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MULTILAYER HALOGEN-FREE BARRIER FILM

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(57) Claim

1. An oxygen and moisture impermeable multilayer barrier film comprising a halogen-free polymeric barrier layer and at least one heat sealable skin layer, said skin layer comprising a thermoplastic polymer having a 2 percent secant modulus of less than 15,000 psi in both the machine and transverse directions, said barrier film exhibiting a noise of less than 85 dB when subjected to flexing through a 65° angle at 0.45 Hz and having a heat seal strength of at least 1.0 lb/inch width of said film.

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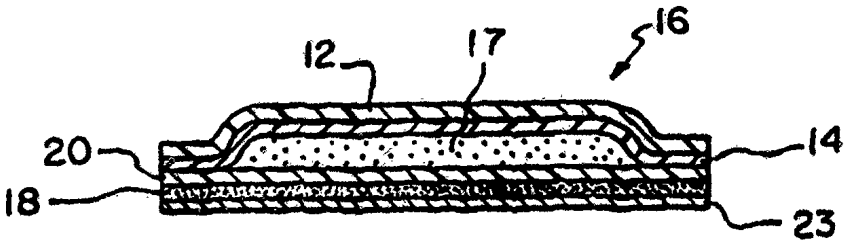
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(54) Title: MULTILAYER HALOGEN-FREE BARRIER FILM

(57) Abstract

An oxygen and moisture impermeable multilayer barrier film (10) which was free of halogens and which may be produced by coextrusion or lamination techniques was provided. The film provides excellent adhesion between layers, has quietness, odor barrier, and softness characteristics, and provides a heat sealable surface for the fabrication of bags.



The barrier film includes a halogen-free barrier layer (12) and at least one heat sealable skin layer (14). The heat sealable skin layer includes either a thermoplastic polyurethane, a substantially linear copolymer of ethylene and an α-olefin having a density in the range of from 0.87-0.92 gm/cc and from 0.01 to 3 long chain branches/1000 carbon atoms along the polymer backbone, a homogeneously-branched linear polyolefin resin, or a blend of an ultra low density polyolefin resin with a copolymer of ethylene and vinyl acetate.

MULTILAYER HALOGEN-FREE BARRIER FILM

The present invention relates to an oxygen and moisture impermeable multilayer barrier film which was free of halogens, and to articles produced therefrom including ostomy bags or pouches and transdermal drug delivery systems.

Plastic film laminates having oxygen and moisture vapor barrier properties were desirable for current packaging requirements, as well as for use in medical applications such as the fabrication of ostomy bags and transdermal drug delivery systems. Where the films were to be used in ostomy applications, they must possess a unique combination of odor and moisture barrier properties as well as low noise, softness, heat or radio-frequency sealability, skin compatibility, and comfort. Such films have been provided in the past through the use of multi-ply film laminates where at least one of the plies was oxygen and moisture vapor impermeable. Typically, the barrier layer in these films comprises a halogen-containing polymer such as chlorinated polyethylene, plasticized polyvinyl chloride, or polyvinylidene chloride copolymers. Others have used multilayered barrier constructions such as ethylene vinyl acetate/polyvinylidene chloride/ethylene vinyl acetate combination films.

While such films have good barrier properties against oxygen, odor, and moisture, one major drawback has been the chlorine content of the films. Such chlorine-containing films were considered to create environmental hazards in their use and disposal in many countries. For example, German Patent No. DD 274,387 describes coextruded composite films for use in the manufacture of colostomy bags having a barrier layer of a copolymer of ethylene and vinyl alcohol and skin layers of a linear low density polyethylene.

Other known multilayer barrier films exist for varied uses including the packaging of meats where oxygen and moisture barrier properties were also important. For example, Lustig et al 5,077,109 and 4,911,963 teach multilayer films using Nylon as the barrier layer with linear low density or very low density polyethylenes as the skin layers. However, such films were taught to be biaxially oriented to improve puncture resistance, making them too noisy for use in ostomy applications.

Accordingly, the need still exists for multilayer barrier films which may be produced by conventional processes without the need for halogen-containing barrier layers and for films which were impermeable to moisture and oxygen, provide odor barrier, softness, and low noise properties, and which have a heat sealable surface for forming ostomy bags or the like.

