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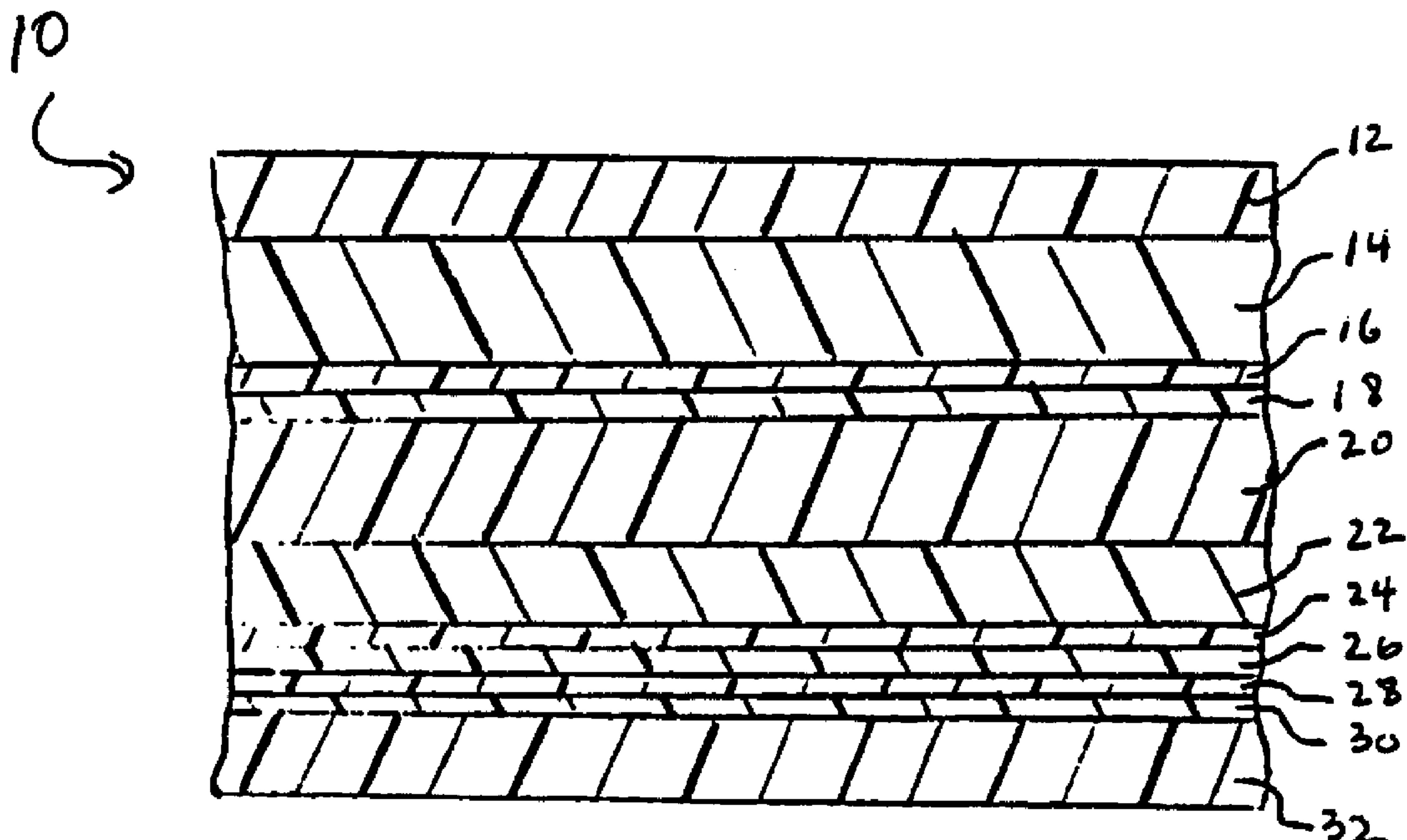
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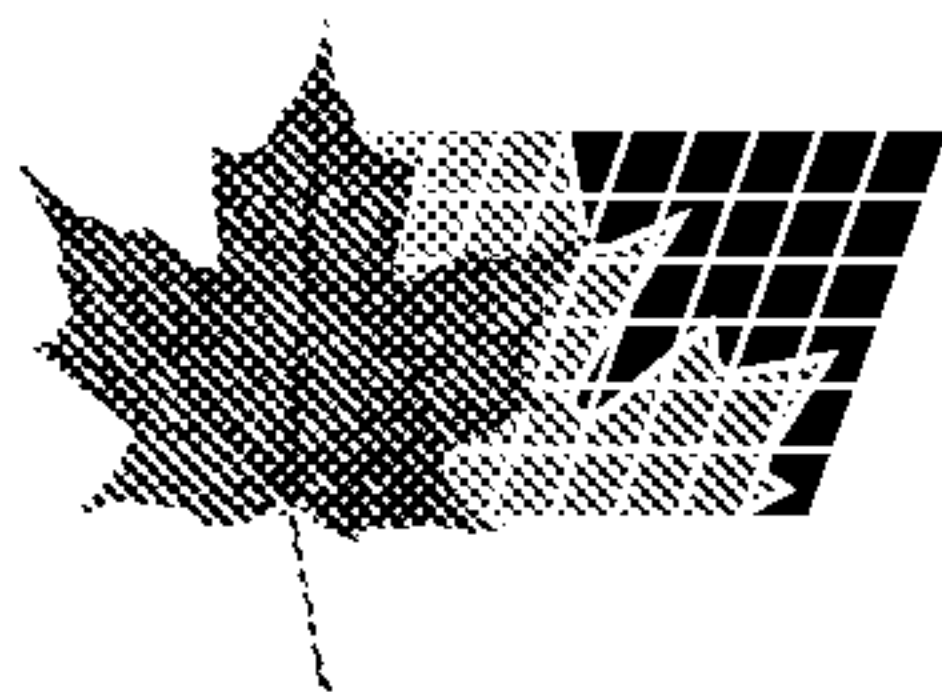
(54) **FILM D'EMBALLAGE MULTICOUCHE HAUTE BARRIERE
RESISTANT AUX MANIPULATIONS ABUSIVES**

(54) **MULTILAYER ABUSE RESISTANT HIGH BARRIER
PACKAGING FILM**



(57) Ce film multicouche possède d'exceptionnelles propriétés de barrière contre le N₂, l'O₂ et le CO₂ sans contenir de feuilles de métal. Ce film peut également être pourvu de propriétés haute barrière contre l'humidité ainsi que d'une forte opacité à la lumière, et il peut également être rendu très résistant aux manipulations abusives, ce qui le rend particulièrement approprié pour l'emballage de bobines relativement lourdes de film photographique non développé. Un film multicouche opaque préféré est particulièrement approprié pour l'emballage de produits sensibles à la lumière, tels que des films photographiques et des papiers

(57) A multilayer film exhibits exceptional N₂-, O₂-, and CO₂-barrier without containing metal foil. The film can also be provided with high moisture-barrier characteristics as well as high opacity to light, and can also be made very abuse-resistant, and can be especially suited for the packaging of relatively heavy rolls of undeveloped photographic film. A preferred opaque multilayer film is especially suited to packaging light-sensitive products such as photographic film and photographic paper, and has an outer seal layer and at least one inner layer containing carbon black, preferably two inner layers containing carbon black. The presence



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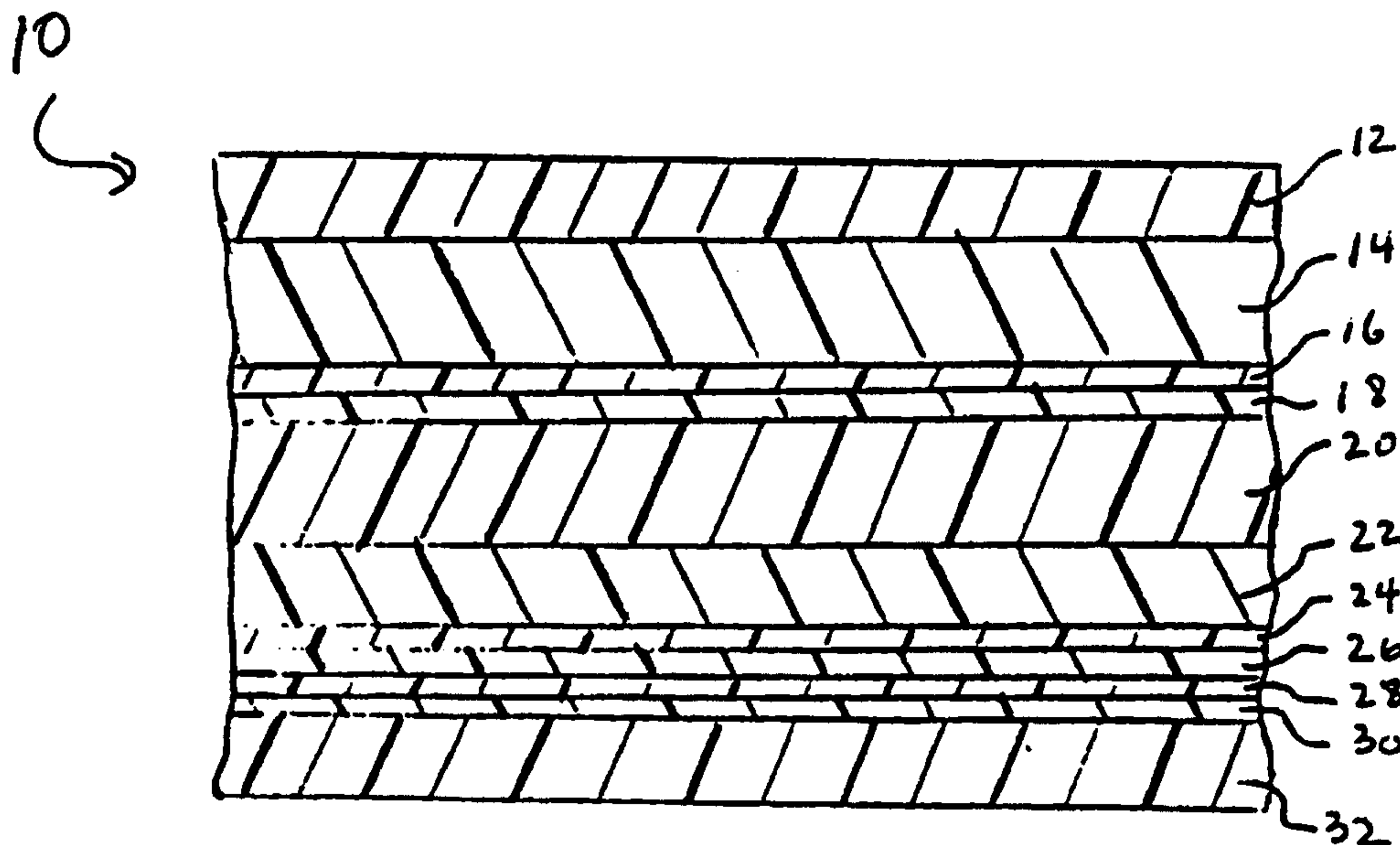
photographiques, et il possède une couche scellante extérieure et au moins une couche intérieure contenant du noir de carbone, de préférence deux couches intérieures contenant du noir de carbone. La ou les couches intérieures du film qui entourent le noir de carbone empêchent le film de frotter contre le noir de carbone sur l'équipement d'emballage et de fabrication du film, ainsi que le produit emballé dans le film. Des articles tels que sacs, étuis et sachets peuvent être fabriqués à partir de ce film.

of the carbon black in one or more inner film layer prevents the carbon black from rubbing off of the film on film-making and packaging equipment, as well as a product packaged in the film. Articles such as bags, casings, and pouches can be made from the film.

