

FILM SUITABLE FOR FOOD PACKAGING

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FIELD OF THE INVENTION

The present invention relates to plastic films having controlled permeability characteristics. The films of the invention are particularly suitable for use in packaging. The invention also concerns methods of making the films, packages comprising such films, and a method for improving the storage life of perishable articles, such as fresh produce.

BACKGROUND OF THE INVENTION

In today's distribution and marketing of products a multitude of different packaging materials are used. One principal category of packaging materials is plastic film. To meet the specific performance requirements for various packaging applications and packaged products, many different kinds of plastic films exist, both in composition and structure.

In the packaging of fresh cut produce, such as fruits and vegetables, preservation of freshness, flavor, texture and eating quality through the time of consumption presents a particular challenge. It has been found that the shelf life of packaged produce may be extended and deterioration in quality and undesired phenomena, such as foul odor, be reduced, when the respiration and maturation rates of such produce can be properly reduced and pathogen growth be inhibited. The specific requirements and recommended conditions for the long-term storage of essentially all types of fresh fruits and vegetables are known in the art. One of the factors which significantly affects the shelf life of packaged produce is the presence of gases, including oxygen and carbon dioxide. Dependent on the storage conditions, such as temperature and relative humidity, each type of produce has its specific optimum ranges of oxygen concentration, carbon dioxide concentration and relative concentrations of carbon dioxide to oxygen, at which respiration can be suitably retarded and quality be maintained to the greatest possible extent.

To provide improved, produce-specific storage conditions, including advantageous concentrations of oxygen and carbon dioxide, plastic films with certain controlled gas permeability characteristics and modified atmosphere packaging have been proposed. For example, U.S. Patent No. 4,879, 078 discloses a controlled packaging atmosphere film comprising a polymer and 36 to 60 weight percent of an inert filler. The films are uniaxially stretched to provide carbon dioxide and oxygen permeabilities in the range of 5,000 to 10,000,000 cc/100 in²-atm-day. However, the relatively high amounts of filler and the required stretching step are disadvantageous. International patent application WO 94/04655 discloses a multilayer film with oxygen permeabilities in the range of from about 150 to 450 cc/100 in²-atm-day or greater up to about 1000 cc/ 100 in²-atm-day comprising a first outer layer of an elastomer and a second layer of a single site catalyst polyethylene. Shortcomings of this film include its limited permeability range and the requirement for a multilayer structure. For ecological and/or economic reasons it is desirable that controlled permeability properties are attainable in a single layer. International patent applications WO 92/02580, WO 95/07949 and WO 99/33658 each disclose controlled permeability films comprising a film forming polymer and filler particles which are larger than the intrinsic film thickness. It is desirable to further improve the properties of such films, for example, with respect to appearance, including visual appearance, printability and safety. Films with excellent clarity which can readily be printed upon are particularly desirable in retail packaging.

There still is the need for plastic films suitable for use in packaging applications, particularly such applications involving perishable articles, which films can afford proper controlled permeability characteristics suitable to extend storage life of the packaged item without compromising safety. Such controlled permeability films should also have excellent optical and haptic properties as well as good mechanical performance to provide adequate protection for the packaged article.

SUMMARY OF THE INVENTION

In one embodiment, the invention is a controlled permeability film comprising:

- A. A polymeric film having an intrinsic thickness, and
- B. A crushed, nonporous, inert filler incorporated into the film and having a average particle size such that the ratio of the average particle size of the filler to the film thickness is 0.67 to 0.99.

In another embodiment, the invention is a controlled permeability film comprising:

- A. A polymeric film having an intrinsic thickness, and
- B. A nonporous, inert, particulate filler incorporated into the film and having
5 an average particle size such that the ratio of the average particle size of the filler to the film thickness is 0.67 to 0.99,

the particulate filler that is incorporated within the film subjected to a compressive force that results in the crushing at least a portion of the particulate filler.

10 In another embodiment, the invention is a compressed, controlled permeability film comprising:

- A. A polymeric film having an intrinsic thickness, and
- B. A nonporous, inert, particulate filler incorporated within the film and
having an average particle size such that the ratio of the average particle
size of the filler to the film thickness is 0.67 to 0.99, and at least a portion
15 of the particulate filler is crushed.

