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(54) **BREATHABLE PACKAGING FILM HAVING ENHANCED THERMOFORMABILITY**

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(57) **ABSTRACT**

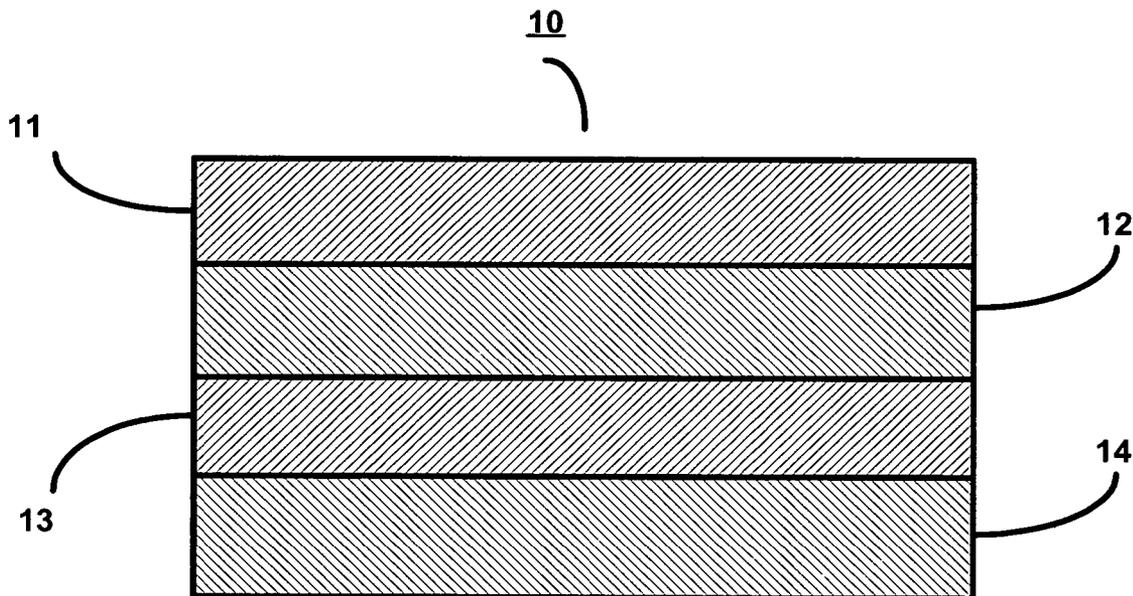
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The present invention describes thermoformable coextruded film suitable for use in packaging applications having at least a first polymeric layer serving as an outermost exterior-film layer and comprising a cycloaliphatic polyester, an aromatic polyester or blends thereof; a second polymeric layer serving as a thermoforming-assist layer and comprising a polyolefin; and a third polymeric layer serving as an innermost exterior-film layer and comprising a heat-sealing polyolefinic material. The films of the present invention are oxygen-permeable in that they exhibit an oxygen transmission rate of between 2-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h.atm.



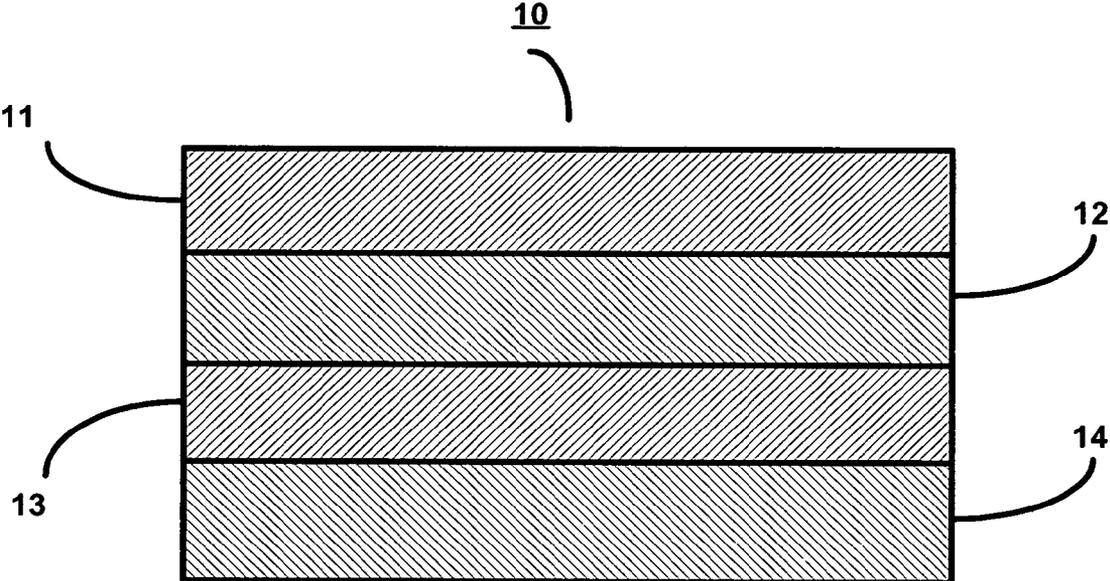
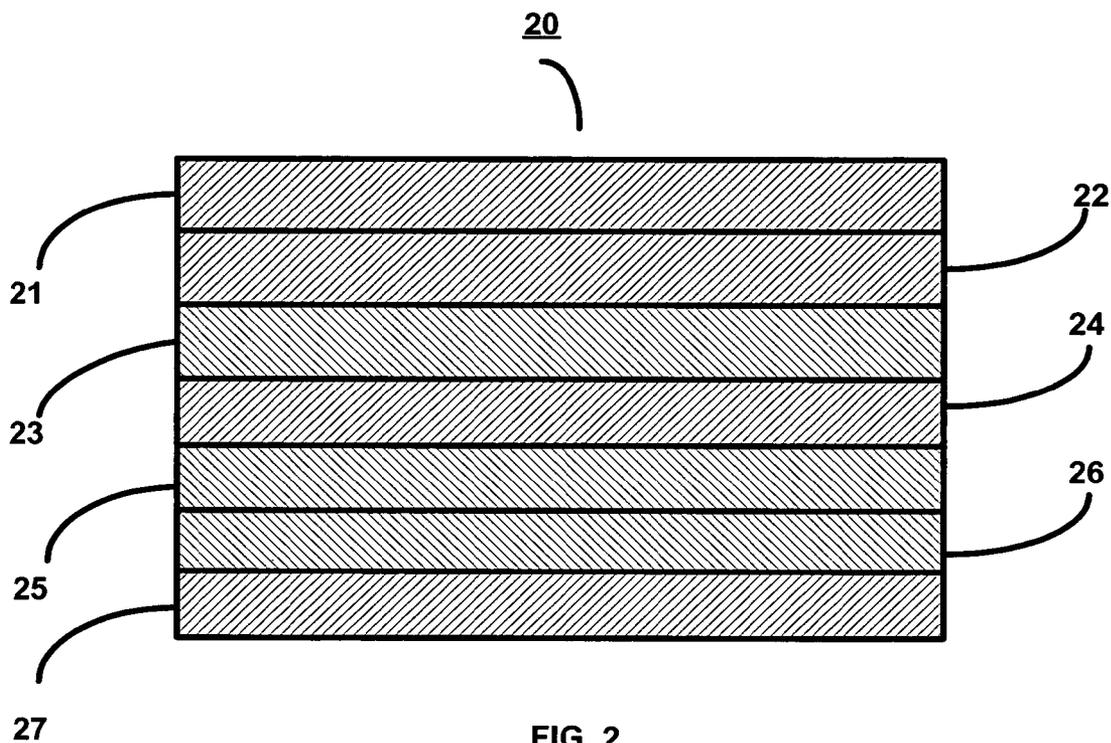