The present invention meets that need by providing an oxygen and moisture impermeable multilayer barrier film which was free of halogens and which may be produced by

coextrusion or lamination techniques. The film provides excellent adhesion between layers, has quietness, odor barrier, and softness characteristics, and provides a heat sealable surface for the fabrication of bags or the like

According to one aspect of the present invention, an oxygen and moisture impermeable multilayer barrier film was provided which includes a halogen-free polymeric barrier layer coextruded with at least one heat sealable skin layer. To provide the desired softness characteristics, the heat sealable skin layer preferably has a 2 percent secant modulus of less than 15,000 psi in both the machine (MD) and transverse(TD) directions. The heat sealable skin layer may comprise either a thermoplastic polyurethane, a substantially linear copolymer resin of ethylene and an α-olefin having a density in the range of from 0.87-0.92 gm/cc and from 0.01 to 3 long chain branches/1000 carbon atoms along the polymer backbone, a homogeneously-branched linear polyolefin resin, or a blend of an ultra low density polyolefin resin with a copolymer of ethylene and vinyl acetate. The barrier film exhibits a noise of less than 85 dB when subjected to flexing through a 65° angle at 0.45 Hz, preferably exhibits a noise of less than 83 dB when subjected to flexing through a 65° angle at 0.45 Hz, and most preferably exhibits a noise of less than 81 dB when subjected to flexing through a 65° angle at 0.45 Hz. The barrier film has a heat seal strength of at least 1.0 lb/inch of film width, and preferably greater than 1.5 lb/inch of film width (ASTM 903 D).

By "oxygen impermeable", it was meant that the film has an oxygen transmission rate of equal to or less than 400 cc/m^2/day·atm. By "moisture impermeable", it was meant that the film has a water vapor transmission rate of equal to or less than 30 gm/m^2/day. The term "heat sealable" was meant also to encompass radio-frequency sealing techniques.

The preferred halogen-free barrier layer material for the present invention comprises Nylon, either an amorphous Nylon resin, a crystalline Nylon resin such as Nylon 6 or Nylon 6/66 resin, or blends of amorphous and crystalline Nylons. Other suitable barrier materials for use in the present invention include copolymers of ethylene and vinyl alcohol (EVOH), blends of Nylon and EVOH, and multiple layers of these barrier materials. In a preferred embodiment of the invention, the heat sealable skin layers were included on both surfaces of the halogen-free barrier layer. As an aid in processing the film, the skin layer(s) may optionally contain from 0.5-5 percent by weight of a slip additive/antiblocking agent package.

In one embodiment of the invention, the barrier layer may be coextruded with at least one heat sealable skin layer comprising either a thermoplastic polyurethane, a substantially linear copolymer of ethylene and an α-olefin having a density in the range of from 0.87-0.92, or a blend of an ultra low density polyolefin resin with a copolymer of ethylene and vinyl acetate. Where the heat sealable skin layer comprises a thermoplastic polyurethane, it may be desirable to coextrude a layer of a chemically modified copolymer of ethylene and vinyl acetate between the barrier and skin layers to improve the adhesion between those layers. Where the heat sealable skin layer comprises a blend of an ultra low density polyolefin resin

with a copolymer of ethylene and vinyl acetate, it may be desirable to coextrude a layer of a copolymer of ethylene and acrylic acid or a chemically modified copolymer of ethylene and vinyl acetate between the barrier and skin layers, again to improve the adhesion between those layers.

In a preferred embodiment of the invention, the barrier layer was coextruded between two heat sealable skin layers, where the skin layers comprise from 70-90 percent by volume (thickness) of the film and the barrier layer comprises from 10-30 percent by volume (thickness) of the film. The barrier and skin layer or layers may also be formed separately and then laminated together using suitable adhesive polymers, liquid adhesives, or hot melt adhesives. This construction may be used to form reusable ostomy bags or pouches. To form the bags, the film was folded over onto itself and the at least one skin layer was heat sealed along its edges.

In another embodiment of the invention, additional layers may be added to the barrier film to form a system for transdermal delivery of drugs. The system preferably comprises a backing layer of the barrier film which functions as a barrier to the drug system. An adhesive containing an active drug was preferably adhered to one surface of the film. Adjacent the adhesive was a controlled release membrane which was adapted to contact a patient's skin and to controllably release the drug. In another form of this embodiment, the backing layer may form a reservoir for containing the active drug with the controlled release membrane covering the opening of the reservoir to control the diffusion of the drug into a patient's skin. A peripheral or overall adhesive may be used to adhere the transdermal delivery system to a patient's skin. Preferably, a release liner overlies the adhesive and membrane to protect the construction prior to use.