In another embodiment, the invention is a method of making a controlled permeability film, the method comprising:

- A. Blending a film-forming polymer with an inert, nonporous particulate filler
having an average particle size;
- 20 B. Forming a film from the blend of (A) to an intrinsic film thickness such
that the ratio of the average particle size of the filler to the film thickness is
0.67 to 0.99, and
- C. Subjecting the film of (B) to a compressive force such that at least a
portion of the particulate filler is crushed.

25 In another embodiment, the invention is a method of making a controlled permeability film, the method comprising:

- A. Blending a film-forming polymer with an inert, nonporous, crushed
particulate filler having an average particle size; and
- 30 B. Forming a film from the blend of (A) to an intrinsic thickness such that the
ratio of the average particle size of the filler to the film thickness is 0.67 to
0.99.

In another embodiment, the invention is a package comprising a controlled permeability film in which the film has an intrinsic thickness and contains an inert,

nonporous, crushed particulate filler of an average particle size, the ratio of the average particle size of the filler to the intrinsic film thickness between 0.67 to 0.99.

5 In another embodiment, the invention is a method for extending the storage time of a perishable article, such as fresh produce, by packaging the article at least partially in a controlled permeability film in which the film has an intrinsic thickness and contains an inert, nonporous, crushed particulate filler of an average particle size, the ratio of the average particle size of the filler to the intrinsic film thickness between 0.67 to 0.99.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the following terms have the specified meanings.

10 The singular generally includes the plural and the plural generally includes the singular.

The term "comprising" means "including".

The term "copolymer" means a polymer in which two different monomers are polymerized to form the copolymer.

15 The term "interpolymer" means a polymer in which at least two different monomers are polymerized to make the interpolymer. This includes, for example, copolymers, terpolymers and the like.

The term "film" means a flat article and includes sheet, strips, tapes, and ribbons.

20 The beta (β) ratio is the ratio of carbon dioxide permeability to oxygen permeability.

The term "nonporous" is used to describe an object, e.g., a filler particle, that is without natural pores, interstices, channels or similar passageways that extend from one surface of the object to another surface of the object or, in the case of a spherical or other one-surface object, from one point on the surface of the object to another point on the surface of the object. The passageways of a porous object are large enough to allow the passage through the object of small molecules of a gas or liquid, e.g., oxygen, nitrogen, water, benzene, etc. Nonporous objects include porous objects with blocked or otherwise obstructed passageways, e.g., hydrated minerals.

The terms "crush", "crushed", "crushing" and similar terms are used to describe a nonporous object, e.g., a filler particle, that has pores, interstices, channels or similar passageways that extend from one surface of the object to another surface of the object such that a gas or liquid can pass through the object; the pores, interstices, etc. in the object the result of activating the object, e.g., subjecting the object to a compressive force of sufficient magnitude so as to create one or more such passageways within the object.

The terms "activation", "activating" and similar terms mean the creation of passageways within a nonporous object, e.g., a filler particle, by any means, but typically by subjecting the object to a compressive force.

The term "intrinsic thickness" refers to the calculated thickness or gauge of a monolayer film, or a layer of a multilayer film. The intrinsic film thickness is the thickness of the film without a filler. Intrinsic thickness is calculated as the product of the weight of the film in grams times the density of the film in grams/cubic centimeter. The density of the film is the sum of the weight percentage of the polymer from which the film is made times the density of the polymer, plus the weight percentage of the filler times the density of the filler.

All parts and percentages are by weight unless indicated otherwise.

Unless otherwise stated, any given range includes both endpoints used to state the range. Moreover, all numerical values, e.g., ranges, include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least two units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as temperature, pressure, etc., is from 10 to 125, preferably from 30 to 75 and more preferably from 40 to 60, it is intended that values such as 20 to 100, 35 to 70 and 50 to 55, etc., are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate for the context in which it is used. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are intended to be specifically enumerated in this specification.

Surprisingly, it has been found that films comprising at least one film-forming polymer and an inert, nonporous filler material which has an average particle size such

that the ratio of the average particle size of the filler material to the intrinsic thickness of the film is 0.67 to 0.99 can be subjected to an activation step so as to effectively modify and control the oxygen and/or carbon dioxide permeabilities of the film. The oxygen and/or carbon dioxide permeabilities of the film can effectively be adjusted to meet the controlled atmosphere requirements or recommendations for a particular packaged product, e.g., in order to extend the shelf life of produce. The controlled permeability films of the invention can be readily printed upon and have excellent optical and mechanical properties. The films provided herein can be produced in a cost-effective manner.