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(21) International Application Number: PCT/US98/13477 (22) International Filing Date: 25 June 1998 (25.06.98) (30) Priority Data: 885,244 30 June 1997 (30.06.97) US (71) Applicant (for all designated States except US): CRYOVAC, INC. [US/US]; 100 Rogers Bridge Road, P.O. Box 464, Duncan, SC 29334 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): SHAH, Gautam, P. [US/US]; 27 English Oak Road, Simpsonville, SC 29681 (US). GARLAND, Steven, B. [US/US]; 225 Block House Road, Greenville, SC 29615 (US). (74) Agents: HURLEY, Rupert, B., Jr. et al.; 100 Rogers Bridge Road, P.O. Box 464, Duncan, SC 29334 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: MULTILAYER ABUSE RESISTANT HIGH BARRIER PACKAGING FILM**(57) Abstract**

A multilayer film exhibits exceptional N₂-, O₂-, and CO₂-barrier without containing metal foil. The film can also be provided with high moisture-barrier characteristics as well as high opacity to light, and can also be made very abuse-resistant, and can be especially suited for the packaging of relatively heavy rolls of undeveloped photographic film. A preferred opaque multilayer film is especially suited to packaging light-sensitive products such as photographic film and photographic paper, and has an outer seal layer and at least one inner layer containing carbon black, preferably two inner layers containing carbon black. The presence of the carbon black in one or more inner film layer prevents the carbon black from rubbing off of the film on film-making and packaging equipment, as well as a product packaged in the film. Articles such as bags, casings, and pouches can be made from the film.

MULTILAYER ABUSE RESISTANT HIGH BARRIER PACKAGING FILM

Field of the Invention

The present invention is related to packaging film suitable for packaging products which are preferably packaged in an abuse-resistant film which provides a barrier to atmospheric gases, i.e., N₂, O₂, CO₂, etc. The film is especially useful for the packaging of light-sensitive, moisture-sensitive, and O₂-sensitive products. The present invention is also related to packaged products, especially to packages in which a photographic film, especially motion picture film, vacuum-packaged in an opaque, moisture-barrier, gas-barrier film.

Background of the Invention

There are a variety of photographic products, such as undeveloped photographic film, which have for some time been vacuum packaged in tough, opaque, high gas-barrier films. One such film has been a multilayer film having the structure:

polyethylene / foil / nylon / polyethylene terephthalate

However, it would be desirable to provide an alternative film which exhibits a high gas-barrier but which does not contain foil, as foil is not as easily recycled, cannot be coextruded with plastics, is expensive, etc. It would also be desirable to reduce or eliminate the use of polyamide, which is relatively expensive in comparison with other thermosetting and thermoplastic polymers, especially polyethylene. Of course, it is also desirable that the film has a very high degree of opacity, high abuse-resistance, and high gas barrier properties.

Very high O₂-barrier packaging films are known in which at least one layer of the film contains a "layer mineral," such as vermiculite. However, these films do not have adequate abuse-resistance for the packaging of hard, heavy articles such as undeveloped photographic film. They also do not have the gas barrier characteristics for the packaging of photographic film products, including undeveloped photographic film. In addition, they do not have the opacity which is desirable for the packaging of light-sensitive products such as photographic film, including undeveloped photographic film.

Summary of the Invention

The present invention provides a multilayer film which exhibits exceptional gas-barrier to N_2 , O_2 , and CO_2 , without containing foil, and can also be provided with high moisture barrier characteristics as well as high opacity to light. The multilayer film of the present invention can also be provided in a form which is very abuse resistant, and is especially suited for the vacuum-packaging of relatively heavy rolls of undeveloped photographic film.

The film of the present invention is especially suited to the packaging of light-sensitive products, especially motion picture film rolls. Optionally, the film can be of a type which, when heat sealed to itself or another film, exhibits a high burst strength, and can hold vacuum well. In addition, the film can be made from relatively inexpensive polymers, and need not require complex production processes, such as cross-lamination.

As a first aspect, the present invention pertains to a multilayer film comprising (A) a first layer comprising at least one member selected from the group consisting of platelet mineral, aluminum oxide, and SiO_x (wherein x is from 1.5 to 4); and (B) a second layer comprising at least one member selected from the group consisting of ethylene/alpha-olefin copolymer, polyethylene homopolymer, polypropylene, polyamide, polycarbonate, polyester; wherein the multilayer film has an instrumented impact strength of at least 10 pounds, based on a total thickness of the multilayer film.

As a second aspect, the present invention pertains to a multilayer film comprising: (A) a first layer comprising at least one member selected from the group consisting of platelet mineral, aluminum oxide, and SiO_x (wherein x is from 1.5 to 4); and (B) a second layer comprising at least one member selected from the group consisting of high density polyethylene, biaxially oriented polypropylene, polyvinylidene chloride, and polyester; and wherein the film has an O_2 -transmission rate of less than $25 \text{ cc/m}^2/\text{day}$ stp at 100% relative humidity (more preferably, from about and an H_2O -transmission rate of less than 1.5 grams/100in² at 100°F and 90% relative humidity).

Preferably, the multilayer film has an impact strength of from about 10 to 300 pounds, based on a total thickness of the multilayer film.

Preferably, the multilayer film comprises: (A) a first layer comprising at least one member selected from the group consisting of polyethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer, ionomer, polyamide, and polyester; (B) a second

layer comprising at least one member selected from the group consisting of ethylene/ester copolymer, modified polyolefin, ionomer, ethylene acrylate copolymer, ethylene acrylic acid, polyamide, and polyurethane; (C) a third layer comprising at least one member selected from the group consisting of ethylene/ester copolymer, modified polyolefin, ionomer, ethylene acrylate copolymer, ethylene acrylic acid, polyamide, and polyurethane; (D) a fourth layer comprising at least one member selected from the group consisting of polyethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer, ionomer, polyamide, and polyester; (E) a fifth layer comprising at least one member selected from the group consisting of platelet mineral, aluminum oxide, and SiO_x (wherein x is from 1.5 to 4); and (F) a sixth layer comprising at least one member selected from the group consisting of high density polyethylene, biaxially oriented polypropylene, polyvinylidene chloride, and polyester, and wherein the fifth layer is between the fourth layer and the sixth layer. Preferably, the second layer is between the first layer and the third layer, the third layer is between the second layer and the fourth layer and is directly adhered to the second layer, and the fourth layer is between the third layer and the fifth layer, and the fifth layer is between the fourth layer and the sixth layer. Preferably, the fifth layer comprises vermiculite.

Preferably, the multilayer film further comprises a primer layer directly adhered to the fifth layer, wherein the primer layer comprises at least one member selected from the group consisting of aminoplast resin, homopolyester, copolyester, styrene/maleic anhydride copolymer, styrene/itaconic acid copolymer, styrene/acrylamide copolymer, copolymer of acrylic acid, copolymer of methacrylic acid, copolymer of acrylic acid/ C_{2-6} ester, functionalized polyolefin, nitrocellulose, ethylcellulose, hydroxyethylcellulose, polyvinyl alcohol, and polyurethane.

Preferably, the fifth layer further comprises at least one member selected from the group consisting of aminoplast resin, homopolyester, copolyester, styrene/maleic anhydride copolymer, styrene/itaconic acid copolymer, styrene/acrylamide copolymer, copolymer of acrylic acid, copolymer of methacrylic acid, copolymer of acrylic acid/ C_{2-6} ester, functionalized polyolefin, nitrocellulose, ethylcellulose, hydroxyethylcellulose, polyvinyl alcohol, and polyurethane.

Preferably, the multilayer film further comprises a seventh layer which comprises at least one member selected from the group consisting of modified polyolefin, ionomer, ethylene acrylate copolymer, ethylene acrylic acid, polyamide, and polyurethane, the seventh

layer being between the fourth layer and the fifth layer. Preferably, the multilayer film further comprises a eighth layer which comprises at least one member selected from the group consisting of modified polyolefin, ionomer, ethylene acrylate copolymer, ethylene acrylic acid, polyamide, and polyurethane, the eighth layer being between the fifth layer and the sixth layer.

Preferably, at least one layer of the multilayer film comprises a pigment. Preferably, the pigment comprises carbon black. Preferably, the carbon black is present in at least one inner film layer. Preferably, the carbon black is present in a seventh film layer which is between the first layer and the second layer, the seventh layer further comprising at least one member selected from the group consisting of polyethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer, ionomer, polyamide, and polyester. Preferably, the carbon black is also present in an eighth film layer which is between the third layer and the fourth layer, the eighth layer further comprising at least one member selected from the group consisting of polyethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer, ionomer, polyamide, and polyester.

Preferably, the multilayer film further comprises a ninth film layer which comprises at least one member selected from the group consisting of modified polyolefin, ionomer, ethylene/acrylate copolymer, ethylene/acrylic acid copolymer, polyamide, and polyurethane, the ninth film layer being between the fourth layer and the fifth layer.

Preferably, the multilayer film further comprises a tenth film layer which comprises at least one member selected from the group consisting of modified polyolefin, ionomer, ethylene acrylate copolymer, ethylene acrylic acid, polyamide, and polyurethane, the tenth film layer being between the fifth layer and the sixth layer.

Preferably, the first, fourth, seventh, and eighth layers of the multilayer film each comprise at least one member selected from the group consisting of (A) homogeneous ethylene/alpha-olefin copolymer having a density of from about 0.89 g/cc to 0.93 g/cc and (B) linear low density polyethylene.

Preferably, the multilayer film has an O₂-transmission rate of less than 25 cc/m²/day stp at 100% relative humidity; more preferably, from about 0.1 to 10 cc/m²/day stp at 100% relative humidity; still more preferably, from about 0.1 to 1 cc/m²/day stp at 100% relative humidity.