FIG. 1



**BREATHABLE PACKAGING FILM HAVING  
ENHANCED THERMOFORMABILITY**

## FIELD OF THE INVENTION

[0001] The present invention generally relates to food packaging films, and particularly, to thermoformable coextruded packaging films having special utility in the packaging of fresh poultry, meats, fruits and vegetables.

## BACKGROUND OF THE INVENTION

[0002] Thermoforming and other similar techniques are well known in the art for packaging products. Suitable thermoforming methods, for example, include a vacuum forming or plug-assist vacuum forming method. In the vacuum forming method, a first film is heated, for example, by a contact heater and a vacuum is applied beneath the film causing the web to be pushed by atmospheric pressure down into a preformed mold. In a plug-assist vacuum forming method, after the first or forming film has been heated and sealed across a mold cavity, a plug shape similar to the mold shape impinges on the forming film and, upon the application of vacuum, the forming film transfers to the mold surface. After the forming film is in place, a product is placed, such as by manual loading, on the forming film and a second, substantially non-thermoforming film is disposed over the product. At a sealing station, the packages are evacuated and fusion sealed with a sealing device such as a heated jaw. The first or thermoforming film encloses a substantial portion, generally more than half, of the product to be packaged.

[0003] Thermoforming is a popular method of making packaging for food products, particularly, fresh and frozen meats. In the packaging of such products, it is desirable to allow oxygen to permeate a film or package so as to contact the meat product contained therein. For example, a package utilizing a permeable film can permit oxygen to permeate to a fresh red meat in the package, thereby allowing the meat product to oxygenate (often referred to as blooming which causes the meat color to change from purple to a consumer desirable red color). This can enhance consumer appeal, and retail vendors of such meat products demand this type of capability. Additionally, many types of produce require the presence of oxygen to suppress anaerobic spoilage.

[0004] Also in packaging of such products, it is desirable to provide a clear package to permit observation of the enclosed product with the packaging having good optical properties such as clarity and gloss in order to enhance package appearance for the consumer.

[0005] Notwithstanding the fairly high state of development in the art, packaging manufacturers are continually striving to improve the functionality of their packaging materials.

## SUMMARY OF THE INVENTION

[0006] This present invention relates to thermoformable coextruded packaging films which provide oxygen permeability, improved thermoformability and good optical characteristics. It is a more particular object of the present invention to provide a material for packaging food products requiring oxygen permeability such as, for example, fresh poultry, fresh and frozen red meat and fresh produce. The

present invention provides such films which have an oxygen transmission rate at 73° C. and 0% R.H. of between 2-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (31-15,500 cm<sup>3</sup>/m<sup>2</sup>/24 h.) as measured in accordance with ASTM D-3985-02 test method.

[0007] It is another object of the present invention to provide a coextruded packaging film having improved thermoformability. The present invention provides such thermoformable multilayer films which are particularly well suited for forming a package in which the film is molded into a cavity in which a product may be placed. Such multilayer films may be characterized as having a linear free shrink at 80° C. of 0-5% in both the machine and transverse directions as measure in accordance with ASTM D-2732-96 test method.

[0008] It is yet another object of the present invention to provide a thermoformable coextruded packaging film which exhibits exceptional optical properties. The present invention provides multilayer films having a gloss value at 45° of at least 60% as measure in accordance with ASTM D-2457-03 test method and a haze value of less than 20% as measured in accordance with ASTM D-1003-00 test method.

[0009] Such objects generally are achieved by a thermoformable coextruded packaging film having a multilayer film structure comprising at least three polymeric layers which includes a first polymeric layer as an outermost exterior-film layer comprising homopolymers or copolymers of polypropylene an aromatic polyester, a cycloaliphatic polyester or blends thereof, a second polymeric layer as an interior-film, thermoforming-assist layer comprising homopolymers or copolymers of polyolefin, preferably, polypropylene or cross-linked polyethylene, and a third polymeric layer as an innermost exterior-film layer comprising a heat-sealing polyolefin.

[0010] Such objects more particularly may be achieved by above-described film structures which include a first polymeric layer comprising an aromatic ester derived from homopolymers and copolymers of alkyl-aromatic esters, such as, for example, polyethylene terephthalate ("PET"), amorphous polyethylene terephthalate ("APET"), crystalline polyethylene terephthalate ("CPET"), glycol-modified polyethylene terephthalate ("PETG"), and polybutylene terephthalate; copolymers of isophthalate, such as, polyethylene terephthalate/isophthalate copolymer, or cycloaliphatic esters, and blends of any of the aforementioned materials. The films may include layers in addition to those described above. For instance, the multilayer films of the present invention may include a film structure comprising a fourth polymeric layer such as a tie layer positioned between the first polymeric layer and the second polymeric layer. Preferably, the fourth layer includes a material derived from polyalkyl acrylate copolymers, more preferably, ethylene/alkyl acrylate copolymers, and most preferably, a material selected from the group consisting of ethylene/methyl acrylate copolymer ("E/MA"), ethylene/ethyl acrylate copolymer ("E/EA"), ethylene/butyl acrylate copolymer ("E/BA"), and ethylene/methyl methacrylate copolymer ("E/MMA").

[0011] These and other aspects, advantages, and features of the invention will be more readily understood and appreciated by reference to the detailed description of the invention and the drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is a partially schematic, cross-sectional view of one embodiment of a multilayer packaging film according to the present invention comprising four layers.