The present invention provides monolayer and multilayer films in which the monolayer film or at least one layer of the multilayer film comprises (i) at least one film forming polymer, and (ii) an inert, nonporous filler material which has an average particle size such that the ratio of the average particle size of the filler to the film thickness is 0.67 to 0.99. The gas permeability of such a film or layer is modified in an activation step. Such a film or film layer that has been subjected to an activation step is referred to as controlled permeability film or controlled permeability layer, which are also subjects of the present invention. In multilayer films, the additional layers are selected such as to impart or enhance certain desired film properties, for example hot tack, heat-sealability and/or structural properties, without substantially interfering with the controlled permeability characteristics of the controlled permeability layer. The multilayer films of the present invention may comprise one or more tie layers, if appropriate. Preferably, the additional layers are chosen so as not to substantially interfere with or substantially adversely impact the controlled permeability characteristics of the controlled permeability layer. For ecological and/or economic reasons, the films of the invention usually have as few layers as possible to meet the desired and/or required performance attributes. Preferred film structures of the present invention are monolayer, twolayer or threelayer films, monolayer films being the more preferred.

In one embodiment, multilayer films of the present invention comprise from two to about seven layers, at least one of which, preferably one, comprises at least one film forming polymer and an inert, nonporous filler material which has a particle size such that the ratio of the average particle size of the filler material to the intrinsic thickness of the layer is 0.67 to 0.99. In another embodiment, multilayer films of the present invention

comprise from two to about seven layers, at least one of which, preferably one, comprises at least one film forming polymer and an inert, nonporous filler material which has a particle size such that the ratio of the average particle size of the filler material to the intrinsic thickness of the multilayer film is 0.67 to 0.99. These multilayer films are typically laminates constructed using conventional techniques, e.g., thermal or adhesive lamination or extrusion coating. In the embodiment in which the ratio of the average particle size of the filler material to the intrinsic thickness of the layer is 0.67 to 0.99, the layer is typically activated before it is joined to the other layers of the film. In the embodiment in which the ratio of the average particle size of the filler material to the intrinsic thickness of the multilayer film is 0.67 to 0.99, activation is after the formation of the multilayer film.

The activation step serves to modify the gas permeability of the film or layer comprising (i) at least one film-forming polymer, and (ii) the inert, nonporous filler material, with a ratio of the average particle size of the filler material to the intrinsic thickness of the film or layer of 0.67 to 0.99. Typical activation steps include a pressure treatment, a heat treatment, or a combination of these treatments. The activation step typically increases the gas permeability, in particular the oxygen transmission rate, of such a film or layer as compared to a film or layer containing a nonactivated, inert, nonporous filler. In other words, a film containing, e.g., between about 0.01 and 15 percent by weight, an activated, inert, nonporous filler material will exhibit increased gas permeability as compared to a film similar in all respects except that it has not been subjected to an activation step. In addition, the activation step can increase the carbon dioxide transmission rate without affecting, at least at low filler concentrations (e.g., 0.01 to 0.025) the water vapor transmission rate. Advantageously, the desired controlled permeability characteristics are obtained without stretching the film.

In a preferred embodiment, the activation step includes subjecting a film comprising at least one layer comprising at least one film-forming polymer and a filler having an average particle size, the ratio of the average particle size of the filler material to the intrinsic thickness of the film of 0.67 to 0.99, to a compressive force, e.g. by contacting the film with a pressure plate or rollers. For example, the pressure treatment may be carried out by passing the film between pressure rollers which, optionally, may be heated. All or only a part of the film may be activated, e.g., only a fraction of the width

of a film, or every other segment of a length of a film, or designated areas within an area of the film, are subjected to a compressive force.

The compressive force or pressure range should exceed the compressive strength of the filler particles. The force is typically in the range of from 2.5 to 100 kg, preferably in the range of 5 to 75 kg. The compressive force should be sufficient to at least partially crush the filler particles, e.g. sufficient to creating cracks, pores or channels within the filler particles that extend from one surface of the particle to another surface of the particle. The contacting step may be conducted at ambient temperature or at elevated temperature. Preferably, the temperature is between room temperature and below the melting point of the polymer with the highest melting point from which the film is made, more preferably 10 to 15C below the melting or softening point of the highest melting point polymer from which the controlled permeability film or layer is made.

Preferably, the controlled permeability films of the present invention which have been subjected to the activation step or which comprise at least one layer which has been subjected to such a step have a beta ratio in the range of from 0.8 to 3.5, more preferably from 0.8 to 2.5, even more preferably from 0.8 to 2.0, and most preferably from 0.8 to 1.5. Methods and suitable equipment to determine the oxygen and carbon dioxide transmission rates are known in the art, for example ASTM D3985.