Preferably, the multilayer film has an H₂O-transmission rate of less than 1.5 grams/100in² at 100°F and 90% relative humidity; more preferably, from about 0.01 to 1.0 grams/100in² at 100°F and 90% relative humidity; still more preferably, from about 0.01 to 0.3 grams/100in² at 100°F and 90% relative humidity.

5 Preferably, the multilayer film has a total thickness of from about 3 mils to about 15 mils; more preferably, from about 4 to 10 mils; still more preferably, from about 4 to 7 mils.

As a third aspect, the present invention pertains to a packaged product which comprises a package and an product within the package. The package comprises a multilayer film in accordance with the present invention, and the product comprises
10 photographic film. Preferably, the multilayer film in the packaged product is a preferred multilayer film in accordance with the present invention. Preferably, the product comprises at least one roll of undeveloped photographic film, with the package preferably being a vacuum package.

Brief Description of the Drawings

15 Figure 1 illustrates a cross-sectional view of a preferred multilayer film suitable for use in the articles illustrated in Figures 1-3.

Figure 2 illustrates a schematic view of a preferred process for making a portion of the film illustrated in Figure 1.

20 Figure 3 illustrates a schematic view of a preferred process for making another portion of the film illustrated in Figure 1.

Detailed Description of the Invention

Films of and used in the present invention have a thickness of 0.25 mm or less, i.e., 10 mils or less. As used herein, the term "package" refers to packaging materials configured
25 around a product being packaged. The phrase "packaged product," as used herein, refers to the combination of a product which is surrounded by a packaging material.

As used herein, the term "seal" refers to any seal of a first region of a film surface to a second region of a film surface, wherein the seal is formed by heating the regions to at least their respective seal initiation temperatures, i.e., a heat seal. The sealing can be performed by
30 any one or more of a wide variety of manners, such as using a heated bar, hot air, hot wire, infrared radiation, ultrasonic sealing, radio frequency sealing, etc.

Heat sealing is the process of joining two or more thermoplastic films or sheets by heating areas in contact with each other to the temperature at which fusion occurs, usually aided by pressure. When the heat is applied by dies or rotating wheels maintained at a constant temperature, the process is called thermal sealing. In melt-bead sealing, a narrow strand of molten polymer is extruded along one surface, trailed by a wheel that presses the two surfaces together. In impulse sealing, heat is applied by resistance elements that are applied to the work when relatively cool, then are rapidly heated. Simultaneous sealing and cutting can be performed in this way. Dielectric sealing is accomplished with polar materials by inducing heat within the films by means of radio-frequency waves. When heating is performed with ultrasonic vibrations, the process is called ultrasonic sealing.

As used herein, the term "barrier", and the phrase "barrier layer", as applied to films and/or film layers, are used with reference to the ability of a film or film layer to serve as a barrier to one or more gases. In the packaging art, oxygen (i.e., gaseous O₂) barrier layers have included, for example, hydrolyzed ethylene/vinyl acetate copolymer (designated by the abbreviations "EVOH" and "HEVA", and also referred to as "ethylene/vinyl alcohol copolymer"), polyvinylidene chloride, polyamide, polyester, polyacrylonitrile, etc., as known to those of skill in the art.

As used herein, the phrase "abuse layer", as well as the phrase "puncture-resistant layer", refer to an outer film layer and/or an inner film layer, so long as the film layer serves to resist abrasion, puncture, and other potential causes of reduction of package integrity, as well as potential causes of reduction of package appearance quality.

As used herein, the phrase "instrumented impact strength" refers to the energy necessary to puncture a restrained specimen of film, similar to ball burst impact strength, as disclosed below. However, the Instrumented Impact Tester has the ability to measure the tensile/elongation curve to break. The "gradient" is the ratio of the change in force to change in elongation in the straight line portion of the curve. "Peak" is a measure of the maximum force exerted on the specimen to impart rupture. "Impact Energy" is a measure of the energy absorbed by the sample prior to rupture. Instrumented Impact is measured by ASTM D 3763, hereby incorporated in its entirety, by reference thereto.

Preferably, the multilayer film for use in the present invention has an impact strength of from about 30 to 300 pounds; more preferably, from about 50 to 300 pounds; still more preferably, from about 75 to 300; yet still more preferably, from about 100 to 300 pounds.

Preferably, the multilayer film for use in the present invention has an energy to break of at least 2 ft-lbs; more preferably, at least 2.5 ft-lbs; still more preferably, at least 3 ft-lbs; yet still more preferably, at least 3.5 ft-lbs. Preferably, the multilayer film preferably has an energy to break of from about 2 to 10 ft-lbs; more preferably, from about 2.5 to 10 ft-lbs; still
5 more preferably, from about 3 to 10 ft-lbs; yet still more preferably, from about 3.5 to 10 ft-lbs.

As used herein, the phrase "impact strength" refers to both the peak load and energy absorbed, regardless of whether the test is carried out via dart drop or via instrumented impact. As known to those of skill in the art, peak load values from dart
10 drop substantially correspond with peak load from instrumented impact, and energy absorbed values obtained via dart drop substantially correspond with energy absorbed values obtained via instrumented impact, so long as the same impingement speed is present. The values reported herein were obtained at an impingement speed of about 12 feet per second.

15 As used herein, the phrase "ball burst strength" refers to the energy necessary to burst and penetrate a restrained specimen of film, and is measured by ASTM D 3420, which is hereby incorporated, in its entirety, by reference thereto.

As used herein, the terms "lamination," "laminate," as well as the phrase "laminated film," refer to the process, and resulting product, made by bonding together two or more
20 layers of film or other materials. Lamination can be accomplished by joining layers with adhesives, joining with heat and pressure, with corona treatment, and even spread coating and extrusion coating. The term laminate is also inclusive of coextruded multilayer films comprising one or more tie layers.

As used herein, the term "oriented" refers to a polymer-containing material which has
25 been elongated (generally at an elevated temperature called the orientation temperature), followed by being "set" in the elongated configuration by cooling the material while substantially retaining the elongated dimensions. This combination of elongation at elevated temperature followed by cooling causes an alignment of the polymer chains to a more parallel configuration, thereby improving the mechanical properties of the film.
30 Upon subsequently heating unrestrained, unannealed, oriented polymer-containing material to its orientation temperature, heat shrinkage is produced almost to the original dimensions,

i.e., pre-elongation dimensions. The term "oriented," is herein used with reference to oriented films, which can undergo orientation in any one or more of a variety of manners.

Orienting in one direction is referred to herein as "uniaxial orientation," while orienting in two directions is referred to herein as "biaxial orientation." In oriented plastic films, there can be internal stress remaining in the plastic sheet which can be relieved by reheating the film to a temperature above that at which it was oriented. Upon reheating such a film, the film tends to shrink back to the original dimensions it had before it was oriented. Films which shrink upon being heated are generally referred to as heat-shrinkable films.

As used herein, the phrase "orientation ratio" refers to the multiplication product of the extent to which the plastic film material is oriented in several directions, usually two directions perpendicular to one another. Orientation in the machine direction is herein referred to as "drawing", whereas orientation in the transverse direction is herein referred to as "stretching". For films extruded through an annular die, stretching is obtained by "blowing" the film to produce a bubble. For such films, drawing is obtained by passing the film through two sets of powered nip rolls, with the downstream set having a higher surface speed than the upstream set, with the resulting draw ratio being the surface speed of the downstream set of nip rolls divided by the surface speed of the upstream set of nip rolls. The degree of orientation is also referred to as the orientation ratio, also known as the "racking ratio".

As used herein, the term "monomer" refers to a relatively simple compound, usually containing carbon and of low molecular weight, which can react to form a polymer by combining with itself or with other similar molecules or compounds.

As used herein, the term "comonomer" refers to a monomer which is copolymerized with at least one different monomer in a copolymerization reaction, the result of which is a copolymer.

As used herein, the term "polymer" refers to the product of a polymerization reaction, and is inclusive of homopolymers, copolymers, terpolymers, tetrapolymers, etc. In general, the layers of a film can consist essentially of a single polymer, or can have additional polymers together therewith, i.e., blended therewith.

As used herein, the term "homopolymer" is used with reference to a polymer resulting from the polymerization of a single monomer, i.e., a polymer consisting essentially of a single type of repeating unit.

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 copolymerization reaction product of ethylene and an alpha-olefin, such as 1-hexene. The term "copolymer" is also inclusive of, for example, the copolymerization of a mixture of ethylene, propylene, 1-hexene, and 1-octene. As used herein, the term "copolymerization" refers to the simultaneous polymerization of two or more monomers. The term "copolymer" is also inclusive of random copolymers, block copolymers, and graft copolymers.

As used herein, the term "polymerization" is inclusive of homopolymerizations, copolymerizations, terpolymerizations, etc., and includes all types of copolymerizations such as random, graft, block, etc. In general, the polymers, in the films used in accordance with the present invention, can be prepared in accordance with any suitable polymerization process, including slurry polymerization, gas phase polymerization, and high pressure polymerization processes.

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 first listed monomer preferably polymerizes in a higher weight percent than the second listed monomer, and, for copolymers which are terpolymers, quadripolymers, etc., preferably the first monomer copolymerizes in a higher weight percent than the second monomer, and the second monomer copolymerizes in a higher weight percent than the third monomer, etc.

As used herein, terminology employing a "/" with respect to the chemical identity of a copolymer (e.g., "an ethylene/alpha-olefin copolymer"), identifies the comonomers which are copolymerized to produce the copolymer. As used herein, "ethylene alpha-olefin copolymer" is the equivalent of "ethylene/alpha-olefin copolymer."

As used herein, copolymers are identified, i.e., named, in terms of the monomers from which the copolymers are produced. For example, the phrase "propylene/ethylene copolymer" refers to a copolymer produced by the copolymerization of both propylene and

ethylene, with or without additional comonomer(s). As used herein, the phrase "mer" refers to a unit of a polymer, as derived from a monomer used in the polymerization reaction. For example, the phrase "alpha-olefin mer" refers to a unit in, for example, an ethylene/alpha-olefin copolymer, the polymerization unit being that "residue" which is derived from the alpha-olefin monomer after it reacts to become a portion of the polymer chain, i.e., that portion of the polymer contributed by an individual alpha-olefin monomer after it reacts to become a portion of the polymer chain.

As used herein, the phrase "heterogeneous polymer" refers to polymerization reaction products of relatively wide variation in molecular weight and relatively wide variation in composition distribution, i.e., polymers made, for example, using conventional Ziegler-Natta catalysts. Heterogeneous polymers are useful in various layers of the film used in the present invention. Such polymers typically contain a relatively wide variety of chain lengths and comonomer percentages.