[0013] FIG. 2 is a partially schematic, cross-sectional view of another embodiment of a multilayer film according to the present invention comprising seven layers.

## DETAILED DESCRIPTION OF THE INVENTION

[0014] As used herein, the term “film” is used in the generic to include plastic web, regardless of whether it is a film or sheet.

[0015] As used herein, the phrase “thermoplastic” refers to a polymer or polymer mixture that softens when exposed to heat and returns to its original condition when cooled to room temperature. In general, thermoplastic materials include, but are not limited to, synthetic polymers such as polyesters, polyolefins, polyamides, polystyrenes, and the like. Thermoplastic materials may also include synthetic polymers that are cross-linked by either radiation or chemical reaction during a manufacturing or post-manufacturing process operation.

[0016] As used herein, the term “polymeric” refers to a material which is the product of a polymerization reaction of natural, synthetic, or natural and synthetic ingredients, and is inclusive of homopolymers, copolymers, terpolymers, etc. In general, the layers of a film or substrate may comprise a single polymer, a mixture of a single polymer and non-polymeric materials, a combination of two or more polymeric materials blended together, or a mixture of a blend of two or more polymeric materials and non-polymeric materials.

[0017] As used herein, the term “copolymer” refers to polymers formed by the polymerization reaction of at least two different monomers. For example, the term “copolymer” includes the co-polymerization reaction product of ethylene and an  $\alpha$ -olefin, such as 1-hexene. The term “copolymer” is also inclusive of, for example, the co-polymerization of a mixture of ethylene, propylene, 1-butene, 1-hexene, and 1-octene. As used herein, a copolymer identified in terms of a plurality of monomers, e.g., “propylene/ethylene copolymer”, refers to a copolymer in which either monomer may copolymerize in a higher weight or molar percent than the other monomer or monomers. However, the term “copolymer” as applied to film layers of the present invention refers to the first listed monomer polymerized in a higher weight percent than the second listed monomer.

[0018] As used herein, terminology employing a “/” with respect to the chemical identity of a copolymer (e.g., polyvinylidene chloride/methyl acrylate copolymer), identifies the comonomers which are copolymerized to produce the copolymer.

[0019] As used herein, the phrase “oxygen transmission rate” also known as “OTR” is measured according to ASTM D-3985-02 test method, a test known to those skilled in the art. The oxygen transmission rate refers to the quantity of oxygen gas passing through a unit area of the parallel surfaces of a film per unit time under the conditions of test, i.e.,  $\text{cm}^3/100 \text{ in.}^2/24 \text{ h.}$  or  $\text{cm}^3/\text{m}^2/24 \text{ h.}$  The OTR of a film

is measured after the film sample has equilibrated in a dry test environment and at standard temperature and pressure conditions (STP) or at temperature and/or pressure conditions as stated otherwise. Standard temperature and pressure conditions for measuring oxygen transmission rate are 32° F. (0° C.) and 1 atmosphere of pressure (0.1013 MPa). The “dry” environment is considered to be one in which the relative humidity is less than 1%.

[0020] As used herein, the term “thermoformable” as applied to the present invention refers to films which are capable of being formed into a desired shape upon the application of heat, and are thermoformed about the product on a support member by means of heat and differential pressure. In the thermoforming process, virtually all of the air is evacuated from the interior of the package so that the film conforms very closely to the contour of the packaged product.

[0021] As used herein, the phrase “unrestrained linear thermal shrinkage”, also known as “linear free heat shrinkage”, refers to the irreversible and rapid reduction in linear dimension in a specified direction occurring in film subjected to elevated temperatures under conditions where nil or negligible restraint to inhibit shrinkage is present. It is normally expressed as a percentage of the original dimension. As a result of the manufacturing process, internal stresses may be locked into the film which can be released by heating. The temperature at which shrinkage will occur is related to the processing techniques employed to manufacture the film and may also be related to a phase transition in the base resin. Thermoformable films according to the present invention may be characterized as having a low unrestrained linear thermal shrinkage, preferably, an unrestrained linear thermal shrinkage at 80° C. of less than 20%, more preferably, less than 10%, and most preferably, between 0-5% in both the machine and the transverse directions, as measured in accordance with ASTM D-2732-96 test method.

[0022] As used herein, the term “coextrusion” refers to the process of extruding two or more materials through a single die with two or more orifices arranged so that the extrudates merge and weld together into a laminar structure before chilling (chilling may also be termed quenching). The thermoformable films of the present invention may be formed using a coextrusion process, preferably, blown film coextrusion, cast film coextrusion, or extrusion coating, more preferably, blown film coextrusion, cast film coextrusion, and most preferably, blown film coextrusion.

[0023] As used herein, the term “polyester” refers to homopolymers or copolymers having an ester linkage between monomer units which may be formed, for example, by condensation polymerization reactions between a dicarboxylic acid and a glycol. The ester can be represented by the general formula:  $[\text{R}-\text{C}(\text{O})\text{O}-\text{R}']$  where R and R'=alkyl group. The dicarboxylic acid may be linear or aliphatic, i.e., oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, and the like; or may be aromatic or alkyl substituted aromatic, i.e., various isomers of phthalic acid, such as paraphthalic acid (or terephthalic acid), isophthalic acid and naphthalic acid. Specific examples of alkyl substituted aromatic acids include the various isomers of dimethylphthalic acid, such as dimethylisophthalic acid, dimethylorthophthalic

acid, dimethylterephthalic acid, the various isomers of diethylphthalic acid, such as diethylisophthalic acid, diethylorthophthalic acid, the various isomers of dimethylnaphthalic acid, such as 2,6-dimethylnaphthalic acid and 2,5-dimethylnaphthalic acid, and the various isomers of diethylnaphthalic acid. The glycols may be straight-chained or branched. Specific examples include ethylene glycol, propylene glycol, trimethylene glycol, 1,4-butane diol, neopentyl glycol and the like. Suitable materials of aromatic polyesters for use in the present invention include, but are not limited to, polyethylene terephthalate (PET), amorphous polyethylene terephthalate (APET), crystalline polyethylene terephthalate (CPET), glycol-modified polyethylene terephthalate (PETG), and polybutylene terephthalate; copolymers of isophthalate, such as, polyethylene terephthalate/isophthalate copolymer; and the like.

[0024] As used herein, the phrase “cycloaliphatic polyester” refers to copolymers derived from a dicarboxylic acid component consisting of 1,4-cyclohexanedicarboxylic, a diol component consists of 1,4-cyclohexanedimethanol and polytetramethyleneether glycol. Cycloaliphatic polyesters are well known in the art and are described, for example, in U.S. Pat. Nos. 3,023,192; 3,261,812; 3,651,014; 4,003,882; 4,221,703; and 4,349,469, all of which are incorporated herein by reference.

