Active Packaging Systems

Active packaging systems that remove or “scalp” volatiles by adsorption or absorption have been previously reported in scientific literature and patent applications. The focus of most of these packaging systems has been oxygen and ethylene removal (1-7). The use of active packaging systems to selectively remove off-flavor compounds and improve the flavor quality of foods is an area only recently being explored. Rooney (4) writes, “Commercially, plastics packaging has not been used to remove selectively components of the flavor or aroma of foods which are considered undesirable, but a potential opportunity has been available for over a decade.”

A classic example of how food packaging can be used to improve the quality of foods in an active form is the incorporation of zinc oxide in tinplate lacquers of canned food items. Protein degradation that occurs in tinplated canned foods causes a phenomenon known as sulfur staining. Sulfur compounds released during protein degradation interact with the tin in these products and cause black areas on the inside of the can. The incorporation of zinc oxide in tinplate lacquers intercepts the sulfur compounds and react with them before they can diffuse to the tinplate surface (4).

Chandler and his coworkers proposed an active packaging system in which an absorbent for limonine was incorporated into the packaging of citrus juices (8,9). Limonene is a tetraterpenoid present in citrus products, which becomes bitter during heating. The active packaging system proposed by Chandler included a 1 L plastic bottle coated internally with cellulose acetate-butyrate. Results of such an active packaging system showed that the limonene content in 500 mL of juice was reduced from 42 to 11 mg/kg after 3 days of refrigeration.

Only two examples are described in literature for the targeted removal of off-flavors based on interactions between an agent in the packaging material and a functional group known to be present in the off-flavor. Rooney (4) describes a product proposed by the ANIC Company Ltd. in Japan that can remove amine odors generated from the breakdown of fish muscle. Films containing ferrous salt and an organic acid such as citric or ascorbic acid are claimed to oxidize the amine or other oxidizable compounds as it is absorbed by the polymer.
DuPont has introduced an interactive packaging resin, Bynel IXP101, that is used as a tie layer and claims to remove aldehydes such as hexanal and heptanal from packaged headspace (4). The chemical mechanism by which this interactive packaging resin removes aldehydes is not described. Rooney (4) suggests the reaction would be the formation of a Schiff base by reaction of an aldehyde with an amino group, Figure (1). The compound containing the free amino group would need to be stable in heat and oxygen in order to process such a packaging material. In addition, the reaction between the aldehyde and amino group needs to be irreversible over the temperature range the package encounters during its shelf-life.

The tainting of foods by package migration continues to be a problem for the food industry. Several approaches have been made by manufacturers of food packaging material to alleviate this problem. A review of patent literature in this area show that these approaches often times include the addition of an active ingredient into a packaging material. The active ingredient interacts or reacts with a specific potential migrant similar to the way in which aldehydes are removed by DuPont’s IXP101. The basis for selecting active agents to be blended into PET for this research was based on a review of patent literature describing mechanisms to reduce residual aldehyde, particularly acetaldehyde, concentrations in polymeric materials.

**Polyamide Active Agents**

Long et al. (10) describes polyester/polyamide blend containers that minimizes the formation of undesirable byproducts in ozonated liquids, particularly acetaldehyde, in U.S. Patent No. 6,042,908. The polyester/polyamide blend consists of a PET or PEN polyester component with a concentration of 99.5-98\% w/w and a polyamide component with a concentration of 0.05-2\% w/w. The polyamide component can be selected from: low molecular weight partially aromatic polyamides having an average molecular weight less than 15,000, low molecular weight aliphatic polyamides having an average molecular weight of less than 7,000, or wholly aromatic polyamides and mixtures thereof. The mechanisms by which the polyamide removes acetaldehyde and other byproducts generated by ozonated liquids is believed to be by the nucleophilic addition of the free amino group on the polyamide to aldehydes or ketones to form imines (also known as Schiff bases). Figure (1) shows this reaction for poly(m-xylylene adipamide) (nylon MXD6) and acetaldehyde.
Low molecular weight partially aromatic polyamides specifically described in U.S. Patent No. 6,042,908 were poly(m-xylylene adipamide) (nylon MXD6), poly(hexamethylene isophthalamide), poly(hexamethylene adipamide-co-isophthalamide), poly(hexamethylene adipamide-co-terephthalamide), and poly(hexamethylen isophthalamide-co-terephthalamide). Low molecular aliphatic polyamides described in U.S. Patent No. 6,042,908 were polycapramide (nylon 6), poly-ω-aminoheptanoic acid (nylon 7), poly-ω-aminonanoic acid (nylon 9), polyundecane-amide (nylon 11), polyaurylactam (nylon 12), polyethylene-adipamide (nylon 2,6), polytetramethylene-adipamide (nylon 4,6), polyhexamethylene-adipamide (nylon 6,6), polyhexamethylene-sebacamide (nylon 6,10), polyhexamethylene-dodecamide (nylon 6,12), polyoctamethylene-adipamide (nylon 8,6), polydecamethylene-adipamide (nylon 10,6), polydodecamethylene-adipamide (nylon 12,6), and polydodecamethylene-sebacamide (nylon 12,8).