Accordingly, it was a feature of the present invention to provide an oxygen and moisture impermeable multilayer halogen-free barrier film which may be produced using coextrusion or lamination processes. Further features of the invention include odor barrier, softness, and low noise properties. Additionally, a heat sealable surface for use in forming bags and pouches was provided. These, and other features and advantages of the present invention will become apparent from the following detailed description, the accompanying drawings, and the appended Claims.

Fig. 1 was a schematic cross-section of the multilayer barrier film of the present invention;

Fig. 2 was a front elevational view of an ostomy bag or pouch formed from the multilayer barrier film of Fig. 1 of the present invention;

Fig. 3 was a schematic cross-section of one embodiment of a transdermal drug delivery system in accordance with the present invention; and

Fig. 4 was a schematic cross-section of another embodiment of a transdermal drug delivery system in accordance with the present invention.

In one embodiment, the multilayer barrier film of the present invention may be produced using standard extrusion techniques such as feedblock coextrusion, multi-manifold die coextrusion, or combinations of the two The volume (thickness) of each individual layer may be controlled as it was extruded. Thus, the overall thickness of the multilayer structure may be controlled. Alternatively, the individual layers may be formed separately and laminated together using suitable adhesive bonding layers.

The polymers in the films were not intentionally stretched or oriented other than as a natural consequence of their manufacture to preserve their ow noise characteristics. For example, films produced by a blown process will inherently have some orientation in both the machine (MD) and transverse (TD) directions, while cast films will remain unoriented in the transverse direction Generally, the less orientation which was introduced into the films, the less noisy they will be. The multilayer barrier films of the present invention exhibit a noise of less than 85 dB when subjected to flexing through a 65° angle at 0.45 Hz, preferably exhibit a noise of less than 83 dB when subjected to flexing through a 65° angle at 0.45 Hz, and most preferably exhibit a noise of less than 81 dB when subjected to flexing through a 65° angle at 0.45 Hz.

Additionally, to provide the desired softness characteristics, the heat sealable skin layer preferably has a 2 percent secant modulus of less than 15,000 psi in both the machine (MD) and transverse (TD) directions. 2 percent secant modulus was a measure of the stiffness or softness of a film. We have found that the lower the value for 2 percent secant modulus for the heat sealable skin layer, the softer the resulting film will be. Generally, it was desirable for the 2 percent secant modulus of the film to be as low as possible and yet still remain processable by conventional equipment. For the overall multilayer film, it was preferable that the 2 percent secant modulus be 30,000 psi or below. The resulting multilayer films possess low oxygen and vapor transmission rates, as well as having the odor barrier, softness, and low noise properties needed for ostomy applications.

Referring now to Fig. 1, an oxygen and moisture impermeable multilayer barrier film 10 was illustrated. The film 10 includes a halogen-free barrier layer 12 which may be either an amorphous Nylon, a crystalline Nylon, blends of amorphous and crystalline Nylons, a copolymer of ethylene and vinyl alcohol (EVOH), blends of EVOH and Nylons, and multiple layers of such barrier materials. A preferred Nylon was an amorphous Nylon Selar (*-Registered Trademark) PA3426, commercially available from E.I. du Pont de Nemours Co., Inc. Other suitable commercially available Nylons include Capron* 1539, a Nylon 6/66 resin from Allied Corporation and Capron* 100F, also available from Allied Corporation. An amorphous Nylon was preferred as we have found the amorphous Nylons to possess superior odor barrier properties.

As shown, the halogen-free barrier layer was preferably coextruded with or laminated to two heat sealable thermoplastic skin layers 14 with adhesive layers 13 sandwiched therebetween. The skin layers comprise either a thermoplastic polyurethane, a substantially

linear copolymer resin of ethylene and an α-olefin having a density in the range of from 0.87-0.92 gm/cc and from 0.01 to 3 long chain branches/1000 carbon atoms along the polymer backbone, a homogeneously-branched linear polyolefin resin, or a blend of an ultra low density polyolefin resin with a copolymer of ethylene and vinyl acetate. Suitable thermoplastic polyurethanes include those based on the reaction of a polyisocyanate (aromatic or aliphatic) with polyester, polyether, or polycaprolactone polyols. Chain extenders such as diols and diamines may also be used in the reaction. Such thermoplastic polyurethanes were commercially available from E.I. du Pont de Nemours Co., Inc. under the trademark Hytrel* , from the B.F. Goodrich Co. under the trademark Estane* , and from The Dow Chemical Company under the trademark Pellathane* . A preferred thermoplastic polyurethane composition was Hytrel* 4056.