[0025] As used herein, the phrase “polyolefin” refers to homopolymers, copolymers, including e.g. bipolymers, terpolymers, block copolymer, grafted copolymers, etc., having a methylene linkage between monomer units which may be formed by any method known to those skill in the art. Examples of polyolefins include polyethylene (“PE”) which include, but are not limited to, low-density polyethylene (“LDPE”), linear low-density polyethylene (“LLDPE”), very low-density polyethylene (“VLDPE”), ultra low-density polyethylene (“ULDPE”), medium-density polyethylene (“MDPE”), high-density polyethylene (“HDPE”), ultra high-density polyethylene (“UHDPE”), and polyethylenes comprising ethylene/ $\alpha$ -olefin (“E/AO”) which are copolymers of ethylene with one or more  $\alpha$ -olefins (alpha-olefins) such as butene-1, hexene-1, octene-1, or the like as a comonomer, and the like.

[0026] As used herein, the phrase “ethylene/ $\alpha$ -olefin”, also known as “EAO” refers to a modified or unmodified copolymer produced by the co-polymerization of ethylene and any one or more  $\alpha$ -olefin. The  $\alpha$ -olefin in the present invention has between 3-20 pendant carbon atoms, preferably, 3-12 pendant carbon atoms and more preferably, 3-6 pendant carbon atoms. The co-polymerization of ethylene and an  $\alpha$ -olefin may be produced by heterogeneous catalysis, i.e., co-polymerization reactions with Ziegler-Natta catalysis systems, for example, metal halides activated by an organometallic catalyst, i.e., titanium chloride, optionally containing magnesium chloride, complexed to trialkyl aluminum and maybe found in patents such as U.S. Pat. No. 4,302,565 to Goeke, et al. and U.S. Pat. No. 4,302,566 to Karol, et al., both of which are hereby incorporated, in their entireties, by reference thereto. Heterogeneous catalyzed copolymers of ethylene and an  $\alpha$ -olefin may include linear low density polyethylene, very low density polyethylene and ultra low density polyethylene. These copolymers of this type are available from, for example, The Dow Chemical Company, of Midland, Mich., U.S.A. and sold under the trademark DOWLEX™ resins. Additionally, the co-poly-

merization of ethylene and a  $\alpha$ -olefin may also be produced by homogeneous catalysis, for example, co-polymerization reactions with metallocene catalysis systems which include constrained geometry catalysts, i.e., monocyclopentadienyl transition-metal complexes taught in U.S. Pat. No. 5,026,798, to Canich, the teachings of which are incorporated herein by reference. Homogeneous catalyzed ethylene/ $\alpha$ -olefin copolymers may include ethylene/ $\alpha$ -olefin copolymers available from The Dow Chemical Company, known as AFFINITY™ and ATTANE™ resins, TAFMER™ linear copolymers obtainable from the Mitsui Petrochemical Corporation of Tokyo, Japan and ethylene/ $\alpha$ -olefin copolymers known as EXACT™ resins obtainable from ExxonMobil Chemical Company of Houston, Tex., U.S.A.

[0027] As used herein, the terms “heat-seal”, “heat-sealing”, “heat-sealable”, and the like refer to a first portion of a film surface (i.e., formed from a single layer or multiple layers) which is capable of forming a fusion bond to a second portion of a film surface. A heat-seal layer is capable of fusion bonding by conventional indirect heating means which generate sufficient heat on at least one film contact surface for conduction to the contiguous film contact surface and formation of a bond interface therebetween without loss of the film integrity. It should be recognized that heat sealing can be performed by any one or more of a wide variety of manners, such as using a heat seal technique (e.g., melt-bead sealing, thermal sealing, impulse sealing, ultrasonic sealing, hot air, hot wire, infrared radiation, etc.) and most often involves application of heat and pressure for a time sufficient to create a seal upon cooling.

[0028] As used herein, the phrase “innermost exterior-film layer” as applied to film layers of the present invention refers to the exterior-film layer which is closest to the product relative to the other layers of the multilayer film. The phrase “exterior-film layer” as applied to film layers refers to any film layer having less than two of its principal surfaces directly adhered to another layer of the substrate or another substrate. In contrast, the phrase “outermost exterior-film layer”, as used herein refers to the exterior-film layer which is furthest from the product relative to the other layers of the multilayer film.

[0029] As used herein, the phrase “interior-film layer” as applied to film layers refers to any film layers having both of its principal surfaces directly adhered to another layer of the film.

[0030] As used herein, the phrase “gloss” refers to the specular gloss of the films of the present invention, which is a measure of the relative luminous reflectance factor of a specimen in the mirror direction. The relative luminous reflectance factor is the amount of light reflected by the surface of the specimen in reference to a standard and the angle of reflection (20°, 45°, 60° or 85°). Gloss as it refers to the present invention, means that property of a film measured according to ASTM D-2457-03 test method. The specular gloss of the films of the present invention are determined by using BYK Gardner micro TRI Glossmeter.

[0031] As used herein, the phrase “haze” refers to that percentage of transmitted light which in passing through the film specimen deviates from the incident beam by forward scattering, and which is measured in accordance with ASTM D-1003-00 test method, a test known to those skilled in the art.

[0032] As used herein, the phrase “tie layer” refer to any film layer which functions to adhere two layers to one another. The tie layer may comprise any polymer, copolymer or blend of polymers having a polar group thereon, or any other polymer, copolymer or blend of polymers which provide sufficient interlayer adhesion to adjacent layers comprising otherwise nonadhering polymers. Suitable materials for use as tie layers in the present invention may include, but are not limited to, ionomers, ethylene/vinyl acetate copolymers (E/VA), anhydride-modified ethylene/vinyl acetate copolymers (“m-E/VA”), ethylene/methacrylic acid copolymers (“E/MAA”), ethylene/methyl acrylate copolymers (E/MA), ethylene/ethyl acrylate copolymers (E/EA), anhydride-modified ethylene/ $\alpha$ -olefin copolymers (“m-E/AO”), anhydride-modified polyolefins, such as anhydride-modified polyethylene (“m-PE”), or a blend thereof.

[0033] As used herein, the term “anhydride-modified” refers to any form of anhydride functionality, such as the anhydride of maleic acid, fumaric acid, etc., whether copolymerized with an anhydride-containing monomer with a second, different monomer, grafted onto a polymer or copolymer, or blended with one or more polymers, and is inclusive of derivatives of such functionalities, such as acids, esters, and metal salts derived therefrom.