As used herein, the phrase "heterogeneous catalyst" refers to a catalyst suitable for use in the polymerization of heterogeneous polymers, as defined above. Heterogeneous catalysts are comprised of several kinds of active sites which differ in Lewis acidity and steric environment. Ziegler-Natta catalysts are heterogeneous catalysts. Examples of Ziegler-Natta heterogeneous systems include metal halides activated by an organometallic co-catalyst, such as titanium chloride, optionally containing magnesium chloride, complexed to trialkyl aluminum and may be found in patents such as U.S. Patent No. 4,302,565, to GOEKE, et. al., and U.S. Patent No. 4,302,566, to KAROL, et. al., both of which are hereby incorporated, in their entireties, by reference thereto.

As used herein, the phrase "homogeneous polymer" refers to polymerization reaction products of relatively narrow molecular weight distribution and relatively narrow composition distribution. Homogeneous polymers can be used in various layers of multilayer films useful in the present invention. Homogeneous polymers are structurally different from heterogeneous polymers, in that homogeneous polymers exhibit a relatively even sequencing of comonomers within a chain, a mirroring of sequence distribution in all chains, and a similarity of length of all chains, i.e., a narrower molecular weight distribution. Furthermore, homogeneous polymers are typically prepared using metallocene, or other single-site type catalysis, rather than using Ziegler Natta catalysts.

More particularly, homogeneous ethylene/alpha-olefin copolymers may be characterized by one or more methods known to those of skill in the art, such as molecular weight distribution (M_w/M_n), composition distribution breadth index (CDBI), narrow melting point range, and single melt point behavior. The molecular weight distribution (M_w/M_n), also known as "polydispersity," may be determined by gel permeation chromatography. Homogeneous ethylene/alpha-olefin copolymers which can be used in the present invention preferably have an M_w/M_n of less than 2.7; more preferably from about 1.9 to 2.5; still more preferably, from about 1.9 to 2.3. The composition distribution breadth index (CDBI) of such homogeneous ethylene/alpha-olefin copolymers will generally be greater than about 70 percent. The CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50 percent (i.e., plus or minus 50%) of the median total molar comonomer content. The CDBI of linear polyethylene, which does not contain a comonomer, is defined to be 100%. The Composition Distribution Breadth Index (CDBI) is determined via the technique of Temperature Rising Elution Fractionation (TREF). CDBI determination clearly distinguishes homogeneous copolymers (i.e., narrow composition distribution as assessed by CDBI values generally above 70%) from VLDPEs available commercially which generally have a broad composition distribution as assessed by CDBI values generally less than 55%. TREF data and calculations therefrom for determination of CDBI of a copolymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation as described, for example, in Wild et. al., J. Poly. Sci. Poly. Phys. Ed., Vol. 20, p.441 (1982). Preferably, the homogeneous ethylene/alpha-olefin copolymers have a CDBI greater than about 70%, i.e., a CDBI of from about 70% to 99%. In general, the homogeneous ethylene/alpha-olefin copolymers useful in the present invention also exhibit a relatively narrow melting point range, in comparison with "heterogeneous copolymers", i.e., polymers having a CDBI of less than 55%. Preferably, the homogeneous ethylene/alpha-olefin copolymers exhibit an essentially singular melting point characteristic, with a peak melting point (T_m), as determined by Differential Scanning Colorimetry (DSC), of from about 60°C to 105°C. Preferably the homogeneous copolymer has a DSC peak T_m of from about 80°C to 100°C. As used herein, the phrase "essentially single melting point" means that at least about 80%, by weight, of the material corresponds to a single T_m peak at a temperature within the range of from about 60°C to 105°C, and essentially no substantial fraction of the material has a peak melting point

in excess of about 115°C., as determined by DSC analysis. DSC measurements are made on a Perkin Elmer System 7 Thermal Analysis System. Melting information reported are second melting data, i.e., the sample is heated at a programmed rate of 10°C./min. to a temperature below its critical range. The sample is then reheated (2nd melting) at a programmed rate of 10°C/min.

A homogeneous ethylene/alpha-olefin copolymer can, in general, be prepared by the copolymerization of ethylene and any one or more alpha-olefin. Preferably, the alpha-olefin is a C₃-C₂₀ alpha-monoolefin, more preferably, a C₄-C₁₂ alpha-monoolefin, still more preferably, a C₄-C₈ alpha-monoolefin. Still more preferably, the alpha-olefin comprises at least one member selected from the group consisting of butene-1, hexene-1, and octene-1, i.e., 1-butene, 1-hexene, and 1-octene, respectively. Most preferably, the alpha-olefin comprises octene-1, and/or a blend of hexene-1 and butene-1.

Processes for preparing and using homogeneous polymers are disclosed in U.S. Patent No. 5,206,075, to HODGSON, Jr., U.S. Patent No. 5,241,031, to MEHTA, and PCT International Application WO 93/03093, each of which is hereby incorporated by reference thereto, in its entirety. Further details regarding the production and use of homogeneous ethylene/alpha-olefin copolymers are disclosed in PCT International Publication Number WO 90/03414, and PCT International Publication Number WO 93/03093, both of which designate Exxon Chemical Patents, Inc. as the Applicant, and both of which are hereby incorporated by reference thereto, in their respective entireties.

Still another species of homogeneous ethylene/alpha-olefin copolymers is disclosed in U.S. Patent No. 5,272,236, to LAI, et. al., and U.S. Patent No. 5,278,272, to LAI, et. al., both of which are hereby incorporated by reference thereto, in their respective entireties.

As used herein, the term "polyolefin" refers to any polymerized olefin, which can be linear, branched, cyclic, aliphatic, aromatic, substituted, or unsubstituted. More specifically, included in the term polyolefin are homopolymers of olefin, copolymers of olefin, copolymers of an olefin and an non-olefinic comonomer copolymerizable with the olefin, such as vinyl monomers, modified polymers thereof, and the like. Specific examples include polyethylene homopolymer, polypropylene homopolymer, polybutene, propylene/butene copolymer, ethylene/alpha-olefin copolymer, propylene/alpha-olefin copolymer, butene/alpha-olefin copolymer, ethylene/vinyl acetate copolymer, ethylene/ethyl acrylate copolymer, ethylene/butyl acrylate copolymer, ethylene/methyl acrylate copolymer, ethylene/acrylic acid

copolymer, ethylene/methacrylic acid copolymer, modified polyolefin resin, ionomer resin, polymethylpentene, etc. Modified polyolefin resin is inclusive of modified polymer prepared by copolymerizing the homopolymer of the olefin or copolymer thereof with an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like. It could also be obtained by incorporating into the olefin homopolymer or copolymer, an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like.

As used herein, terms identifying polymers, such as "polyamide", "polyester", "polyurethane", etc. are inclusive of not only polymers comprising repeating units derived from monomers known to polymerize to form a polymer of the named type, but are also inclusive of comonomers, derivatives, etc. which can copolymerize with monomers known to polymerize to produce the named polymer. For example, the term "polyamide" encompasses both polymers comprising repeating units derived from monomers, such as caprolactam, which polymerize to form a polyamide, as well as copolymers derived from the copolymerization of caprolactam with a comonomer which when polymerized alone does not result in the formation of a polyamide. Furthermore, terms identifying polymers are also inclusive of "blends" of such polymers with other polymers of a different type.

As used herein, the phrases "ethylene alpha-olefin copolymer", and "ethylene/alpha-olefin copolymer", refer to such heterogeneous materials as low density polyethylene (LDPE), medium density polyethylene (MDPE), linear low density polyethylene (LLDPE), and very low and ultra low density polyethylene (VLDPE and ULDPE); as well as to such homogeneous ethylene/alpha olefin copolymers as: metallocene-catalyzed EXACT[®] linear homogeneous ethylene/alpha olefin copolymer resins obtainable from the Exxon Chemical Company, of Baytown, Texas, homogeneous substantially linear ethylene/alpha-olefin copolymers having long chain branching (e.g., copolymers known as AFFINITY[®] resins, and ENGAGE[®] resins, available from the Dow Chemical Company, of Midland, Michigan), as well as TAFMER[®] linear homogeneous ethylene/alpha-olefin copolymer resins obtainable from the Mitsui Petrochemical Corporation. Both the heterogeneous polymers and homogeneous polymers referred to above generally include copolymers of ethylene with one or more comonomers selected from C₄ to C₁₀ alpha-olefin such as butene-1 (i.e., 1-butene), hexene-1, octene-1, etc. While LDPE and MDPE are more highly branched than LLDPE,

VLDPE, ULDPE, EXACT™ resin, and TAFMER™ resin, this latter group of resins has a relatively large number of short branches rather than the longer branches present in LDPE and MDPE. AFFINITY™ resins and ENGAGE™ resins have a relatively large number of short branches in combination with a relatively small number of long-chain branches.

5 LLDPE has a density usually in the range of from about 0.91 grams per cubic centimeter to about 0.94 grams per cubic centimeter.

In general, the ethylene/alpha-olefin copolymer comprises a copolymer resulting from the copolymerization of from about 80 to 99 weight percent ethylene and from 1 to 20 weight percent alpha-olefin. Preferably, the ethylene alpha-olefin copolymer comprises a

10 copolymer resulting from the copolymerization of from about 85 to 95 weight percent ethylene and from 5 to 15 weight percent alpha-olefin.

As used herein, the phrases "inner layer" and "internal layer" refer to any layer, of a multilayer film, having both of its principal surfaces directly adhered to another layer of the film.

15 As used herein, the phrase "inside layer" refers to an outer film layer, of a multilayer film packaging a product, which is closest to the product, relative to the other layers of the multilayer film. "Inside layer" also is used with reference to the innermost layer of a plurality of concentrically arranged layers simultaneously coextruded through an annular die.

As used herein, the phrase "outer layer" refers to any film layer of film having less

20 than two of its principal surfaces directly adhered to another layer of the film. The phrase is inclusive of monolayer and multilayer films. All multilayer films have two, and only two, outer layers, each of which has a principal surface adhered to only one other layer of the multilayer film. In monolayer films, there is only one layer, which, of course, is an outer layer in that neither of its two principal surfaces are adhered to another layer of the film.

25 As used herein, the phrase "outside layer" refers to the outer layer, of a multilayer film packaging a product, which is furthest from the product relative to the other layers of the multilayer film. "Outside layer" also is used with reference to the outermost layer of a plurality of concentrically arranged layers simultaneously coextruded through an annular die.

As used herein, the phrase "directly adhered", as applied to film layers, is defined as

30 adhesion of the subject film layer to the object film layer, without a tie layer, adhesive, or other layer therebetween. In contrast, as used herein, the word "between", as applied to a film layer expressed as being between two other specified layers, includes both direct

adherence of the subject layer between to the two other layers it is between, as well as including a lack of direct adherence to either or both of the two other layers the subject layer is between, i.e., one or more additional layers can be imposed between the subject layer and one or more of the layers the subject layer is between.