To aid in processing of the thermoplastic polyurethane skin layers, the skin layers may contain from 0 to 10 percent by weight of a copolymer of ethylene and vinyl acetate, and more preferably, from 0.5-5 percent by weight. In addition, the skin layers may contain from 0.5-6 percent by weight of a slip additive such as 16SFI, commercially available from Akzo Chemical Inc. The thermoplastic polyurethane skin layers used in the present invention typically will provide a heat seal strength in the range of from 7 to 9 lb/inch of film width (ASTM 903 D).

It may also be desirable to coextrude or otherwise position an adhesive layer 13 of a copolymer of ethylene and vinyl acetate between the barrier and thermoplastic polyurethane skin layers to improve the adhesion between those layers. A preferred adhesive was Plexar* 3342, commercially available from Quantum Chemical Corp.

Suitable homogeneously-branched linear polyolefin resins were commercially available from Exxon Corporation under the trademark Exact* or from Mitsui Chemical Co. under the trademark Tafmer* .

A suitable substantially linear copolymer resin of ethylene and an α-olefin was taught in commonly-assigned published PCT application PCT/US92/08812, published April 27, 1993, the disclosure of which was hereby incorporated by reference. These copolymer resins were commercially available from The Dow Chemical Company as polymer resins made using Insite™ constrained geometry catalyst technology (CGCT). The constrained geometry catalysts were described in commonly-assigned copending U.S. application Serial Nos. 545,403, filed July 3, 1990, 758,654, filed September 12, 1991, 758,660, filed September 12, 1991, and 720,041, filed June 24, 1991. The catalysts may be generally characterized as comprising a metal coordination complex of a metal of Groups 3-10 or the Lanthanide series of the Periodic Table of Elements and a delocalized π-bonded moiety substituted with a constrain-inducing moiety.

Such substantially linear copolymers have the strength and toughness of linear low density polyethylene (LLDPE) but with processability similar to highly branched low density polyethylene (LDPE). Thus, the polymers have processing indices (PI's) less than or equal to 70

percent of those of a comparable linear olefin polymer and a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at onset of surface melt fracture of a traditional linear olefin polymer at the same I_2 and M_w/M_n, where I_2 was the melt index measured according to ASTM D-1238, Condition 190°C/2.16 kg (formerly known as "Condition E"), M_w was the weight average molecular weight, and M_n was the number average molecular weight of the polymer. The substantially linear copolymers will have from 0.01 to 3 long chain branches/1000 carbon atoms along the polymer backbone, where long chains were defined as a chain length of at least 6 carbon atoms.

Moreover, these substantially linear copolymers have desirable quietness for use in ostomy applications. Such substantially linear ethylene/α-olefin copolymers typically will provide a heat seal strength in the range of from 2 to 3 lb/inch of film width (ASTM 903 D). Thus, these substantially linear copolymers were preferred for use in the present invention because they possess a unique combination of processability, quietness, and heat seal strength.

A suitable blend of an ultra low density polyolefin resin with a copolymer of ethylene and vinyl acetate for use as a heat sealable skin layer in the present invention includes from 5-95 percent by weight of ultra low density polyolefin resin blended with from 95-5 percent by weight copolymer of ethylene and vinyl acetate. Preferably, from 0.5-6 percent by weight of a slip additive/antiblocking agent package was also included in the blend. A preferred blend of components contains 55 percent of a copolymer of ethylene and vinyl acetate, 40 percent ultra low density polyolefin resin, and 5 percent slip additive.

A suitable class of ultra low density polyolefin resins were Attane* resins, commercially available from The Dow Chemical Company. A suitable class of copolymers of ethylene and vinyl acetate were Elvax* resins, commercially available from E.I. du Pont de Nemours Co., Inc. The slip additive may be any of a number of well known materials commercially available from a variety of sources.