[0034] As used herein, the phrase “bulk layer” refers to any film layer which serves to increase the abuse resistance, toughness, and modulus of a multilayer film.

[0035] As used herein, the phrase “thermoforming-assist layer” refers to any interior-film layer which functions to increase the integrity of the multilayer film while the film is heated and drawn into a cavity during the thermoforming process.

[0036] As used herein, the phrase “machine direction” refers to a direction “along the length” of the film, i.e., in the elongate direction of the film as the film is formed during extrusion, lamination, and/or coating.

[0037] As used herein, the phrase “transverse direction” refers to a direction across the film, perpendicular to the machine or longitudinal direction.

[0038] The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete and will fully convey the scope of the invention to those skilled in the art.

[0039] Referring to FIG. 1, film 10 is a schematic, cross-sectional view of one embodiment of a multilayered film according to the present invention comprising a first polymeric layer 11, a second polymeric layer 12, a third polymeric layer 13, and a fourth polymeric layer 14. Film 10 has four layers: two exterior-film layers (11, 14); and two interior-film layers (12, 13). As depicted, polymeric first layer 11 is an innermost exterior-film layer which may comprise either a cycloaliphatic polyester or an aromatic polyester, such as, for example, polyethylene terephthalate (PET). Layer 12 is an interior-film tie layer and may comprise any adhesive material which serves to adhere layer 11 and 13 to itself. Preferably, layer 12 comprises an

adhesive material derived from copolymers of ethylene and an alkyl acrylate, i.e., for example, ethylene/methacrylate copolymers (E/MA). Layer 13 serves as a thermoforming-assist layer and may comprise any polyolefin, preferably, either a homopolymer or copolymer of polypropylene (PP) or a homopolymer or a copolymer of a cross-linked polyethylene (PE). Layer 14 is an innermost exterior-film layer which includes a heat-sealing material, preferably, a heat-sealing polyolefin. Suitable heat-sealable polyolefins for use in layer 14 may include, but are not limited to, for example, polyethylene (PE), which includes ultra low-density polyethylene (ULDPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), medium-density polyethylene (MDPE), polypropylene (PP), ethylene/vinyl acetate (E/VA), copolymers of ethylene or propylene with one or more  $\alpha$ -olefins, and ionomers. Other examples of suitable heat-sealable polyolefins include cyclic olefin copolymers (COC), ethylene/propylene copolymers (PE/P), polypropylene (PP), propylene/ethylene copolymer (PP/E), polyisoprene, polybutylene (PB), polybutene-1, poly-3-methylbutene-1, and copolymers of ethylene and 4-methylpentene-1, and the like.

[0040] It will be appreciated that films according to the present invention are not limited to the four-layered structure, i.e., layers 11, 12, 13, and 14, provided that layers 11 and 14 are positioned as exterior-film layers and layer 13 is an interior-film layer which functions as a thermoforming-assist layer. Layer 13 may be placed in any position within the film structure and, preferably, is in direct contact with layer 11, by either a fusion bond to layer 11 or through contact with tie layer 12. It is within the scope of the present invention that additional interior layers may be included in the film structure provided that the oxygen transmittability of the entire structure does not decrease below  $2 \text{ cm}^3/100 \text{ in}^2/24 \text{ h.}$  ( $31 \text{ cm}^3/\text{m}^2/24 \text{ h.}$ ) as measured in accordance with ASTM D-3985-02. Thus, the film of this invention may include any number of additional layers in any position between either outermost exterior-film layer 11 and innermost exterior-film layer 14 or between interior-film layer 13 and innermost exterior-film layer 14. It is contemplated that the films of the present invention may comprise at least three layers, and may include a total of four layers, five layers, seven layers, or any number of layers so desired.

[0041] Turning now to FIG. 2, film 20 is schematic, cross-sectional view of one embodiment of a multilayered film according to the present invention comprising a seven-layer film structure. Film 20 includes a first polymeric layer 21, a second polymeric layer 22, a third polymeric layer 23, a fourth polymeric layer 24, a fifth polymeric layer 25, a sixth polymeric layer 26, and a seventh polymeric layer 27, in which there exists two exterior-film layers (21, 27), and five interior-film layers (22, 23, 24, 25, 26). Layers 21, 22 and 23 may each have identical compositions and substructure as described for layers 11, 12 and 13, respectively, of film 10, as described hereinabove. As depicted, layer 21 is an outermost exterior-film layer and layers 22 and 23 being both interior-film layers which serve as a tie layer and thermoforming-assist layer, respectively. Layers 24 and layer 25 function as bulk layers and may both be formed from the same material or different materials. Preferably, layers 24 and 25 comprise any thermoplastic material, more preferably, any polyolefin resin, and most preferably, homopolymers and copolymers of polyethylene (PE), polypropylene (PP), polybutylene (PB) or blends thereof.

Layer **26** is an interior-film layer which may serve as either a bulk layer or a tie layer. As a bulk layer, layer **26** preferably comprises any thermoplastic material, more preferably, any polyolefin resin, and most preferably, homopolymers and copolymers of polyethylene (PE), polypropylene (PP), polybutylene (PB) or blends thereof. As a tie layer, layer **26** preferably comprises any adhesive material which bonds layers **25** and **27** to itself. Suitable polyolefins include, but are not limited to, for example, homopolymers and copolymers of polyethylene (PE), polypropylene (PP), polybutylene (PB) or blends thereof. It is preferred that the modified polyolefin comprise anhydride-modified polyolefin, which, but are not limited to, ionomers, ethylene/vinyl acetate copolymers (E/VA), anhydride-modified ethylene/vinyl acetate copolymers (m-E/VA), ethylene/methacrylic acid copolymers (E/EAA), ethylene/methyl acrylate copolymers (E/MA), ethylene/ethyl acrylate copolymers (E/EA), anhydride-modified ethylene/ $\alpha$ -olefin copolymers (m-E/AO), anhydride-modified polyolefins, such as anhydride-modified polyethylene (m-PE), or a blend thereof.

[0042] It will also be recognized by those skilled in the art that films **10**, **20** and any variations thereof may be used to form flexible, semi-rigid and rigid containers, packages, pouches or any portion thereof. In general the films and packages of the present invention can be used in the packaging of any product, the films and packages of the present invention are especially advantageous for the packaging of food products, especially fresh meat products. Among the fresh meat product which can be packaged in the films and packages according to the present invention are poultry, pork, beef, lamb, goat, horse, and fish.