The films of the invention may be of any thickness or gauge appropriate for the intended use of the film. For economic and/or ecological reasons it may be desirable to minimize film thickness. Monolayer films according to the present invention typically have a thickness in the range of from about 10 microns (0.4 mil) to about 125 microns (5 mils), preferably from about 30 microns (1.2 mils) to about 75 microns (3 mils). Multilayer films according to the invention typically have a total thickness in the range of from about 25 microns (1 mil) to about 250 microns (10 mils). The controlled permeability films according to the invention may be printed on an outer and/or inner surface. Printing may be imparted to the film, preferably after activation, for example, by a flexographic or rotogravure apparatus. If appropriate, the employed ink is suitable for food packaging. Advantageously, the controlled permeability films according to the present invention are designed to have excellent optical clarity, be flexible and tough.

The films of the present invention can be prepared by any suitable fabrication process, and their properties can be designed to accommodate any particular end use. Suitable fabrication processes include, for example, blown film extrusion, flat die extrusion, coextrusion, extrusion coating and lamination techniques. The films can be made available to wholesalers and retailers in any suitable form, for example roll stock, and be used on conventional equipment. Preferably, the films according to the present invention are designed to be easily machinable at cost effective line speeds.

The film forming polymer may be of any suitable type and generally includes, but is not limited to, homopolymers, copolymers, interpolymers, such as for example block, graft, random and alternating copolymers or interpolymers. The term "polymer" includes all possible geometrical configurations of the material, including isotactic, syndiotactic and random symmetries. Suitable types of polymers include, for example, polyolefins, such as homopolymers, copolymers, interpolymers and blends thereof of ethylene and linear or branched α -mono-olefins having at least three, preferably three to ten carbon atoms. Examples of homopolymers which may be used in the present invention are polyethylene, polypropylene and poly(1-butene). Representative examples of suitable copolymers are ethylene/propylene, ethylene/butene, ethylene/pentene, ethylene/hexene, ethylene/heptene and ethylene/octene copolymers. Suitable categories of polyethylenes include, but are not limited to, high pressure low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE). Examples of other homopolymers, copolymers and interpolymers which can be used are polyesters, including polyethylene terephthalate and polybutene terephthalate, nylon, polystyrene, vinyl polymers, such as polyvinyl chloride, polyvinyl acetate, ethylene vinyl-acetate copolymers and ethylene-vinyl alcohol copolymers, ethylene methacrylic acid copolymers (ionomers), ethylene/styrene interpolymers, polyalkylene oxide polymers, and polycarbonate. Representative examples of blends are blends of homopolymers, such as polyethylene or polypropylene, and copolymers, such as ethylene/butene or ethylene/octene and blends of copolymers.

The selection of the film-forming polymer should be consistent with the film requirements, for example with respect to processability and physical properties. Preferably, the film-forming polymer is suitable for use in food packaging applications and meets the respective requirements set forth by the competent regulatory authorities.

Such preferred polymers include, for example, polyethylene polymers, polypropylene polymers, ethylene vinyl alcohol copolymers and ethylene vinyl acetate copolymers.

In the compositions employed to form the controlled permeability films according to the present invention, the amount of film-forming polymer is preferably 99.99 weight percent or less (based on the amount of film-forming polymer and filler in the film or layer). Preferably, the amount of film-forming polymer is 85 weight percent or higher, more preferably 90 weight percent or higher, and most preferably 96 weight percent or higher. Particularly preferred embodiment, the amount of film-forming polymer is in the range of from 98 weight percent to 99.975 weight percent based on the combined weight of the film and filler.

The filler materials used in the present invention are inert to the film forming polymer or polymers, meaning that they do not chemically interfere with or adversely affect the film. Suitable fillers are organic or, preferably inorganic particulate materials. The fillers may be natural or synthetic materials. The filler particles are nonporous. Preferably, the particles are substantially spherical with a length to diameter ratio of from about one to about two. Preferred are fillers with a suitably low compressive strength so that they are relatively easy to crush during the activation process, but which are not substantially damaged during compounding or film fabrication. Suitable filler materials may have an average particle size in the range of from 30 to 70 microns. For monolayer films, the average particle size typically is in the range of from about 8 to about 113 microns.