5 As used herein, the term "core", and the phrase "core layer", as applied to multilayer films, refer to any inner film layer which has a primary function other than serving as an adhesive or compatibilizer for adhering two layers to one another. Usually, the core layer or layers provide the multilayer film with a desired level of strength, i.e., modulus, and/or optics, and/or added abuse resistance, and/or specific impermeability.

10 As used herein, the phrases "seal layer," "sealing layer," "heat seal layer," and "sealant layer," refer to an outer film layer, or layers, involved in the sealing of the film to itself, another film layer of the same or another film, and/or another article which is not a film. It should also be recognized that in general, up to the outer 3 mils of a film can be involved in the sealing of the film to itself or another layer. With respect to packages having only fin-
15 type seals, as opposed to lap-type seals, the phrase "sealant layer" generally refers to the inside film layer of a package, as well as supporting layers within 3 mils of the inside surface of the sealant layer, the inside layer frequently also serving as a food contact layer in the packaging of foods. In general, sealant layers employed in the packaging art have included thermoplastic polymers, such as polyolefin, polyamide, polyester, and polyvinyl chloride.

20 As used herein, the phrase "tie layer" refers to any inner film layer having the primary purpose of adhering two layers to one another. Tie layers can comprise any polymer having a polar group thereon, or any other polymer which provides sufficient interlayer adhesion to adjacent layers comprising otherwise nonadhering polymers.

25 As used herein, the phrase "bulk layer" refers to any layer of a film which is present for the purpose of increasing the abuse-resistance, toughness, modulus, etc., of a multilayer film. Bulk layers generally comprise polymers which are inexpensive relative to other polymers in the film which provide some specific purpose unrelated to abuse-resistance, modulus, etc.

30 The names "first layer", "second layer", as used herein, are generally indicative of the manner in which a multilayer film structure is built up. That is, in general, the first layer can be present without any of the additional layers described, or the first and second layers can be present without any of the additional layers described, etc.

As used herein, the term "extrusion" is used with reference to the process of forming continuous shapes by forcing a molten plastic material through a die, followed by cooling or chemical hardening. Immediately prior to extrusion through the die, the relatively high-viscosity polymeric material is fed into a rotating screw of variable pitch, i.e., an extruder, which forces the polymeric material through the die.

As used herein, the term "coextrusion" refers to the process by which the outputs of two or more extruders are brought smoothly together in a feed block, to form a multilayer stream that is fed to a die to produce a layered extrudate. Coextrusion can be employed in film blowing, sheet and flat film extrusion, blow molding, and extrusion coating.

As used herein, the phrase "machine direction", herein abbreviated "MD", refers to a direction "along the length" of the film, i.e., in the direction of the film as the film is formed during extrusion and/or coating. As used herein, the phrase "transverse direction", herein abbreviated "TD", refers to a direction across the film, perpendicular to the machine or longitudinal direction.

Although the film useful in the article of the present invention has at least 2 layers (more preferably, from 2 to 20 layers), more preferably the film has from 2 to 15 layers, still more preferably, from 5 to 12 layers. However, so long as the multilayer film has at least 2 layers, the multilayer film can have any further number of additional layers desired, so long as the film provides the desired properties for the particular packaging operation in which the film is used, e.g., N_2 -, O_2 -, and CO_2 -barrier characteristics, self-weld capability (i.e., a symmetrical film, or film portion, having two identical tie layers bonded directly to one another), etc. The multilayer film illustrated in Figure 1 has eleven layers. Layers 1 through 6 are preferably formed from the collapsing of a three-layer tubing film upon itself. Layers 3 and 4, which were originally the inside layer of the tubing, formed two identical directly-adhered-together tie layers in the center of a symmetrical structure.

The film used in the present invention has a thickness of at least 3 mils (1 mil equals 0.001 inch); preferably, a thickness of from about 3 to 15 mils; more preferably, from about 4 to 10 mils; still more preferably, from about 4 to 7 mils. Of course, the preferred thickness varies depending upon the desired properties for the particular packaging operation in which the film is used.

Figure 1 illustrates a cross-sectional view of preferred 11-layer film in accordance with the present invention. Film preferably has:

(1) layer 12, which is an outer layer which serves as a seal and abuse layer, and which preferably comprises a blend of EVA and LLDPE or 100% LLDPE, but is free of carbon black;

5 (2) layer 14, which is an inner layer which serves a bulk and opacity layer, and which preferably comprises a blend of EVA and LLDPE or 100% LLDPE, and which further comprises carbon black;

(3) layer 16, which is also an inner layer and which serves as a self-weld layer, and which preferably comprises 100% EVA, and which is free of carbon black;

10 (4) layer 18, which is also an inner layer and which also serves as a self-weld layer, and which preferably comprises 100% EVA, and which is free of carbon black;

(5) layer 20, which is an inner layer which serves a bulk and opacity layer, and which preferably comprises a blend of EVA and LLDPE or 100% LLDPE, and which further comprises carbon black;

15 (6) layer 22, which is an inner layer which serves as a bulk layer and which preferably comprises a blend of EVA and LLDPE or 100% LLDPE, but is free of carbon black;

(7) layer 24, which is an inner layer which serves as an adhesive layer, and which preferably comprises a urethane-based adhesive;

(8) layer 26, which is an inner layer which serves as a gas-barrier layer, and which preferably comprises vermiculite particulates and polyester;

20 (9) layer 28, which is an inner film layer which serves as a primer layer, and which preferably comprises an acrylamide copolymer;

(10) layer 30, which is an inner film layer which serves as an adhesive layer, and which preferably comprises a urethane-based adhesive; and

25 (11) layer 32, which is an outer film layer which serves as a moisture barrier layer, and which preferably comprises high density polyethylene and/or biaxially oriented polypropylene.

Figure 2 illustrates a schematic of a preferred process for producing a substrate film which makes up at least the first, second, third, ninth, and tenth layers of the multilayer films of Figure 1. In the process illustrated in Figure 2, solid polymer beads (not illustrated) are
30 fed to a plurality of extruders 66 (for simplicity, only one extruder is illustrated). Inside extruders 66, the polymer beads are forwarded, melted, and degassed, following which the resulting bubble-free melt is forwarded into die head 68, and extruded through annular die,

resulting in tubing 70, which is 5-40 mils thick, more preferably 20-30 mils thick, still more preferably, about 25 mils thick.

After cooling or quenching by water spray from cooling ring 72, tubing 70 is collapsed by pinch rolls 74, and is thereafter fed through irradiation vault 76 surrounded by shielding 78, where tubing 70 is irradiated with high energy electrons (i.e., ionizing radiation) from iron core transformer accelerator 80. Tubing 70 is guided through irradiation vault 76 on rolls 82. Preferably, the irradiation of tubing 70 is at a level of from about 2 to 10 megarads (hereinafter "MR"); more preferably, from about 3.5-4 MR.

After irradiation, irradiated tubing 84 is directed over guide roll 86, after which irradiated tubing 84 passes into hot water bath tank 88 containing water 90. The now-collapsed irradiated tubing 84 is submersed in the hot water for a retention time of at least about 5 seconds, i.e., for a time period in order to bring the film up to the desired temperature, following which supplemental heating means (not illustrated) including a plurality of steam rolls around which irradiated tubing 84 is partially wound, and optional hot air blowers, elevate the temperature of irradiated tubing 84 to a desired orientation temperature of from about 240°F-250°F. Thereafter, irradiated film 84 is directed through nip rolls 92, and bubble 94 is blown, thereby transversely stretching irradiated tubing 84 to form oriented blown tubing film 96. Furthermore, while being blown, i.e., transversely stretched, irradiated tubing 84 is drawn (i.e., in the longitudinal direction) between nip rolls 88 and nip rolls 98, as nip rolls 98 have a higher surface speed than the surface speed of nip rolls 92. As a result of the transverse stretching and longitudinal drawing, irradiated, biaxially-oriented, blown tubing film 96 is produced, this blown tubing preferably having been both stretched at a ratio of from about 1:1.5 - 1:6, and drawn at a ratio of from about 1:1.5-1:6. More preferably, the stretching and drawing are each performed at a ratio of from about 1:2 - 1:4. The result is a biaxial orientation of from about 1:2.25 - 1:36, more preferably, 1:4 - 1:16. While bubble 94 is maintained between pinch rolls 92 and 98, blown tubing film 96 is collapsed by converging rolls 100, and thereafter conveyed through pinch rolls 98 and across guide roll 102, and then rolled onto wind-up roller 104. Idler roll 106 assures a good wind-up.

The film of the present invention is preferably irradiated to induce crosslinking (i.e., form a crosslinked polymer network), as well as corona treated to roughen the surface of the films which are to be adhered to one another. In the irradiation process, the film is subjected

to an energetic radiation treatment, such as corona discharge, plasma, flame, ultraviolet, X-ray, gamma ray, beta ray, and high energy electron treatment, which induce cross-linking between molecules of the irradiated material. The irradiation of polymeric films is disclosed in U.S. Patent NO. 4,064,296, to BORNSTEIN, et. al., which is hereby incorporated in its entirety, by reference thereto. BORNSTEIN, et. al. discloses the use of ionizing radiation for crosslinking the polymer present in the film.

The corona treatment of a film is performed by subjecting the surfaces of the film to corona discharge, i.e., the ionization of a gas such as air in close proximity to a film surface, the ionization initiated by a high voltage passed through a nearby electrode, and causing oxidation and other changes to the film surface, such as surface roughness. Corona treatment of polymeric materials is disclosed in U.S. Patent No. 4,120,716, to BONET, issued October 17, 1978, herein incorporated in its entirety by reference thereto, discloses improved adherence characteristics of the surface of polyethylene by corona treatment, to oxidize the polyethylene surface. U.S. Patent No. 4,879,430, to HOFFMAN, also hereby incorporated in its entirety by reference thereto, discloses the use of corona discharge for the treatment of plastic webs for use in meat cook-in packaging, with the corona treatment of the inside surface of the web to increase the adhesion of the meat to the adhesion of the meat to the proteinaceous material.

Although the multilayer film of the present invention can be produced by a full coextrusion method or extrusion coating method, a preferred method of making the multilayer film is by laminating together at least two separate films, preferably three separate films. The lamination is carried out using a conventional laminating process as known to those of skill in the art, and suitable laminating adhesives as are also known to those of skill in the art.