[0043] It will be appreciated that the thicknesses of each of films **10**, **20** and any variations thereof may vary and equal thicknesses in the **FIGS. 1 and 2** are presented only to facilitate illustration.

[0044] It will also be appreciated that the films of the present invention have an oxygen transmission rate at 73° C. and 0% R.H. of preferably between 2-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (31-15,500 cm<sup>3</sup>/m<sup>2</sup>/24 h.), more preferably, between 10-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (155-15,500 cm<sup>3</sup>/m<sup>2</sup>/24 h.), and most preferably, between 20-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (310-15,500 cm<sup>3</sup>/m<sup>2</sup>/24 h.) as measured in accordance with ASTM D-3985-02 test method.

[0045] The films of the present invention may be formed by any conventional technique for forming films, including extrusion lamination, cast extrusion, extrusion coating, and coextrusion, preferably, extrusion coating, cast coextrusion or blown film coextrusion, and more preferably, cast coextrusion or blown film coextrusion, most preferably, blown coextrusion. In blown coextrusion, for example, the films of the present invention may be produced by a single-bubble blown film process. In this process a tubular film is produced using one or more extruders (the number of extruders depends upon the number of layers in the film and each layer composition). The polymer resins extruded by the extruders are fed to a circular die head through which the film layers are forced and formed into a cylindrical multilayer film bubble. The bubble is extruded therefrom through an air ring and quenched e.g., via cooled water bath, solid surface and/or air, and then ultimately collapsed and formed into a multilayer film.

[0046] In the practice of this invention, it may be desirable to have one or more layers of the entire film cross-linked to

improve the thermoformability, abuse and/or puncture resistance and/or other physical characteristics of the entire film. Crosslinking is the predominant reaction which results in the formation of carbon-carbon bonds between polymer chains. Crosslinking may be accomplished, for example, by ionized radiation means such as high energy electrons, gamma-rays, beta particles and the like, or through chemical means by use of peroxides and the like. More particularly, for crosslinking with ionizing radiation, the energy source can be any electron beam generator operating in a range of about 150 kilovolts to about 6 megavolts with a power output capable of supplying the desired dosage. The voltage can be adjusted to appropriate levels which may be for example 1 to 6 million volts or higher or lower. Many apparatus for irradiating films are known to those skilled in the art. The films of the present invention may be irradiated at a level of from 2-12 MRads, more preferably 2-5 MRads. The most preferred amount of radiation is dependent upon the film and its end use.

[0047] One method for determining the degree of "crosslinking" or the amount of radiation absorbed by a material is to measure the gel content in accordance with ASTM D-2765-01 which is hereby incorporated, in its entirety, by reference. Gel content corresponds to the relative extent of crosslinking within a polymeric material having undergone irradiation.

[0048] Preferably, the coextruded multilayered packaging film of the present invention can have any total film thickness desired, preferably thicknesses may range between 0.8-15 mils (20.32-381  $\mu$ m), more preferably, between 0.8-10 mils (20.32-254  $\mu$ m), and most preferably, between 0.8-8.0 mil (20.32-203.2  $\mu$ m).

#### EXAMPLES

[0049] The invention is illustrated by the following examples, which are provided for the purpose of representation, and are not to be construed as limiting the scope of the invention.

[0050] Unless otherwise noted, the thermoplastic resins utilized in the present invention are generally commercially available in pellet form and, as generally recognized in the art, may be melt blended or mechanically mixed by well-known methods using commercially available equipment including tumblers, mixers or blenders. Also, if desired, well known additives such as processing aids, slip agents, anti-blocking agents and pigments, and mixtures thereof may be incorporated into the film, by blending prior to extrusion. The resins and any additives are introduced to an extruder where the resins are melt plastified by heating and then transferred to an extrusion (or coextrusion) die for formation into a tube. Extruder and die temperatures will generally depend upon the particular resin or resin containing mixtures being processed and suitable temperature ranges for commercially available resins are generally known in the art, or are provided in technical bulletins made available by resin manufacturers. Processing temperatures may vary depending upon other processing parameters chosen.

[0051] For the following examples, a single slash, "/", represents the division between individual layers within a film structure.

#### Example 1

[0052] Example 1 is one embodiment of the present invention of a film having seven layers (see film **20** in **FIG. 2**).

The first polymeric layer (21) comprised a mixture of polyester, anti-block additive and slip additive. The polyester comprised polyethylene terephthalate copolymer having a density of 1.4 g/cm<sup>3</sup>, a melting point of 240° C., a tensile strength at break (machine direction/transverse direction) of 8.4/5.6 kpsi, and is available under the trademark Voridian™ Polymer 9921 from Eastman Chemical Company, Kingsport, Tenn., U.S.A. In Example 1, the second layer (22) was a tie layer comprising ethylene/methyl acrylate copolymer (E/MA) and modified linear low-density polyethylene (m-LLDPE). The ethylene/methyl acrylate copolymer has a density of 0.948 g/cm<sup>3</sup>, a melting point of 49° C., a melt index of 2.0 g/10 min., and is available from Eastman Chemical Company, Kingsport, Tenn., U.S.A. The modified linear low-density polyethylene was an anhydride linear low-density polyethylene having a density of 0.92 g/cm<sup>3</sup>, a melting point of 125° C., a melt index of 1.5 g/10 min., a Vicat softening point of 102° C., and is available under the trademark Bynel® from E. I. du Pont de Nemours and Company, Wilmington, Del., U.S.A. The third layer (23) and the sixth layer (26) each comprised a polypropylene random copolymer (PP) having a melt index of 2 g/10 min., a tensile strength at break of 4.5 kpsi, and is sold as Grade 8244 from BP Amoco Polymers, Inc., Naperville, Ill., U.S.A. The fourth layer (24) and the fifth layer (25) each comprised an ultra low-density polyethylene (ULDPE), particularly, an ethylene/octene  $\alpha$ -olefin copolymer (E/AO) having a density of 0.912 g/cm<sup>3</sup>, a melting point of 123° C., a melt index of 1.0 g/10 min., a Vicat softening point of 93° C., a is available under the trademark Attane 4201G from The Dow Chemical Company, Midland, Mich., U.S.A. The seventh layer (27) comprised polyethylene (PE) and anti-block additive. The polyethylene was identical to that used in the fourth and fifth layers of the film. The Example 1 was produced having an overall film thickness of about 5 mil and with the following structure and relative layer thicknesses, beginning with the outermost exterior-film layer and going to the innermost exterior-film layer (left to right):

**[0053]** 5% PET/15% E/MA/10% PP/12% PE/8% PE/27% PP/23% PE

Example 1 had an oxygen transmission rate at 73° C. and 0% R.H. of 40 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (620 cm<sup>3</sup>/m<sup>2</sup>/24 h.) as measured in accordance with ASTM D-3985-02 test method.