Nonporous filler materials suitable for use in the present invention include, for example, pumice, tuff, rhyolite, dacite, reticulite, scoria, lapilli, perlite, coal, silicas, metal oxides, such as aluminum oxide, sulfates, such as barium sulfate, carbonates, such as calcium carbonates and clays. Particularly preferred fillers are mineral, spherulitic materials, such as nonporous silicas, e.g., glass beads. The use of mixtures of different filler materials is also envisioned. Advantageously, the filler materials are uniformly dispersed throughout the film-forming polymer used to make the films and/or layers of the present invention.

In one, less preferred embodiment of the invention, the inert, nonporous filler particles are crushed before they are blended with the film-forming polymer from which

the film or layer is made. In this embodiment, the particles are first activated by any suitable means, e.g., crushed between plates or rollers, and then blended with the film-forming polymer, and then the blend is made into a film or layer by any suitable process. This method of making the controlled permeability film is less preferred than crushing the particles after the film is made because crushing of the particles outside of the film often results in the disintegration of the particles. In other words, the particles simply break along the created passageways into smaller, nonporous particles, e.g., shards and the like. When crushed within the film matrix, the particles retain their physical integrity despite the formation of the desired passageways from one surface to another surface. In the case of spheres, of course, the particle has a single surface and the passageways course from one point on the surface to another point on the surface.

Important to the present invention is the particle size of the filler material relative to the intrinsic thickness of the film or layer which attains the controlled permeability as a result of activation, or relative to the intrinsic thickness of the overall multilayer structure. The average particle size of the filler material is less than the intrinsic thickness of the film, layer or multilayer structure before activation. Advantageously, the activation step does not change the intrinsic thickness of the controlled permeability layer or of the controlled permeability film. The intrinsic thickness before activation is substantially the same as the film thickness or gauge after activation.

The average particle size of the filler material is at least two thirds of the intrinsic thickness of the film or layer. Preferably, the ratio of the average particle size to film thickness or gauge is at least 0.70, and more preferably at least 0.80. The average particle size is less than the intrinsic thickness of the film or layer, i.e., the ratio of the average particle size to the film thickness or gauge is 0.99 or less, and preferably the ratio of the average particle size to the film thickness or gauge is 0.90 or less.

Preferred are filler materials which have a narrow particle size distribution. A narrow particle size distribution is found to be particularly suitable for achieving consistent activation results. Particularly preferred are filler materials for which the average particle size, as well as the size of 90 percent of all particles, meet the general and preferred requirements relative to the intrinsic film thickness described in the preceding paragraph. The desired particle size of the filler material is dependent on the

intrinsic thickness. For example, for monolayer films the preferred filler size is in the range of from 14 to 68 microns.

The particle size of a filler material can be determined by methods known in the art, for example by a Coulter counter method or by microscopy.

5 The amount of filler in the film of the invention is chosen such that it is sufficient to provide the desired controlled permeability after subjection of the film to the activation step. Preferably, the amount of filler in the controlled permeability layer -- based on the total weight of filler and film forming polymer present in said layer -- is at least 0.01 weight percent or more, preferably 0.05 percent or more, more preferably at least 0.1
10 weight percent or more. The amount of filler in the controlled permeability layer should be 15 weight percent or lower, preferably 10 weight percent or lower, more preferably 8 percent or lower, most preferably 6 weight percent or lower, particularly preferably 4 weight percent or lower. The particularly preferred range for the amount of filler is from 0.025 weight percent to 8 weight percent.

15 The filler surface may be modified, for example such that it is more hydrophobic, using a surface modifying agent. Surface modification may serve to improve the dispersion of the filler and/or its adhesion to the polymer matrix. Advantageously, the fillers are uniformly dispersed in the polymer matrix. Suitable agents are known in the art and include, for examples, polymers and fatty acids. Preferred surface modifying agents
20 are FDA compliant and include, for example, calcium stearate.

 The compositions for the films according to the present invention comprising the film-forming polymer and the filler material may further comprise additives to impart or enhance certain properties of the film, including, without limitation, pigments, antioxidants, stabilizers, antifogging agents, plasticizers, tackifiers, waxes, flow
25 promoters, surfactants, materials added to enhance the processability of the composition, and the like. These additives typically have little, if any, affect on the permeability of the film resulting from the activation step because this permeability is the result of creating porosity in the filler. These additives typically have more affect on the permeability of a film in those instances in which the permeability is primarily a function of
30 solution/diffusion transport mechanisms. The compositions can be prepared by

conventional blending techniques using such equipment as two-roll mills, Banbury mixers, and single and twin-screw extruders.