In a preferred lamination-type method in which three separate films are laminated together to result in the multilayer film, the separate film which serves as that portion of the multilayer film which provides the N_2 -, O_2 -, and CO_2 -barrier, is preferably MELINEX[®] D888 polyester film, which can be obtained from ICI Polyester, Melinex Commercial, Wilton Centre, P.O Box 90, Middlesbrough, England. The composition of this film, its method of production, and various alternative embodiments thereof, are believed to be described in detail in PCT published patent application WO 94/25511 (i.e., international application number PCT/GB94/00874, having an international filing

date of 25 April 1994, published 10 November 1994), which is hereby incorporated in its entirety, by reference thereto. Other ICI patent documents which pertain to gas-barrier films which contain platelet-type mineral in a gas barrier layer include: European Patent Application 0 498 569 A2 filed February 4, 1991, published August 12, 1992;
5 European Patent Application 0 518 646 A1 filed June 10, 1991, published December 16, 1992; European Patent Application 0 518 647 A1, filed June 14, 1991, published December 16, 1992; and European Patent Application 0 605 130 A1, filed December 13, 1993, published July 6, 1994. Each of these patent documents is hereby incorporated in its entirety, by reference thereto.

10 Based on PCT application WO 94/25511, MELINEX™ D888 film is believed to be a composite sheet which is produced by applying a coating layer (which comprises a mineral) to at least one surface of a substrate which has been primed with a primer layer. Thereafter, a flexible adherent layer is applied to the surface of the coating layer which is not adhered to the substrate. The various materials from which the substrate layer, the
15 primer layer, the coating layer (including the mineral therein), and the adherent layer, are all disclosed in detail in WO 94/25511. In any event, the preferred film for use in laminating to form the multilayer film is MELINEX™ polyester film, identified above.

20 The layer mineral present in the film preferably comprises platelets of a film-forming, 2:1 phyllosilicate layer mineral. For information on the composition and structure of phyllosilicate layer minerals, reference can be made to "Clay minerals: Their Structure, Behavior & Use", Proceedings of a Royal Society Discussion Meeting, 9 & 10 November 1983, London, The Royal Society, 1984, the entirety of which is hereby incorporated by reference thereto. See particularly Pages 222 through 223, and 232 through 235.

25 SiO_x is a mineral which can be used as a gas barrier in the multilayer film of the present invention. As used herein, the term "SiO_x" refers to silica and variations thereof. More particularly, in "x" is from 1.5 to 4. Preferably, the SiO_x comprises silica (SiO₂) and/or silicon monoxide (SiO).

30 The term "platelets" as used in this specification refers to tiny particles of the layer mineral obtained by subjecting the mineral to a chemical delaminating process to form an aqueous colloidal dispersion of high aspect ratio particles of the mineral from which a film can be formed. Preferably, the layer mineral is selected from the group

consisting of smectites, preferably hectorite and montmorillonite, and particularly vermiculite. The term "vermiculite" as used in this specification, refers to all materials known mineralogically and commercially as vermiculite. Vermiculite ore is a naturally-occurring mineral contains a mixture of phases) eg vermiculite, biotite, hydrobiotite etc.) and a mixture of interlayer cations (eg Mg^{2+} , Ca^{2+} , K^{+}). Production of aqueous suspensions or slurries of vermiculite platelets rely on ion exchange (normally incomplete) to generate adequate macroscopic swelling. The swollen, fully- or partially-exchanged vermiculite gel can then be milled to produce a film-forming aqueous suspension of vermiculite platelets. Treatment of vermiculite particles with one or more aqueous solutions of metal (especially alkali metal) salts or alkyl ammonium slats followed by swelling in water and then milling to delaminate the vermiculite is well known and is described for example in GB-A-1016385, GB-A-1119305, GB-A-1585104 and GB-A-1593382, and in US-A-4130687, each of which is hereby incorporated, in its entirety, by reference thereto.

Vermiculite is a particularly suitable layer mineral to provide gas barrier characteristics, especially to provide a barrier to gaseous O_2 . The multilayer film according to the present invention preferably has an oxygen permeability of less than 50 $cc/m^2/day$, more preferably less than 20 $cc/m^2/day$, still more preferably less than 10 $cc/m^2/day$, yet still more particularly less than 5, and even yet still more preferably less than 1 $cc/m^2/day$.

A preferred embodiment of the invention comprises a coating layer of vermiculite platelets wherein preferably greater than 50%, more preferably 55 to 99%, still more preferably 60 to 90%, and yet still more preferably 70 to 95%, by number of the platelets have a particle size (by which is meant the size of the maximum width of a platelet) in the range 0.5 to 5.0 μm . It is preferred that 80 to 99.9%, more preferably 85 to 99.9%, and still more preferably 90 to 99.9% by number of the vermiculite platelets have a particle size in the range 0.1 to 5.0 μm . The mean particle size (by which is meant the mean value of the maximum width of the platelets) of vermiculite platelets is preferably 1.0 to 3.0 μm , more preferably 1.2 to 2.2 μm , and especially 1.3 to 1.6 μm . It is also preferred that the vermiculite platelets have a thickness in the range from approximately 10 to 60 A, especially from approximately 25 to 40 A. In addition, it is

preferred than from 60 to 100%, more preferably from 70 to 99%, and particularly from 90 to 95% by number of vermiculite platelets have a thickness in the range 10 to 60 Å. The mean thickness of vermiculite platelets is preferably 25 to 50 Å, more preferably 25 to 40 Å, and especially 25 to 30 Å.

5 Although the coating layer can comprise a substantially continuous layer of platelets of any practical thickness, suitably up to 5 µm, preferably up to 2 µm, and more preferably up to 0.5 µm, composite sheets exhibiting desired properties, for example improved barrier property against atmospheric oxygen, comprise a substantially continuous layer of platelets at very low thickness, eg as low as 0.01 µm, especially in
10 the range from 0.02 µm to 0.3 µm, and particularly in the range from 0.1 µm to 0.25 µm.

Figure 3 illustrates a schematic view of a process useful in making a blow film which can be laminated to at least one other film in the production of a multilayer film in accordance with the present invention. At least one extruder supplies molten polymer to coextrusion die
15 196 for the formation of a monolayer film of high density polyethylene. The extruder is preferably equipped with a screen pack 198, a breaker plate 200, and a plurality of heaters 202. The monolayer film is extruded between mandrel 204 and die 196, and the extrudate is cooled by cool air flowing from air ring 206. The resulting blown bubble 207 is thereafter guided into a collapsed configuration by nip rolls 208, via guide rolls 210. The collapsed
20 tube is optionally passed over treater bar 212, and is thereafter passed over idler rolls 214, and around dancer roll 216 which imparts tension control to collapsed tube 218, after which the collapsed tube is wound into roll 220 via winding mechanism 222.

The multilayer film produced by the process illustrated in Figure 2, described above, and a monolayer film produced by the process illustrated in Figure 3, also described above,
25 are each laminated to opposite sides of a film comprising polyester and a platelet mineral believed to be vermiculite, i.e., MELINEX™ D888 polyester film, using a polyurethane based adhesive for each of the laminations. The resulting film, having a thickness of about 5 mils, is highly opaque (effectively providing 0% light transmission using ASTM Test D 589 sec
15.09, which is hereby incorporated by reference thereto, in its entirety), highly abuse-
30 resistant, and relatively O₂, CO₂, N₂, and water vapor impermeable. The laminate was free of metal foil, and was suited for the vacuum packaging of rolls of undeveloped photographic film.

In general, the multilayer film in accordance with the present invention can be sealed to form a bag, pouch, casing, lidstock, etc. The sealing of film can be to itself or to another film or a non-film article. A preferred means for sealing is the use of a hot bar (heat seal) or a nichrome wire fixed to a chilled metal bar (impulse seal), as is known to those of skill in the art, or any other sealing means known to those of skill in the art, such as ultrasonic radiation, radio frequency radiation, and laser. The preferred sealing means is an impulse sealer. Films which are predominantly polyethylene are generally sealed using impulse sealing or hot bar sealing. Both linear and shaped seals can be formed, as is known to those of skill in the art. In general, sealing and cutting of tubing to produce bags is disclosed in U.S. Patent No. 3,552,090, U.S. Patent No. 3,383,746, and U.S. Serial No. 844,883, filed July 25, 1969, to OWEN, each of these two U.S. Patents as well as the U.S. Patent application, hereby being incorporated by reference thereto, in their entireties.

Various films suitable in accordance with the present invention are described below. Unless stated otherwise, all percentages, parts, etc. are by weight.

15

Example

A coextruded, three-ply tubular tape was cast, the tape having a thickness of 29 mils, the tape having an A (outside) layer making up 25 percent of the tape thickness, and a B (inner) layer making up 60 percent of the tape thickness, and a C (inside) layer making up 15% of the tape thickness. The A layer was composed of: (a) 90 weight percent DOWLEX 2045 (TM) linear low density polyethylene having a density of 0.920 g/cc, obtained from The Dow Chemical Company, of Midland, Michigan (hereinafter "LLDPE #1"), (b) 10 weight percent ESCORENE[®] LD 318.92 ethylene/vinyl acetate copolymer having a vinyl acetate content of 9 percent, obtained from the Exxon Chemical Company of Houston, Texas "EVA #1." The B layer was composed of: (a) 65 weight percent LLDPE #1; (b) 10 weight percent EVA #1; and (c) 25 weight percent 19153-S black low density polyethylene-based masterbatch, obtained from Ampacet Corporation, of Tarrytown, New York, hereinafter "Black Masterbatch #1." The C layer was composed of 100 percent ESCORENE[®] LD-761.36 ethylene/vinyl acetate copolymer having a vinyl acetate content of 28 percent, obtained from the Exxon Chemical Company, of Houston, Texas, hereinafter "EVA #2."

30

The three-ply tubing was cooled to a solid phase in a water bath and then electronically crosslinked to a level of from about 53.2 milliamps (i.e., 7 to 8 megareads "MR"). The resulting crosslinked three-ply tubing was heated by steam cans and hot air at

about 237°F, and was subsequently oriented by being drawn and stretched approximately 350%, in each of the machine and transverse directions, respectively, using a trapped bubble of air held between two nip rolls. The orientation produced a 2.38 mil three-ply film in the form of a tube.

5 After drawing, the resulting coextruded, hot-water-shrinkable lay-flat film tubing was passed through a pair of nip rolls, causing the inside C layer to bond to itself upon tube collapse, rendering a final six-ply film, with the two central plies being the inside C layer bonded to itself (i.e., resulting in a "self-welded 6-ply film" having a thickness of 4.76 mils), as follows:

10 A / B / C / C / B / A

This "self-welded" film is then laminated to a MELINEX™ D888 film having a thickness of 20 microns which is a non aluminum metal, non chlorine containing high oxygen barrier film containing polyethylene terephthalate and a lamellar particulate (believed to be vermiculite particulates) which imparts to the film high O₂, CO₂, N₂, and moisture barrier characteristics. The MELINEX™ D888 film is believed to comprise a coating layer containing the vermiculite particulates in a polyester resin, with a primer layer containing a resin component believed to comprise acrylamide and/or a derivative thereof and/or a styrene copolymer, and/or an acrylic or methacrylic resin (as discussed above), together with a freefunctional acid (also as discussed above). The lamination of the MELINEX™ D888 to the 6-layer substrate film results in a 9-layer laminate intermediate, as the MELINEX™ D888 is a 2-layer film and one layer of laminating adhesive (described immediately below) is utilized to carry out the lamination.

