptanes and H_2S developing in certain packaged foods during distribution (Vermeiren *et al.*,1999).

2-in-1™ from United Desiccants (USA) is a combination of silica gel and activated carbon packaged together for use in controlling moisture, gas and odour within packaged products. Furthermore, a whole range of freshness-retaining mineral-based ethylene scavengers, mentioned in Table 3.4 also claim to absorb ammonia, hydrogen sulphide and other unpleasant odours. Ecofresh and Profresh® (E-I-A Warenhandels GmbH, Vienna) are claimed to be fresh keeping and malodour control master batches (Vermeiren *et al.*, 1999; Brody *et al.*, 2001).

UOP Corporation reported on the odour absorbing properties of a molecular-sieve technology 'Smellrite/Abscents'. This material, a crystalline zeolite, has molecular sized pores that trap odour within its structure (Brody *et al.*, 2001). Vitamin E or alpha-tocopherol has been marketed as a food-grade odour remover in packaging materials. Michigan State University researchers concluded that alpha-tocopherol should be considered for incorporation into package materials for food products such as crackers or potato chips (crisps) in which lipid oxidation is a major concern (Brody *et al.*, 2001).

Flavour incorporation in packaging material might be used to minimise flavour scalping. Flavour release might also provide a means to mask off-odours coming from the food or the packaging. It is of importance that this technology is not misused to mask the development of microbial off-odours thereby concealing the marketing of products that are below standard or even dangerous for the consumer (Nielsen, 1997).

3.6 Future trends

Although more successfully applied in the US, Japan and Australia than in Europe, active packaging is still in its early stages and has a distance to travel before being applied on a large scale. However, the group of the scavengers seems to have the best chance to become popular. The effectiveness of these types of active systems has been studied profoundly and a whole range of scavenging technologies has been patented and/or commercialised. However, consumers are not always very keen on the use of sachets in food packaging. This centres around fear of ingestion of the sachet even though the content is safe. Precautions to minimise the risk have been taken by clearly stating 'Do not eat' on the label and by legislating a minimum size of the sachets. Another concern is that the content of the sachet could leak out and adulterate the product (Smith *et al.*, 1995; Nielsen, 1997; Hurme and Ahvenainen, 1998). To avoid mishandling, abuse and resistance to sachets, scavengers can be incorporated in labels, oxygen scavenging films or crown corks. In Finland a consumer survey conducted in order to determine consumer attitudes towards O_2 scavengers revealed that the new concepts would be accepted if consumers are informed well by using reliable information channels. When the consumers understand the quality improvement and/or the assurance function of the scavengers, they will have more confidence in the safety of the food they buy (Mikkola *et al.*, 1997). In Europe, the introduction of scavenging technologies is limited because of legislative restrictions. Active compounds need to be registered on positive lists and the overall and specific migration limits need to be respected. Moreover, traditional migration testing is not always a realistic simulation of the real use of the scavenging system and could result in a serious overestimation of the migration of the active compound. The solution for this legislative issue is complex and will probably require some more time.

As legislative barriers disappear and more companies become aware of the economic advantages of using absorbent technology, and consumers accept this approach, the technology will be very likely to emerge as an important preservation technology.

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