The films of the present invention are particularly suitable for use in packaging applications, such as fresh cut produce packaging. Preferred are films suitable for use in food and horticultural packaging, most preferably packaging of fresh produce including, for example, fruits, vegetables and flowers. Fresh produce can be packaged in a controlled atmosphere, the beta ratio maintained at the optimum level for the packaged item to improve its storage life, preserve quality and/or reduce or prevent foul odor.

The package according to the present invention comprises a controlled permeability film of the present invention and one or more articles, preferably at least one article which benefits from controlled permeability or modified atmosphere packaging. Such articles include, for example, food, such as vegetables and fresh fruits, flowers or microorganisms, and especially those articles which tend to respire or oxidize, e.g., cut fruits and vegetables. As used herein, "packaged" and the like terms mean that one or more articles are wrapped or enclosed by the controlled permeability film according to the invention in a manner that the film provides a barrier between the article and the environment. Preferred packages encompass fresh and/or pre-cut produce, such as fruits, vegetables or flowers. Produce which benefits from being packaged with a film of the present invention includes, but is not limited to, carrots, broccoli, cauliflower, cabbage, mushrooms, brussel sprouts, beans, chicory, celery, radish, spinach, asparagus, parsley, okra, artichoke, tomato, vegetable blends, nashi, pear, plum, berries, grape, apricot, orange, banana, nectarine, kiwi, grapefruit, peach or mango. The films according to the present invention allow the maintenance of a modified atmosphere within the package consistent with the need for a produce to respire, produce ethylene and ripen. The optimum atmosphere for each produce is different. The controlled permeability films or packages of the present invention can be designed such as to provide a relatively high oxygen transmission rate. Such high OTR films are particularly suitable for packaging produce with high respiration requirements, avoiding or significantly reducing undesirable phenomena associated with low package oxygen levels, such as foul odor. Alternatively, the controlled permeability films or packages of the present invention may be designed to permit relatively low oxygen transmission, as desirable e.g. for relatively lower oxygen transmission produce, such as Romaine lettuce.

If appropriate, the package may contain one or more components other than the film and the packaged article, such as a board, a tray, or a container-like or a box-like component. The package may be in any suitable form, for example, in the form of a bag, a wrap, a pouch or a container, e.g. a container wherein the controlled permeability film according to the present invention is a panel in at least one side of said container. Bags as provided by the present invention include, for example, unfilled or filled retail-consumer-disposable bags with a zipper or other interlocking closure, open-mouth bags, food-storage bags, household storage bags, freezer bags, sandwich bags and trash bags. One specific embodiment of the present invention relates to food freshness bags comprising a controlled permeability film according to the present invention and, optionally, one or more food items. Wraps as provided by the present invention include, for example, retail-consumer-disposable wrap for packaging a wide variety of goods, e.g., meat, produce and the like, either prior to sale of those goods or for household storage.

The package according to the present invention can be made by methods known in the art, for example by heat sealing a film according to the invention at the periphery, or by means of a form, fill and seal apparatus. The package may include a resealing means, such as a zipper or "zip-lock" type means, allowing the consumer to repeatedly reseal the package. The film and packages of the present invention are suitable for retail packaging and the food service industry, for example, schools, restaurants, hospitals and the like, where appearance, long shelf life and safety are essential.

The present invention also provides a package which is a controlled permeability container wherein the permeability inside the container is controlled by the use of a film according to the invention as a gas-permeable panel in a window in one or more of the walls of the container. Otherwise the container is made from a substantially gas-impermeable material. The permeability and area of the panel may be designed such as to provide a flux of oxygen and carbon dioxide which is about equal to the predicted respiration rate of the amount of packaged fresh produce.

The applications of the controlled permeability film of the present invention are not restricted to the packaging of produce or organisms, but may also include other uses, including further packaging applications as well as non-packaging applications, for example:

- monitoring respiration rates where the respiration rate can be determined from the known permeability of the film and accumulation of respiration gases;
- enhancing sorbent, scavenging, or indicating polymer additives where permeation of gases or liquids through the polymer is limiting the effectiveness of the additive;
- fresh red meat packaging applications;
- building and construction house wraps;
- medical applications, including disposable healthcare drapes and gowns, and personal hygiene applications
- packaging of meat (other than fresh red meat), poultry, dairy or fish products;
- packaging of medicines, pharmaceuticals and microorganism culture media;
- packaging of live organs.