Suitable laminating adhesives include laminating adhesives as known to those of skill in the art for the laminating of films to one another. A preferred laminating adhesive comprises polyurethane-based adhesive. A particularly preferred polyurethane-based adhesive comprises a blend of: (1) 39.7% ethyl acetate and 5.0% methylene bisphenyl isocyanate, with (2) 25% ethyl acetate and 9.4% gamma-aminopropyltriethoxysilane and 9.4% diethylene glycol, with (3) the ethyl ester of acetic acid as a solvent. This laminating adhesive can be obtained from Morton International of Woodstock, Illinois.

30 Thereafter, a third film is laminated to the 9-layer laminate intermediate described above. The third film serving as a moisture barrier, and preferably is a monolayer film comprising 100 weight percent high density polyethylene. Preferably, the high density

polyethylene has a density of about 0.962 g/cc and a melt index of about 1.0, and having a thickness of about 2 mils, and preferably comprises Chevron HiD 9659 HDPE resin, obtained from the Chevron Chemical Company of Houston, Texas.

5 In the packaging of photography-related products, the film and article of the present invention are especially useful for the packaging of 10 to 100 pound rolls of photographic paper and photographic film, as well as for the packaging of various sizes of motion picture film rolls. The layer(s) of embedded carbon black, which are blended with polymer, to prevent a light-sensitive product in the package from being exposed to light.

10 Although the present invention has been described in connection with the preferred embodiments, it is to be understood that modifications and variations may be utilized without departing from the principles and scope of the invention, as those skilled in the art will readily understand. Accordingly, such modifications may be practiced within the scope of the following claims. Moreover, Applicants hereby disclose all subranges of all ranges disclosed herein. These subranges are also useful in carrying out the present invention.

WHAT IS CLAIMED IS:

1. A multilayer film comprising:

(A) a first layer comprising at least one member selected from the group consisting of
5 platelet mineral, aluminum oxide, and SiO_x ; and

(B) a second layer comprising at least one member selected from the group consisting of
ethylene/alpha-olefin copolymer, polyethylene homopolymer, polypropylene,
polyamide, polycarbonate, polyester; and

wherein the multilayer film has an instrumented impact strength of at least 10 pounds, based
10 on a total thickness of the multilayer film.

2. A multilayer film comprising:

(A) a first layer comprising at least one member selected from the group consisting of
platelet mineral, aluminum oxide, and SiO_x ; and

15 (B) a second layer comprising at least one member selected from the group consisting of
high density polyethylene, biaxially oriented polypropylene, polyvinylidene chloride,
and polyester; and

wherein the film has an O_2 -transmission rate of less than $25 \text{ cc/m}^2/\text{day}$ stp at 100%
relative humidity, and an H_2O -transmission rate of less than $1.5 \text{ grams}/100\text{in}^2$ at
20 100°F and 90% relative humidity.

3. The multilayer film according to Claim 2, wherein the multilayer film has an
instrumented impact strength of from about 10 to 300 pounds, based on a total thickness of
the multilayer film.

4. The multilayer film according to Claim 3, comprising:

(A) a first layer comprising at least one member selected from the group consisting of
polyethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester
copolymer, ionomer, polyamide, and polyester;

30 (B) a second layer comprising at least one member selected from the group consisting of
ethylene/ester copolymer, modified polyolefin, ionomer, ethylene acrylate copolymer,
ethylene acrylic acid, polyamide, and polyurethane;

(C) a third layer comprising at least one member selected from the group consisting of ethylene/ester copolymer, modified polyolefin, ionomer, ethylene acrylate copolymer, ethylene acrylic acid, polyamide, and polyurethane;

(D) a fourth layer comprising at least one member selected from the group consisting of polyethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer, ionomer, polyamide, and polyester;

(E) a fifth layer comprising at least one member selected from the group consisting of platelet mineral, aluminum oxide, and SiO_x ; and

(F) a sixth layer comprising at least one member selected from the group consisting of high density polyethylene, biaxially oriented polypropylene, polyvinylidene chloride, and polyester, and wherein the fifth layer is between the fourth layer and the sixth layer; and

wherein the second layer is between the first layer and the third layer, the third layer is between the second layer and the fourth layer and is directly adhered to the second layer, and the fourth layer is between the third layer and the fifth layer, and the fifth layer is between the fourth layer and the sixth layer.

5. The multilayer film according to Claim 4, wherein the fifth layer comprises vermiculite.

6. The multilayer film according to Claim 5, further comprising a primer layer directly adhered to the fifth layer, wherein the primer layer comprises at least one member selected from the group consisting of aminoplast resin, homopolyester, copolyester, styrene/maleic anhydride copolymer, styrene/itaconic acid copolymer, styrene/acrylamide copolymer, copolymer of acrylic acid, copolymer of methacrylic acid, copolymer of acrylic acid/ C_{2-6} ester, functionalized polyolefin, nitrocellulose, ethylcellulose, hydroxyethylcellulose, polyvinyl alcohol, and polyurethane.

7. The multilayer film according to Claim 5, wherein the fifth layer further comprises at least one member selected from the group consisting of aminoplast resin, homopolyester, copolyester, styrene/maleic anhydride copolymer, styrene/itaconic acid copolymer, styrene/acrylamide copolymer, copolymer of acrylic acid, copolymer of methacrylic acid,

copolymer of acrylic acid/C₂₋₆ ester, functionalized polyolefin, nitrocellulose, ethylcellulose, hydroxyethylcellulose, polyvinyl alcohol, and polyurethane.

8. The multilayer film according to Claim 7 further comprising a primer layer directly
5 adhered to the fifth layer, wherein the primer layer comprises at least one member selected from the group consisting of at least one member selected from the group consisting of aminoplast resin, homopolyester, copolyester, styrene/maleic anhydride copolymer, styrene/itaconic acid copolymer, styrene/acrylamide copolymer, copolymer of acrylic acid, copolymer of methacrylic acid, copolymer of acrylic acid/C₂₋₆ ester, functionalized polyolefin,
10 nitrocellulose, ethylcellulose, hydroxyethylcellulose, polyvinyl alcohol, and polyurethane.

9. The multilayer film according to Claim 8, further comprising a seventh layer which comprises at least one member selected from the group consisting of modified polyolefin, ionomer, ethylene acrylate copolymer, ethylene acrylic acid, polyamide, and polyurethane,
15 the seventh layer being between the fourth layer and the fifth layer.

10. The multilayer film according to Claim 9, further comprising a eighth layer which comprises at least one member selected from the group consisting of modified polyolefin, ionomer, ethylene acrylate copolymer, ethylene acrylic acid, polyamide, and polyurethane,
20 the eighth layer being between the fifth layer and the sixth layer.

11. The multilayer film according to Claim 5, wherein at least one layer of the film comprises a pigment.

25 12. The multilayer film according to Claim 11, wherein the pigment comprises carbon black.

13. The multilayer film according to Claim 12, wherein the carbon black is present in at least one inner film layer.

30

14. The multilayer film according to Claim 13, wherein the carbon black is present in a seventh film layer which is between the first layer and the second layer, the seventh layer

further comprising at least one member selected from the group consisting of polyethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer, ionomer, polyamide, and polyester.

5 15. The multilayer film according to Claim 14, wherein the carbon black is also present in an eighth film layer which is between the third layer and the fourth layer, the eighth layer further comprising at least one member selected from the group consisting of polyethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer, ionomer, polyamide, and polyester.

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16. The multilayer film according to Claim 15, further comprising a ninth film layer which comprises at least one member selected from the group consisting of modified polyolefin, ionomer, ethylene/acrylate copolymer, ethylene/acrylic acid copolymer, polyamide, and polyurethane, the ninth film layer being between the fourth layer and the fifth layer.

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17. The multilayer film according to Claim 16, further comprising a tenth film layer which comprises at least one member selected from the group consisting of modified polyolefin, ionomer, ethylene acrylate copolymer, ethylene acrylic acid, polyamide, and polyurethane, the tenth film layer being between the fifth layer and the sixth layer.

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18. The multilayer film according to Claim 17, wherein the first, fourth, seventh, and eighth layers each comprise at least one member selected from the group consisting of (A) homogeneous ethylene/alpha-olefin copolymer having a density of from about 0.89 g/cc to 0.93 g/cc and (B) linear low density polyethylene.

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19. The multilayer film according to Claim 18, wherein the film has a total thickness of from about 3 mils to about 15 mils.

20. The multilayer film according to Claim 18, wherein the film has an H₂O-transmission rate of less than 0.3 grams/100in² at 100°F and 90% relative humidity.

30

21. The multilayer film according to Claim 18, wherein the multilayer film has an impact strength of at least 10 pounds per mil, based on a total thickness of the multilayer film.

22. A packaged product comprising a package and an product within the package:

5 (A) the package comprising a multilayer film which comprises:

(1) a first layer comprising at least one member selected from the group consisting of polyethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer, ionomer, polyamide, and polyester;

10 (2) a second layer comprising at least one member selected from the group consisting of ethylene/ester copolymer, modified polyolefin, ionomer, ethylene acrylate copolymer, ethylene acrylic acid, polyamide, and polyurethane;

(3) a third layer comprising at least one member selected from the group consisting of ethylene/ester copolymer, modified polyolefin, ionomer, ethylene acrylate copolymer, ethylene acrylic acid, polyamide, and polyurethane;

15 (4) a fourth layer comprising at least one member selected from the group consisting of polyethylene homopolymer, ethylene/alpha-olefin copolymer, ethylene/ester copolymer, ionomer, polyamide, and polyester; and

(5) a fifth layer comprising at least one member selected from the group consisting of platelet mineral, aluminum oxide, and SiO_x; and

20 wherein the second layer is between the first layer and the third layer, the third layer is between the second layer and the fourth layer and is directly adhered to the third layer, and the fourth layer is between the third layer and the fifth layer, and at least one layer comprises an opaque pigment; and

(B) the product comprises photographic film.

25

23. The packaged product according to Claim 22, wherein the fifth layer comprises vermiculite.

24. The packaged product according to Claim 23, wherein the pigment comprises

30 carbon black.

25. The packaged product according to Claim 24, wherein the film comprises at least two layers which comprise carbon black pigment.

5 26. The packaged product according to Claim 25, wherein the photographic film comprises at least one roll of undeveloped photographic film.