Long et al. (10) suggest that the most desirable polyamides to be blended with PET or PEN to reduce residual acetaldehyde were poly(m-xylylene adipamide) having a average molecular weight of 4,000-7,000 and an inherent viscosity of 0.3-0.6 dL/g and poly(hexamethylene adipamide) having an average molecular weight of 3,000-6,000 and an inherent viscosity of 0.4-0.9 dL/g (10). In addition, U.S. Patent No. 6,042,908 claims that aromatic polyamides are preferred over aliphatic polyamides because they produce less haze and are more dispersible.

Usilton and Mark (11) describe in WO Patent No. 0123475 that polyacrylamide, polymethacrylamide or compolymers of polyacrylamide and polymethacrylamide can be extruded into PET and act as an acetaldehyde scavenger. The acetaldehyde scavenging ability of polyacrylamides and polymethacrylamides is similar to that of nylons.

Turner and Nicely (12) describe in WO Patent No. 9728218 polyester/polyesteramide blends with reduced acetaldehyde concentrations. The mechanism by which polyesteramides reduces acetaldehyde is not understood by this author because these compounds have no terminal amino group.

A review of patent literature shows that many other researchers and companies have proposed the use of polyesters blended with polyamides to reduce residual concentrations of acetaldehyde and other byproducts formed during the melt processing and forming of polyester
films and containers (10,13-21). Unfortunately, the high level of terminal amino groups present in PET/polyamide blends causes yellowing and adversely affects the color of the blend (15).

**Polyamine Active Agents**

Speer et al. (22) describes in U.S. Patent No. 5,942,297 that copolymers of allylamine (or diallylamine) can be added to oxygen scavenging systems to remove aldehyde and alcohol by-products from these reactions. Polyallylamines and aldehydes form higher molecular weight imine products through a condensation reaction similar to the one described in Figure (1).

In a similar patent application, Ching et al. (23) describes a multi-layer oxygen scavenging film inclusive with neutralizing compounds for by-products of the oxygen scavenging system in U.S. Patent No. 6,057,013. Inorganic and organic bases were identified as suitable neutralizing compounds for acid, alcohol, and aldehyde by-products generated from an oxygen-scavenging system. Examples of inorganic bases described in this patent include: calcium carbonate, calcium hydroxide, potassium bicarbonate, and calcium oxide. Examples of organic amine compounds described in this patent include: dipropylentriamine, tris(3-aminopropylene)amine, N,N,N’N’-tetrais(3-aminopropyl)ethylenediamine and 1,12 dodecanediamine. Examples of amine-containing polymers described in this patent include: glycols containing amine groups such as polyethylene glycol with two amines and polypropylene glycol with two amines, and dimethylaminoethanol grafted ethylene-methyl acrylate copolymers. Examples of polyamines described in this patent include: pentaethylene hexamine (PEHA), triethylene tetraamine, polyvinyl oxazoline, and similar higher molecular weight compounds.

**Polyimine Active Agents**

Brodie et al. (24) describes the incorporation of polyalkylene imines, particularly polyethylene imine, in polyesters to scavenge unwanted aldehydes in U.S. Patent No. 5,362,784. The authors describe polyester/polyalkylene imine blends in which polyethylene imine is added to PET in a weight ratio of 0.001-30:100. A weight ratio of 0.01-10:100 is preferred. It is also suggested in this patent that polyalkylene imines with an average molecular weight of about 2,500 be used for blending. Furthermore, it is recommended that the polyalkylene imine not be branched and preferable have a relatively low percentage of tertiary amines. Binding agents can be added to polyester/polyalkylene imine blends to prevent migration of polyalkylene imines.
from the matrix, however this does not seem to be problematic. In fact, migration or surface blooming of liquid polyethylene imine within a polyester polymer did not occur in their studies.

The mechanism by which polyalkylene imines are able to remove aldehydes is not discussed in U.S. Patent No. 5,362,784. This author is skeptical of its ability to react with carbonyl compounds because polyalkylene imines are not primary amines and have no available free amino group.