EXAMPLES

The following Examples are illustrative of the invention, but are not to be construed as limiting the scope of the invention in any manner.

The following methods are used to determine the following parameters:

Density (g/cm³): ASTM D-792

Melt Index (g/10 min): ASTM D-1238, at 190°C/2.16 kg load (condition E);

Dart Impact A (g): ASTM D-1709 (66 cm (26 in) drop height)

Elmendorf tear strength (g): ASTM D-1922, Method A.

Tensile Properties including 1% and 2% Secant Modulus: ASTM D-882. The tensile properties and moduli are measured on 2.54 cm x 20.3 cm (1 in x 8 in) specimens with a 10 cm (4 in) gauge length. Crosshead speed is 50.8 cm/min (20 in/min) for the tensile properties and 2.54 cm/min (1 in/min) for the moduli.

“MD” means machine direction, “CD” means cross direction.

The film-forming polymer used in these examples is a commercially available high pressure LDPE (ethylene homopolymer) having a density of 0.923 g/cc and a melt index (I₂) of 1.9 g/10 min. The fillers used in these examples are nonporous silica beads available from Potters Industries (a division of PQ Industries, U.S.A.). Monolayer films are blown on an Egan extruder with a 3-inch die and 70-mil die gap. The maximum mesh size on the screen pack is 120 (about 200 microns) to prevent build-up of the silica beads prior to exiting the die. The melt temperature is about 220C with an extruder profile of 150/160/171/177/182/193/204C with a blow-up ratio of 2.5.

For activation, the films are run through a set of calendering rolls stacked parallel to one another and running at the same speed. The temperature of 23C and the pressure of 0.41 N/mm are set to control the level of permeability achieved in the film. The film gauge is not changed in the activation step. The oxygen transmission rates of the non-activated film Samples 1 to 3 are 900 nmol m⁻¹ s⁻¹ GPa⁻¹. The composition of the film samples is given in Table 1. Sample 4 is not a sample according to the present invention.

TABLE 1

Sample	Filler	Mean Particle Size (μm)	Filler Loading (wt. %)	Film Gauge (μm)	Particle Size to Film Gauge Ratio
1	SPHERIGLASS 3000, Type A	35	0.025	41	0.9
2	Spacer Beads 602590	38	0.05	38	1.0
3	Spacer Beads 602590	38	0.1	38	1.0
4	SPHERIGLASS 2900, Type A	42	0.	69	0.6

The controlled permeability characteristics of the activated films are listed in Table 2.

TABLE 2

Sample	Oxygen Transmission Rate [nmol/m ² s* Gp _a (cc*mil/100 in ² /day/atm)]	Carbon Dioxide Transmission Rate [nmol/m ² s* GP _a (cc*mil/100 in ² /day/atm)]	Beta Ratio
1	48860 (17450)	50120 (17900)	1.0
2	6440 (2300)	8960 (3200)	1.4
3	15400 (5500)	18060 (6450)	1.2
4	3360 (1200)	N/M	N/M

N/M means "not measured".

The mechanical properties of film samples 1-3 after activation are listed in Table 3.

5

TABLE 3

Sample Number	1	2	3
Dart Impact A	64	93	84
Elmendorf A, CD (g)	198	226	201
Elmendorf A, MD (g)	170	126	137
1% Secant Modulus, CD (ksi/MPa)	41.5/286	33.3/230	34.7/239
2% Secant Modulus, CD (ksi/MPa)	35.7/246	28.6/197	29.6/204
1% Secant Modulus, MD (ksi/MPa)	29.9/207	28.3/195	32.4/223
2% Secant Modulus, MD (ksi/MPa)	27.3/188	25.8/178	28.3/195
CD Tensile			
Yield (psi/MPa)	1567/10.8	1735/12.0	1757/12.1
Yield Strain	13	14	15
Ultimate Strength (psi/MPa)	2136/14.7	2572/17.7	2284/15.8
Strain at break	420	522	446
Toughness (ft*lb/cu. In/ kJ/cm ³)	1225/14.9	1576/19.1	1348/16.3
MD Tensile			
Yield (psi/Mpa)	1766/12.2	1877/12.9	1947/13.4
Yield Strain	14	15	16
Ultimate Strength (psi/Mpa)	3331/23.0	3063/21.2	2741/18.9
% Strain at Break	176	222	168
Toughness (ft*lb/cu. In/kJ/cm ³)	807/9.8	975/11.8	736/8.9

Table 4 reports comparative oxygen transmission data for a number of different films both within and without the invention. This data demonstrates the importance of the nonporous glass bead size/film thickness ratio, activation and presence of glass beads.