27. The packaged product according to Claim 26, wherein the package is a vacuum package.

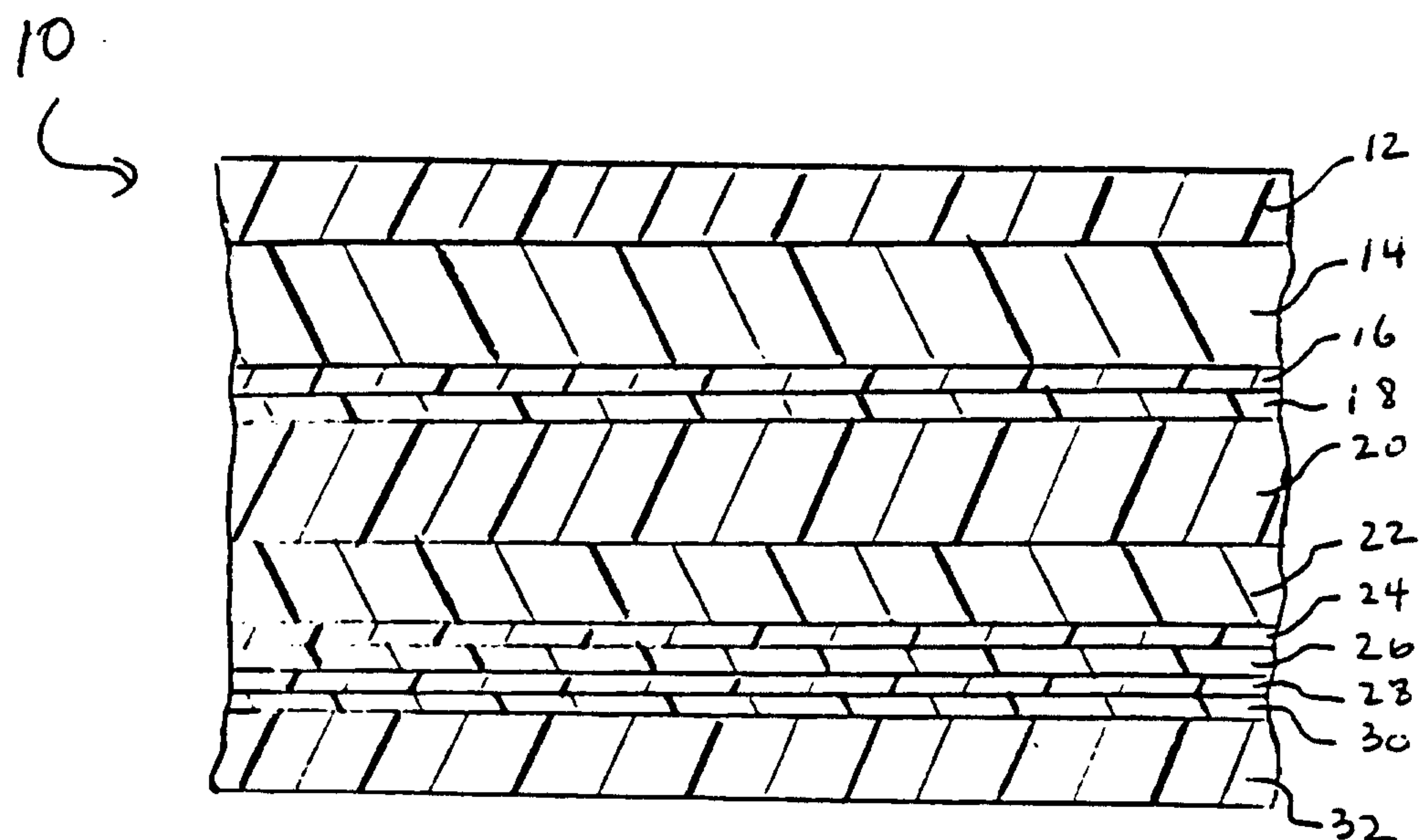


Fig. 1

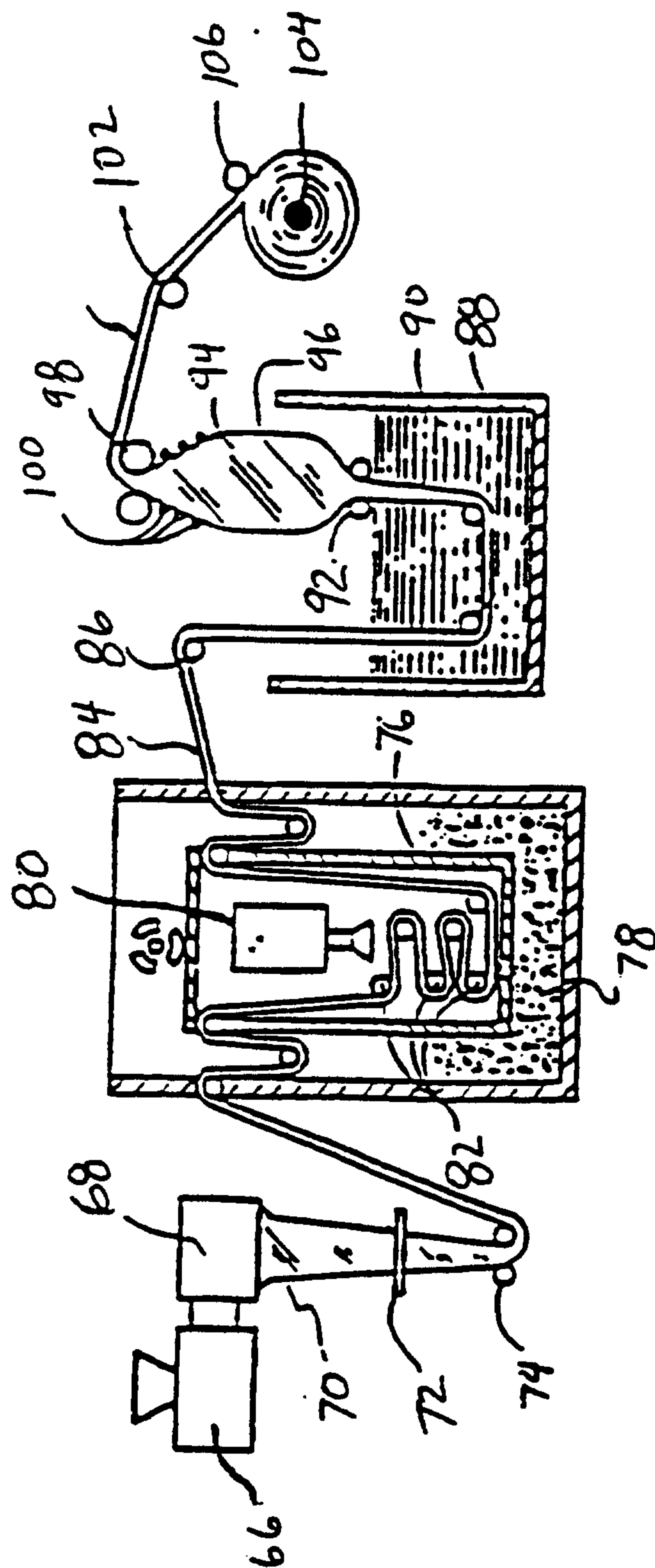


FIG 2

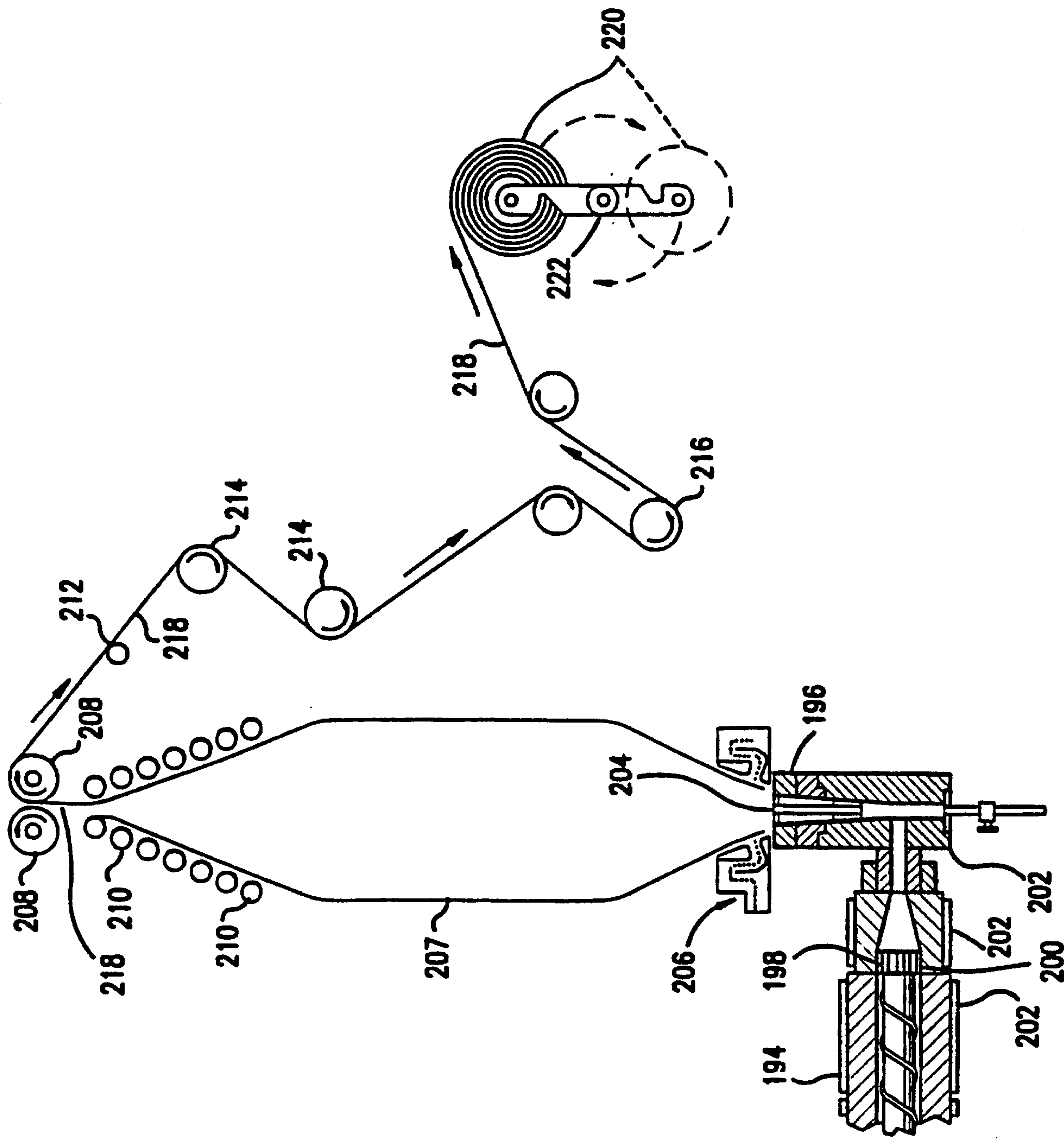


FIG. 3