It also may be desirable to coextrude or otherwise position an adhesive tie layer 13 of a copolymer of ethylene and acrylic acid between the barrier and blend of ultra low density polyolefin resin and copolymer of ethylene and vinyl acetate skin layers, again to improve the adhesion between those layers. A preferred adhesive was Primacor* 1410XT, a copolymer of ethylene and acrylic acid which was commercially available from The Dow Chemical Compan

The barrier film 10 may be used to form a reusable ostomy bag or pouch by folding the film and heat sealing either the thermoplastic polyurethane, substantially linear ethylene/α-olefin copolymer, or blend of ultra low density polyolefin resin and copolymer of ethylene and vinyl acetate skin layers to each other. Preferably, the bag will have an oxygen permeability of less than 400 cc/m^2/day·atm (26 cc/100 in^2/day·atm). The barrier film 10 may have a total thickness of between 35 and 100 micrometers, with the barrier layer 12 making up from 10 to 30 percent of the total thickness (volume) of the film. The skin layers (and adhesive

layers, if needed) will typically make up 70 to 90 percent of the total thickness (volume) of the film.

The multilayer barrier films of the present invention may also be formed by lamination techniques using suitable adhesives. For example, the barrier and skin layer or layers may be formed separately and then laminated together using adhesive polymers, liquid adhesives, or hot melt adhesives. Suitable adhesive polymers to bond the barrier and skin layers include, but were not limited to, ethylenically unsaturated copolymers of vinyl acetate, ethyl acrylate, ethyl methacrylate, methyl acrylic acid, acrylic acid, and carbon monoxide. Other examples include ionomers of ethylene and methyl acrylic acid or acrylic acid and grafted anhydride copolymers. Suitable liquid or hot melt adhesives include, but were not limited to, adhesives based on urethanes, copolyesters, and copolymers of amide acrylates.

Fig. 2 illustrates a typical reusable ostomy bag 24 including an opening 26 formed from the multilayer barrier films of Fig. 1. The bag may be formed by folding and heat sealing the edges of multilayer film 10. The film was preferably folded and sealed such that one heat sealable skin layer provides the inner surface of the bag or pouch 24. The halogen-free barrier film of the present invention provides softness and quietness features which were desirable for ostomy applications, as well as moisture resistance and odor and oxygen barrier properties. As will be appreciated by those skilled in the art, the barrier films of the present invention may also find use in other packaging applications where moisture and oxygen barrier properties were required.

Fig. 3 illustrates another embodiment of the invention in which additional layers were included with the barrier film to form a system 16 for transdermal delivery of drugs. In its simplest form, the barrier layer 12 and skin layers 14 of the film serve as a backing film that was a barrier to the drug system. The barrier film further includes an adhesive layer 18 containing an active drug blended in a matrix therein adhered to one surface of the film. The adhesive which was selected should be compatible with the active drug and permeable to the drug. There were many active drugs which can be administered to a patient in this manner including, for example, estrogen, nitroglycerin, nicotine, and scopolamine. In theory, almost any drug may be administered in this manner.

A controlled release membrane 20 adapted to contact a patient's skin and to controllably release the drug overlies adhesive layer 18. An additional adhesive layer 22, which may be applied peripherally or over the entire surface of membrane 20, may also be present to secure the transdermal delivery system 16 to a patient's skin. The adhesives used in the practice of this embodiment of the invention should be medical grade adhesives such as silicone, acrylic, or vinyl acetate adhesives. Generally, in this embodiment, the system 16 will be sealed in a package or secured to a second barrier film which was removed prior to use.

Fig 4 illustrates an alternative form of a transdermal drug delivery system 16 in accordance with the present invention. Barrier layer 12 and skin layer 14 form a barrier film

which was formed into a reservoir to contain active drug 17 therein. The opening to the reservoir was covered by a controlled release membrane 20. An adhesive 18, which may either be peripherally applied or applied over the entire area of membrane 20, acts to secure system 16 to a patient's skin. Again, the adhesive which was selected should be compatible with the active drug and permeable to the drug. Preferably, a release liner 23 or the like covers and protects the adhesive 18 and membrane 20 prior to use.

"Throughout the description and claims of the specification the word "comprise" and variations of the word, such as "comprising" and "comprises" is not intended to exclude other additives, components, integers or steps".