#### Example 2

**[0054]** In Example 2, the film is another example of a seven-layer embodiment of the present invention. All the film layers are identical in structure and relative layer thickness as that used in Example 1, except that the overall film thickness was about 8 mil.

**[0055]** Example 2 had an oxygen transmission rate at 73° C. and 0% R.H. of 20 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (310 cm<sup>3</sup>/m<sup>2</sup>/24 h.) as measured in accordance with ASTM D-3985-02 test method.

**[0056]** Unless otherwise noted, the physical properties and performance characteristics reported herein were measured by test procedures similar to the following methods. The following ASTM test procedures are each incorporated herein by reference in their entireties.

Density	ASTM D-1505
Gel Content	ASTM D-2765-01
Gloss	ASTM D-2457-03
Haze	ASTM D-1003-00
Unrestrained Linear Thermal Shrinkage	ASTM D-2732-96
Melt Index	ASTM D-1238
Melting Point	ASTM D-3417
Oxygen Transmission Rate	ASTM D-3985-02
Tensile Strength at Break	ASTM D-882
Vicat Softening Temperature	ASTM D-1525

**[0057]** Many modifications and other embodiments of the invention will come to mind to one skilled in the art to which this invention pertains having the benefit of the teachings presented in the foregoing descriptions and the associated drawings. Therefore, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

What is claimed is:

1. A thermoformable coextruded packaging film comprising:
  - (a) at least a first polymeric layer, a second polymeric layer, and a third polymeric layer;
  - (b) wherein said first polymeric layer is an outermost exterior-film layer and comprises a material selected from the group consisting of cycloaliphatic polyesters, polyethylene terephthalate (PET), polyethylene terephthalate glycol (PETG), polypropylene terephthalate (PPT), polybutylene terephthalate (PBT) and blends thereof;
  - (c) wherein said second polymeric layer comprises polypropylene or cross-linked polyethylene;
  - (d) wherein said third polymeric layer is an innermost exterior-film layer comprising a heat-sealable polyolefin;
  - (e) wherein said film has an oxygen transmission rate at 73° C. and 0% R.H. of between 2-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (31-15,500 cm<sup>3</sup>/m<sup>2</sup>/24 h.) as measured in accordance with ASTM D-3985-02 test method; and
  - (f) wherein said film comprises an unrestrained linear thermal shrinkage at 80° C. of 0-20% in both the machine and transverse direction as measured in accordance with ASTM D-2732-96 test method.
2. A thermoformable coextruded packaging film according to claim 1, wherein said film is formed by blown film coextrusion.
3. A thermoformable coextruded packaging film according to claim 1, wherein said first polymeric layer, said second polymeric layer, and said third polymeric layer are free of polyamide.
4. A thermoformable coextruded packaging film according to claim 1, wherein said film comprises an unrestrained linear thermal shrinkage at 80° C. of 0-10% in both the machine and transverse direction as measured in accordance with ASTM D-2732-96 test method.

5. A thermoformable coextruded packaging film according to claim 4, wherein said film comprises an unrestrained linear thermal shrinkage at 80° C. of 0-5% in both the machine and transverse direction as measured in accordance with ASTM D-2732-96 test method.

6. A thermoformable coextruded packaging film according to claim 1, wherein said film comprises a gloss value at 45° of at least 60% as measured in accordance ASTM D-2457-03 test method.

7. A thermoformable coextruded packaging film according to claim 1, wherein said film comprises a haze value of less than 20% as measured in accordance with ASTM D-1003-00 test method.

8. A thermoformable coextruded packaging film according to claim 1, wherein said film has an oxygen transmission rate at 73° C. and 0% R.H. of between 10-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (155-15,500 cm<sup>3</sup>/m<sup>2</sup>/24 h.) as measured in accordance with ASTM D-3985-02 test method.

9. A thermoformable coextruded packaging film according to claim 1, wherein said film has an oxygen transmission rate at 73° C. and 0% R.H. of between 20-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (310-15,500 cm<sup>3</sup>/m<sup>2</sup>/24 h.) as measured in accordance with ASTM D-3985-02 test method.

10. A thermoformable coextruded packaging film according to claim 1, wherein said third polymeric layer comprises polyethylene.

11. A thermoformable multilayer packaging film according to claim 1, wherein said film further comprises a fourth polymeric layer disposed between said first and second polymeric layers.

12. A thermoformable coextruded packaging film according to claim 11, wherein said film further comprises a fifth polymeric layer disposed between said second and third polymeric layers.

13. A thermoformable coextruded packaging film according to claim 11, wherein said fourth polymeric layer comprises a polyalkyl acrylate copolymer or blend thereof.

14. A thermoformable coextruded packaging film according to claim 13, wherein said polyalkyl acrylate copolymer comprises an ethylene/alkyl acrylate copolymer or blends thereof.

15. A thermoformable coextruded packaging film according to claim 14, wherein said ethylene/alkyl acrylate copolymers comprise a material selected from the group consisting of ethylene/methyl acrylate copolymer (E/MA), ethylene/ethyl acrylate copolymer (E/EA), ethylene/butyl acrylate copolymer (E/BA), and ethylene/methyl methacrylate copolymer (E/MMA).

16. A thermoformable coextruded packaging film according to claim 12, wherein said fifth polymeric layer comprises a material selected from the group consisting of polypropylene, polyethylene, anhydride-modified polyolefin and blends thereof.

17. A thermoformable coextruded packaging film according to claim 12, wherein said film further comprises a sixth polymeric layer and a seventh polymeric layer.

18. A thermoformable coextruded packaging film according to claim 17, wherein said sixth and seventh polymeric layers each comprises a material selected from the group consisting of polyethylene, polypropylene and blends thereof.

19. A thermoformable coextruded packaging film according to claim 1, wherein said film has a thickness range between 0.8-15 mils (20.32-381 μm).

20. A thermoformable coextruded packaging film according to claim 19, wherein said film has a thickness range between 0.8-10 mils (20.32-254 μm).

21. A thermoformable coextruded packaging film according to claim 20, wherein said film has a thickness range between 0.8-8.0 mil (20.32-203.2 μm).

22. A thermoformable coextruded packaging film according to claim 1, wherein said film forms a package or a portions thereof.