**Polyol and Alkoylated Polyol Active Agents**

Eckert et al. (25) describes in WO Patent No. 0100724 that polyols with at least one primary hydroxy function in the 2 and/or 3 position can be used as additives in concentrations of 50-5,000 ppm in order to reduce the acetaldehyde content of extruded products of PET. Preferred polyols include the sugar alcohols: sorbitol, mannitol, and xylitol. PET/polyol blends with polyol contents as high as 25% by weight can be pelletized.

Sorbitol and other alcohols react with aldehydes and ketones in a reversible nucleophilic addition reaction. An acid catalyst protonates the carbonyl oxygen and subsequently eliminates water from a hemiacetal intermediate to produce an acetal. Figure (2) shows this reaction for sorbitol and valeraldehyde. The acetal formed from sorbitol and other higher molecular weight alcohols is less volatile then the aldehyde or ketone reactant.

Al-Malaika (26) similarly describes in WO Patent No. 0066659 the addition of D-mannitol, D-sorbitoal, and xylitol in PET blends to reduce residual acetaldehyde. In addition, WO Patent No. 0066659 suggests using other hydroxylic additives to reduce residual acetaldehyde including: triglycerin, trimethylolpropane, dipentaerythritol, and tripentaerythritol.

McNeely et al. (27) describes in U.S. Patent No. 5,250,333 a modified PET incorporated with an alkoxylated polyol to reduce residual acetaldehyde. The inventors specifically discuss the use of alkoxylated trimethylethane, alkoxylated trimethylolpropane, alkoxylated pentaerythritol, and the alkoxylated dimmer of pentaerythritol. These additives may be used in the amount of 2-5%, based upon the total acid units.

**Oxidation Catalyst Active Agents**

Rule (28) describes in WO Patent No. 013090 that acetaldehyde can be reduced to acetic acid in polyester based packaging with the addition of an oxidation catalyst. The reduction of
acetaldehyde to acetic acid is favorable because the flavor threshold of acetic acid is more than 1,000 greater than the flavor threshold of acetaldehyde. The addition of oxidation catalysts to polyester packaging are two-fold, they reduce or eliminate acetaldehyde migration and simultaneously reduce or eliminate the migration of oxygen. Oxidation catalysts mentioned in WO Patent No. 013090 include cobalt octoate and cobalt naphthenate.

Go et al. (29) describes in U.S. Patent No. 4,357,461 a process for preparing low-acetaldehyde polyesters showing good stability by incorporating an alkali metal salt or ethylenediaminetetraacetic acid (EDTA) during the melt polymerization reaction.

**Cyclodextrin Active Agents**

Cyclodextrin is a cyclic oligosaccharide consisting of at least five, but more often by six, seven, or eight glucopyranose units joined by alpha linkages. The three most common homologs are α-, β-, and γ-cyclodextrin having 6, 7, and 8 glucopyranose units. Figure (3) shows the structure of α-cyclodextrin. The arrangement of the glucose monomers resembles a donut shaped ring. The specific coupling of the glucose monomers gives cyclodextrin a rigid, truncated conical molecular structure with a hollow interior of a specific volume. The internal cavity of cyclodextrin is lipophilic whereas its exterior is hydrophobic. This structural feature of cyclodextrin is unique and allows cyclodextrin to complex molecules (e.g., aromatics, alcohols, halides, and hydrogen halides, carboxylic acids and their esters, etc.).

In order for molecules to form an inclusion complex with cyclodextrin, they must satisfy the size criterion of fitting at least partially into the cyclodextrin internal cavity (30). The size-fit concept, predicts the highest complex stabilities for the best size-matched host-guest pairs and supports thermodynamic studies investigating complexation of natural cyclodextrins. For instance, the forces induced by complexation of straight-chain guests such as aliphatic aldehydes with α-cyclodextrin are greater than β-cyclodextrin. Van der Waals forces are critically dependent on the distance of separation in cyclodextrins and therefore can be used to predict the inclusion forces (31). Figure (4) is a graphical representation of cyclodextrin’s cone shaped cavity and ability to form inclusion complexes (32). Figure (5) is a proposed fitting of caproaldehyde in the internal cavity of cyclodextrin. Figure (6) is a graphical representation of α-, β-, and γ-cyclodextrin and their dimensions (30).
Wood and Beaverson (30) describe a rigid thermoplastic beverage bottle containing a substituted or modified cyclodextrin that prevents the passage of a permeant, or the elution of a soluble material from the thermoplastic into the liquid container contents in U.S. Patent No. 6,136,354. The inventors claim that the addition of 0.1-5% modified or derivatized cyclodextrin to biaxially oriented thermoformed polyolefin or polyester thermoplastic beverage containers improves the gas barrier properties and reduces overall migration of these products. Cyclodextrin forms inclusion complexes with permeants and migrants and binds these species within the polymer matrix. The mechanism of sorption is both physical adsorption in the polymer network and the formation of an inclusion complex between cyclodextrin and guest molecules (33,34).