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which was formed into a reservoir to contain active drug 17 therein. The opening to the reservoir was covered by a controlled release membrane 20. An adhesive 18, which may either be peripherally applied or applied over the entire area of membrane 20, acts to secure system 16 to a patient's skin. Again, the adhesive which was selected should be compatible with the active drug and permeable to the drug. Preferably, a release liner 23 or the like covers and protects the adhesive 18 and membrane 20 prior to use.

In order that the invention may be more readily understood, reference was made to the following examples, which were intended to be illustrative of the invention, but were not intended to be limiting in scope.

Example 1

A five-layer barrier film was produced in accordance with the present invention and included a core barrier layer, two outer skin layers, and two intermediate adhesive tie layers joining the core and outer skin layers together. The layers were coextruded using conventional techniques. The core barrier layer was Capron* 1539, a Nylon 6/66 resin commercially available from Allied Corporation. The two outer skin layers comprised a blend of 50 percent Elvax* 3165 (E.I. du Pont de Nemours and Co., Inc.), 40 percent Attane* 4202 (The Dow Chemical Company), and 5 percent of a slip additive such as CN4420. The two intermediate tie layers were Primacor* 1410XT (The Dow Chemical Company).

The resulting five layer halogen-free barrier film had a thickness of approximately 3.0 mils and an ultimate tensile strength (ASTM D-882) of 4,404 (MD) and 3,737 (TD) psi, respectively. The film had an oxygen transmission rate (ASTM D-3985) of 22.2 cc/100 in^2/day·atm and a water vapor transmission rate (Permatran W) of 0.94 gm/100^2/day. The film also had a 2 percent secant modulus (ASTM method D-882 using an Instron tensile tester) of 15,170 psi (MD) and 14,640 psi (TD).

The five layer film was tested for quietness by forming a 4"x4" piece of the film having a 3.0 mil thickness into a cylinder and flexing the film through an angle of 65° at a frequency of 0.45 Hz and measuring the sound level in decibels (dB). Over several tests, the measured noise varied from 78.7 to 82.7 dB.

Example 2

A five-layer barrier film was produced in accordance with the present invention and included a core barrier layer, two outer skin layers, and two intermediate adhesive tie layers joining the core and outer skin layers together. The layers were coextruded using conventional techniques. The core barrier layer was Capron* 100F, a Nylon 6 resin commercially available from Allied Corporation. The two outer skin layers comprised Hytrel* 4056, a thermoplastic polyurethane from E.I. du Pont de Nemours and Co., Inc. and 6 percent of a slip additive 16SFI (Akzo Chemical Inc.). The two intermediate adhesive tie layers were Plexar* 3342 (Quantum Chemical Corp.)

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The resulting five layer halogen-free barrier film had a thickness of approximately 3.0 mils and an ultimate tensile strength (ASTM D-882) of 4,079 (MD) and 3,262 (TD) psi, respectively. The film had an oxygen transmission rate (ASTM D-3985) of 18.8 cc/100 in^2/day·atm and a water vapor transmission rate (Permatran W) of 1.59 gm/100^2/day. The film also had a 2 percent secant modulus (ASTM method D-882 using an Instron tensile tester) of 18,070 psi (MD) and 17,490 psi (TD).

The five layer film was tested for quietness by forming a 4"x4" piece of the film having a 3 0 mil thickness into a cylinder and flexing the film through an angle of 65° at a frequency of 0.45 Hz and measuring the sound level in decibels (dB). Over several tests, the measured noise varied from 82.0 to 84.0 dB.

Example 3

A five-layer barrier film was produced in accordance with the present invention and included a core barrier layer, two outer skin layers, and two intermediate adhesive tie layers joining the core and outer skin layers together. The layers were coextruded using conventional techniques. The core barrier layer was an amorphous Nylon resin, Selar* PA3426 commercially available from E.I. du Pont de Nemours Co., Inc. The two outer skin layers comprised a blend of 55 percent Elvax* 3165D (E.I. du Pont de Nemours and Co., Inc.), 40 percent Attane* 4202 (The Dow Chemical Company), and 5 percent of a slip additive such as CN4420. The two intermediate adhesive tie layers were Plexar* 3342 (Quantum Chemical Corp.).