23. A thermoformable coextruded packaging film comprising:

(a) at least a first polymeric layer, a second polymeric layer, a third polymeric layer, a fourth polymeric layer, and a fifth polymeric layer;

(b) wherein said first polymeric layer is an outermost exterior-film layer and comprises a material selected from the group consisting of cycloaliphatic polyesters, polyethylene terephthalate (PET), polyethylene terephthalate glycol (PETG), polypropylene terephthalate (PPT), polybutylene terephthalate (PBT) and blends thereof;

(c) wherein said second polymeric layer is directly contacting said first and third polymeric layers and comprises an polyalkyl acrylate copolymer or blend thereof;

(d) wherein said third polymeric layer is directly contacting said second and fourth polymeric layers and comprises either polypropylene or cross-linked polyethylene;

(e) wherein said fourth polymeric layer is directly contacting said third and fifth polymeric layers and comprises a material selected from the group consisting of polyethylene, polypropylene, anhydride-modified polyolefin and blends thereof;

(f) wherein said fifth polymeric layer is directly contacting said fourth and sixth polymeric layers and comprises a heat-sealable polyolefin;

(g) wherein said film has an oxygen transmission rate at 73° C. and 0% R.H. of between 2-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (31-15,500 cm<sup>3</sup>/m<sup>2</sup>/24 h.) as measured in accordance with ASTM D-3985-02 test method; and

(h) wherein said film comprises an unrestrained linear thermal shrinkage at 80° C. of 0-5% in both the machine and transverse direction as measured in accordance with ASTM D-2732-96 test method.

24. A thermoformable coextruded packaging film according to claim 23, wherein said film is formed by blown film coextrusion.

25. A thermoformable coextruded packaging film comprising:

(a) at least a first polymeric layer, a second polymeric layer, a third polymeric layer, a fourth polymeric layer, a fifth polymeric layer, a sixth polymeric layer, and a seventh polymeric layer;

(b) wherein said first polymeric layer is an outermost exterior-film layer and comprises a material selected from the group consisting of cycloaliphatic polyesters, polyethylene terephthalate (PET), polyethylene tereph-

thalate glycol (PETG), polypropylene terephthalate (PPT), polybutylene terephthalate (PBT) and blends thereof.;

- (c) wherein said second polymeric layer is directly contacting said first and third polymeric layers and comprises a polyalkyl acrylate copolymer of blend thereof;
- (d) wherein said third polymeric layer is directly contacting said second and fourth polymeric layers and comprises either polypropylene or cross-linked polyethylene;
- (e) wherein said fourth polymeric layer is directly contacting said third and fifth polymeric layers and comprises a material selected from the group consisting of polyethylene, polypropylene and blends thereof;
- (f) wherein said fifth polymeric layer is directly contacting said fourth and sixth polymeric layers and comprises a material selected from the group consisting of polyethylene, polypropylene and blends thereof;
- (g) wherein said sixth polymeric layer is directly contacting said fifth and seventh polymeric layers and comprises a material selected from the group consisting of polyethylene, polypropylene, anhydride-modified polyolefin and blends thereof;
- (h) wherein said seventh polymeric layer is an innermost exterior-film layer comprising a heat-sealable polyolefin;
- (i) wherein said film has an oxygen transmission rate at 73° C. and 0% R.H. of between 2-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (31-15,500 cm<sup>3</sup>/m<sup>2</sup>/24 h.) as measured in with ASTM D-3985-02 test method; and
- (j) wherein said film comprises an unrestrained linear thermal shrinkage at 80° C. of 0-5% in both the machine and transverse direction as measured in accordance with ASTM D-2732-96 test method.

**26.** A thermoformable coextruded packaging film according to claim 25, wherein said film is formed by blown film coextrusion.

**27.** A thermoformable coextruded packaging film according to claim 25, wherein said first polymeric layer, said second polymeric layer, said third polymeric layer, said fourth polymeric layer, said fifth polymeric layer, said sixth polymeric layer, and said seventh polymeric layer are free of polyamide.

**28.** A thermoformable coextruded packaging film according to claim 25, wherein said film comprises a gloss value at 45° of at least 60% as measured in accordance ASTM D-2457 test method.

**29.** A thermoformable coextruded packaging film according to claim 25, wherein said film comprises a haze value of less than 20% as measured in accordance with ASTM D-1003-00 test method.

**30.** A thermoformable coextruded packaging film according to claim 25, wherein said film has an oxygen transmission rate at 73° C. and 0% R.H. of between 10-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (155-15,500 cm<sup>3</sup>/m<sup>2</sup>/24 h.) as measured in accordance with ASTM D-3985-02 test method.

**31.** A thermoformable coextruded packaging film according to claim 30, wherein said film has an oxygen transmission rate at 73° C. and 0% R.H. of between 20-1000 cm<sup>3</sup>/100 in<sup>2</sup>/24 h. (310-15,500 cm<sup>3</sup>/m<sup>2</sup>/24 h.) as measured in accordance with ASTM D-3985-02 test method.

**32.** A thermoformable coextruded packaging film according to claim 25, wherein said fourth polymeric layer comprises a polyalkyl acrylate copolymer or blend thereof.

**33.** A thermoformable coextruded packaging film according to claim 32, wherein said polyalkyl acrylate copolymer comprises an ethylene/alkyl acrylate copolymers or blends thereof.

**34.** A thermoformable coextruded packaging film according to claim 33, wherein said ethylene/alkyl acrylate copolymers comprise a material selected from the group consisting of ethylene/methyl acrylate copolymer (E/MA), ethylene/ethyl acrylate copolymer (E/EA), ethylene/butyl acrylate copolymer (E/BA), and ethylene/methyl methacrylate copolymer (E/MMA).

**35.** A thermoformable coextruded packaging film according to claim 25, wherein said anhydride-modified polyolefin comprise an anhydride modified-polyethylene.

**36.** A thermoformable coextruded packaging film according to claim 25, wherein said heat-sealable polyolefin comprises polyethylene.

**37.** A thermoformable coextruded packaging film according to claim 25, wherein said film has a thickness range between 0.8-15 mils (20.32-381 μm).

**38.** A thermoformable coextruded packaging film according to claim 37, wherein said film has a thickness range between 0.8-10 mils (20.32-254 μm).

**39.** A thermoformable coextruded packaging film according to claim 38, wherein said film has a thickness range between 0.8-8.0 mil (20.32-203.2 μm).

**40.** A thermoformable coextruded packaging film according to claim 25, wherein said film forms a package or a portion thereof.

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