TABLE 4

<u>Sample</u>	<u>Bead^{±±}/Film Ratio</u>	<u>Activated/Not Activated</u>	<u>OTR^{**}</u>
5*	0.61	Activated	500
6.1*	0.9	Activated	7500
6.2*	0.9	Not Activated	350
7*	1.0	Activated	2300
8*	1.1	Activated	4000
9 [±]	No Beads	---	800
10 ^{*±}	No Beads	---	1080

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*LDPE 503A (0.923 g/cc, I₂ of 1.9)

[±]ELITE* 5400G, (0.916 g/cc, I₂ of 1.0), 1.5 mil gauge

^{*±}AFFINITY* PL 1850, (0.902 g/cc, I₂ of 3.0), 0.8 mil gauge

^{±±}Nonporous glass beads

10 *Trademark of The Dow Chemical Company

WHAT IS CLAIMED IS:

1. A controlled permeability film comprising:
 - A. A polymeric film having an intrinsic thickness, and
 - B. A crushed, nonporous, inert filler incorporated into the film and having an
5 average particle size such that the ratio of the average particle size of the
filler to the film thickness is 0.67 to 0.99.
2. A controlled permeability film comprising:
 - A. A polymeric film having an intrinsic thickness, and
 - B. A nonporous, inert, particulate filler incorporated into the film and having
10 an average particle size such that the ratio of the average particle size of
the filler to the film thickness is 0.67 to 0.99, the particulate filler
subjected to a compressive force sufficient to crush at least a portion of the
particulate filler.
3. A controlled permeability film comprising:
 - A. A polymeric film having an intrinsic thickness, and
 - B. A nonporous, inert, particulate filler incorporated into the film and having
15 an average particle size such that the ratio of the average particle size of
the filler to the film thickness is 0.67 to 0.99, the film subjected to a
compressive force sufficient to crush at least a portion of the particulate
20 filler.
4. A compressed, controlled permeability film comprising:
 - A. A polymeric film having an intrinsic thickness, and
 - B. A nonporous, inert, particulate filler incorporated into the film and having
25 an average particle size such that the ratio of the average particle size of
the filler to the film thickness is 0.67 to 0.99, at least a portion of the
particulate filler in a crushed state.
5. A method of making a controlled permeability film, the method comprising:
 - A. Blending a film-forming polymer with an inert, nonporous particulate filler
having an average particle size;
 - B. Forming a film from the blend of (A) with an intrinsic thickness such that
30 the ratio of the average particle size of the filler to the film thickness is
0.67 to 0.99, and

- C. Subjecting the film of (B) to a compressive force sufficient to crush at least a portion of the particulate filler.
6. A method of making a controlled permeability film, the method comprising:
- 5 A. Blending a film-forming polymer with an inert, nonporous, crushed particulate filler having an average particle size; and
- B. Forming a film from the blend of (A) with an intrinsic thickness such that the ratio of the average particle size of the filler to the film thickness is 0.67 to 0.99.
7. The film of Claim 1 in which the filler comprises from 0.01 to 15 weight percent of the film.
- 10 8. The film of Claim 1 having a beta ratio of 0.5 to 2.5.
9. The film of Claim 1 comprising a polyolefin polymer.
10. The film of Claim 1 having an intrinsic film thickness of 10 to 125 microns.
11. The film of Claim 1 having a monolayer construction.
- 15 12. The film of Claim 1 having a multilayer construction in which filler is incorporated into a single layer.
13. The film of Claim 1 having a multilayer construction in which the filler is incorporated into at least two layers.
14. The film of Claim 1 in which the filler has an average particle size of 30 to 70 microns.
- 20 15. The film of Claim 1 in which the filler is a spherulitic mineral.
16. The film of Claim 1 in which the filler is a siliceous material.
17. The film of Claim 1 in the form of a bag or a pouch.
18. A package comprising the controlled permeability film of Claim 1.
- 25 19. A method of improving the storage life of a perishable article comprising packaging the article with a controlled permeability film of Claim 1.
20. The film of Claim 1 in which the filler comprises from 0.01 to 5 weight percent of the film.
21. The film of Claim 1 in which the filler comprises from 0.01 to 2 weight percent of the film.
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