The resulting five layer halogen-free barrier film had a thickness of approximately 4.0 mils and an ultimate tensile strength (ASTM D-882) of 2,300 (MD) and 1,800 (TD) psi, respectively. The film had an oxygen transmission rate (ASTM D-3985) of 10.0 cc/100 in^2/day·atm and a water vapor transmission rate (Permatran W) of 0.703 gm/100 in^2/day. The film also had a 2 percent secant modulus (ASTM method D-882 using an Instron tensile tester) of 27,000 psi (MD) and 25,000 psi (TD).

Example 4

To demonstrate the quietness of the skin layers used in the multilayer barrier films of the present invention, a number of monolayer films were prepared using a cast film process. Monolayer films of a thermoplastic polyurethane and a substantially linear ethylene/α-olefin copolymer of the present invention were cast and tested for comparison purposes against prior art chlorinated polyethylene and homogeneously-branched polyethylene films.

The five layer films were tested for quietness by forming a 4"x4" piece of the film into a cylinder and flexing the film through an angle of 65° at a frequency of 0.45 Hz and measuring the sound level in decibels (dB). Data were reported in Table 1 below. The measured noise was comparable in quietness to other films in commercial use.

TABLE 1

Sample # (psi)	Polymer Resin	Noise (dB)	2% secant Modulus	
			MD (psi)	TD(psi)
1	Chlorinated polyethylene	80.0	4,000	4,000
2	Ultra low density polyethylene (Dow Attane* 4202, 0.912 g/cc, 3.2 MI)	83.5	12,500	12,500
3	CGCT linear ethylene/ α-olefin copolymer (0.909 g/cc, 3.2 MI)	83.5	12,000	12,000
4	Blend of 33% CGCT substantially linear ethylene/ α-olefin copolymer (0.871 g/cc, 1.0 MI) 67% CGCT substantially linear ethylene/ α-olefin copolymer (0.8995 g/cc, 2.7 MI) and 6% CN315	80.0	5,000	5,500
5	Blend of 50% CGCT substantially linear ethylene/ α-olefin copolymer (0.871 g/cc, 1.0 MI) 50% CGCT substantially linear ethylene/ α-olefin copolymer (0.8995 g/cc, 2.7 MI) and 6% CN315	81.0	4,000	4,500
6	Blend of 67% CGCT substantially linear ethylene/ α-olefin copolymer (0.871 g/cc, 1.0 MI) 33% CGCT substantially linear ethylene/ α-olefin copolymer (0.8995 g/cc, 2.7 MI) and 6% CN315	80.0	3,000	3,500
7	Blend of 89% CGCT substantially linear ethylene/ α-olefin copolymer (0.871 g/cc, 1.0 MI) 11% CGCT substantially linear ethylene/ α-olefin copolymer (0.8995 g/cc, 2.7 MI) and 6% CN315	81.0	2,500	3,000

TABLE 1

Sample # (psi)	Polymer Resin	Noise (dB)	2% secant Modulus	
			MD (psi)	TD(psi)
8	CGCT substantially linear ethylene/ α-olefin copolymer (0.8995 g/cc, 2.7 MI) and 6% CN315	82.0	7,500	7,720
9	Tafmer* 4090 (Mitsui) (0.89 g/cc, 3.6 MI) and 6% CN315	83.0	6,670	7,080
10	Tafmer* 4085 (Mitsui) (0.88 g/cc, 3.6 MI) and 6% CN315	81.0	4,600	4,920
11	Tafmer* 4080 (Mitsui) (0.87 g/cc, 1.1 MI) and 6% CN315	79.0	3,060	2,900
12	Thermoplastic polyurethane (Dow Pellathane* 2355-95AE)	81.5	6,900	7,000
13	Thermoplastic polyurethane (Dow Pellathane* 2363-90AE)	79.5	4,900	5,000

While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the methods and apparatus disclosed herein may be made without departing from the scope of the invention, which was defined in the appended Claims.

The claims defining the invention are as follows:

1. An oxygen and moisture impermeable multilayer barrier film comprising a halogen-free polymeric barrier layer and at least one heat sealable skin layer, said skin layer comprising a thermoplastic polymer having a 2 percent secant modulus of less than 15,000 psi in both the machine and transverse directions, said barrier film exhibiting a noise of less than 85 dB when subjected to flexing through a 65° angle at 0.45 Hz and having a heat seal strength of at least 1.0 lb/inch width of said film.