Bobo (35) describes in U.S. Patent No. 5,177,129 that cyclodextrins can be used in can coatings and enamels for use on the interior surface of containers in order to protect foods and beverages stored in the containers from contaminants which adversely affect taste. Interior can coatings described include synthetic thermoplastic or thermosetting film forming resin blended with 0.5 to 5% by weight of cyclodextrin. The uses of such can coatings are specifically designed for coating beer containers to prevent the development of an off-taste similar to stale beer. These flavors are caused by trace amounts of aldehydes and ketones containing 6 to 18 carbon atoms.

A review of patent literature reveals numerous patents describing the use of cyclodextrins as odor emitters or absorbers. The use of cyclodextrins to control pet odor, body odor, and odors associated with garbage are examples of how cyclodextrins are used as odor absorbers. Cyclodextrins are also used as carriers of fragrances in perfumes and deodorants (36-40).

**Zeolite Active Agents**

Zeolites are natural hydrated silicate of aluminum and either sodium, calcium, potassium, or any combination thereof. Zeolites are highly polar and crystalline in structure. They are often used as molecular sieves because of their ability to undergo dehydration with little or no change in crystalline structure. The dehydrated crystals are interlaced with regular spaced channels of molecular dimension. Figure (7) shows the structure of the aluminosilicate framework. This network of uniform pores comprises of approximately 50% of the total volume of crystals. The empty cavities in activated zeolite have a strong tendency to recapture the water molecules that
have been driven off. The tendency for the zeolite material to recapture water is so strong that if no water is present, they will accept any material that can be accepted into the cavity. However, only those molecules that are small enough to pass through pores of the zeolite crystal can enter the cavities and be adsorbed on the interior surface (41).

Mills et al. (1994) describes in WO Patent No. 9429378 a polyester/zeolite admixture with improved gas barrier and flavor retaining properties. Improved flavor retaining properties were attributed to the reduction in residual acetaldehyde concentration. The inventors found that the addition of small- or medium-pore zeolites at a concentration of 100 to 1,000 ppm in PET reduced acetaldehyde concentration without producing haze. Medium-pore zeolites have a 10-ring system with an elliposoidal tubular diameter of 5.5 angstroms x 5.6 angstroms and are often referred to as pentasil zeolites. Examples of medium-pore zeolites specifically mentioned in WO Patent No. 9429378 as suitable additives include: ZSM-5, ZSM-11, ZSM-22, NU-10, Theta 1, ZSM-23, ZSM-48, TS-1, and silicalite. Small-pore zeolites have an eight tetrahedral form with a ring of diameter 4.1 angstroms and are often referred to as A-zeolites. Examples of small-pore zeolites specifically mentioned in WO Patent No. 9429378 as suitable additives include: A-zeolites such as 3A, 4A, and 5A, mordenite (small-pore type) such as AW-300 and ZEOLON-300, erionite, chabazite, zeolite F such as IONSIV F80, and zeolite W such as IONSIV W85. Many of the zeolites mentioned in this document are available from Union Carbide and the Norton Company, the two largest producers of zeolites (42).

Massey et al. (41) describes a method of improving the brightness and color of a polyester resin and reducing acetaldehyde content by passing the resin through zeolite molecular sieves in U.S. Patent No. 4,391,971. In this disclosure, the zeolite is not admixed with the polyester.

Jenkins et al. (43) explains in U.S. Patent No. 5,104,965 that the incorporation of certain zeolites into PET results in a polymer, which has greatly increased rates of crystallization. The PET/zeolite blend consists of PET with a concentration of 99.9-75% w/w and zeolite with a concentration of 0.1-25% w/w. Zeolites that were shown to be effective for crystallization of PET included: 3A, 4A, 5A, NaY, 13X, and mordenite. The inventors concluded that zeolites were effective as crystallization aids of PET because of their ability to strongly attract polymer chain units and hold them in a conformation comparable with the chain conformation of the crystalline polymer, and thus provide a site for polymer crystallization.
References


Figure 1. Nucleophilic addition reaction of nylon MXD6 to acetaldehyde to form imine.
Figure 2. Nucleophilic addition of D-sorbitol to valeraldehyde to form acetal.
Figure 3. Structure of $\alpha$-cyclodextrin
Figure 4. Graphical representation of cyclodextrin’s cone shaped cavity and ability to form inclusion complexes (32).
Figure 5. Proposed fitting of caproaldehyde and cyclodextrin
Figure 6. Graphical representation of α-, β-, and γ-cyclodextrin and their dimensions.
Figure 7. Structural representations of aluminosilicate framework.