2. The multilayer barrier film of Claim 1 wherein said skin layer comprises either a thermoplastic polyurethane, a substantially linear copolymer of ethylene and an α-olefin resin having a density in the range of from 0.87-0.92 gm/cc and from 0.01 to 3 long chain branches/1000 carbon atoms along the polymer backbone, a homogeneously-branched linear olefin resin, or a blend of an ultra low density polyolefin resin with a copolymer of ethylene and vinyl acetate.

3. The multilayer barrier film of Claim 1 or Claim 2 wherein said halogen-free barrier layer was selected from the group consisting of amorphous Nylon, crystalline Nylon, copolymers of ethylene and vinyl alcohol, and blends thereof.

4. The multilayer barrier film of any one of the preceding claims including heat sealable skin layers on both surfaces of said halogen-free barrier layer.

5. The multilayer barrier film of any one of the preceding claims wherein said skin layer contains from 0.5 to 6 percent by weight of a slip additive/antiblocking agent package.

6. The multilayer barrier film of any one of the preceding claims wherein said halogen-free barrier layer comprises an amorphous Nylon resin.

7. The multilayer barrier film of Claim 6 wherein said heat sealable skin layer comprises a thermoplastic polyurethane.

8. The multilayer barrier film of Claim 7 including an intermediate adhesive tie layer of a chemically modified copolymer of ethylene and vinyl acetate between said barrier layer and said skin layer.

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9. The multilayer barrier film of any one of the preceding claims wherein said heat sealable skin layer comprises a blend of an ultra low density polyolefin resin with a copolymer of ethylene and vinyl acetate.

10. The multilayer barrier film of Claim 9 including an intermediate adhesive tie layer of a copolymer of ethylene and acrylic acid or a chemically modified copolymer of ethylene and vinyl acetate between said barrier layer and said skin layer.

11. The multilayer barrier film of any one of the preceding claims wherein said skin layers comprise from 70-90 percent by volume of said film and said halogen-free barrier layer comprises from 10-30 percent by volume of said film.

12. The multilayer barrier film of any one of the preceding claims wherein said film has an oxygen transmission rate of less than 400 $cc/m^2/day.atm$.

13. The multilayer barrier film of any one of the preceding claims wherein said skin layer is a substantially linear copolymer of ethylene and an α-olefin having a density in the range of from 0.87-0.92 gm/cc, from 0.01 to 3 long chain branches/1000 carbon atoms along the polymer backbone.

14. The multilayer barrier film of any one of the preceding claims wherein said at least one skin layer was heat sealed along its edges to form a bag or pouch.

15. The multilayer barrier film of any one of the preceding claims wherein said barrier film further includes:

a) an adhesive containing an active drug adhered to one surface of said barrier film; and

b) a controlled release membrane adjacent said adhesive and adapted to controllably release said drug to a patient's skin.

16. The multilayer barrier film of Claim 15 further including an adhesive adhered to a least portion of said controlled release membrane and a release liner overlying said adhesive and release membrane to form a system for transdermal delivery of drugs.

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17. A multilayer barrier film according to Claim 1 as substantially hereinbefore described with reference to any one of Examples 1 to 3 and/or Figures 1, 3 and 40.

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DATED: 14 October 1997

PHILLIPS ORMONDE & FITZPATRICK

Attorneys for:

THE DOW CHEMICAL COMPANY

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FIG-1

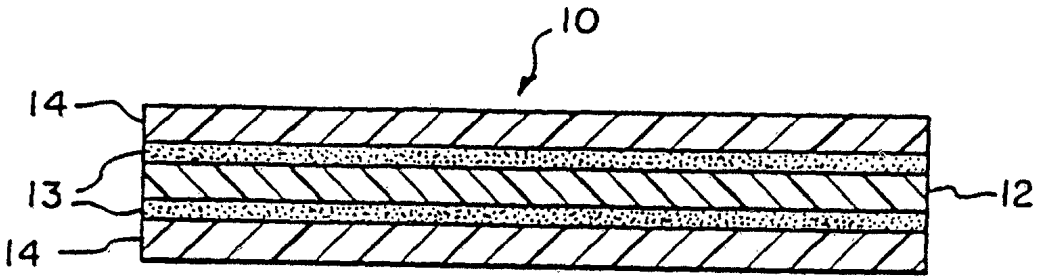


FIG-2

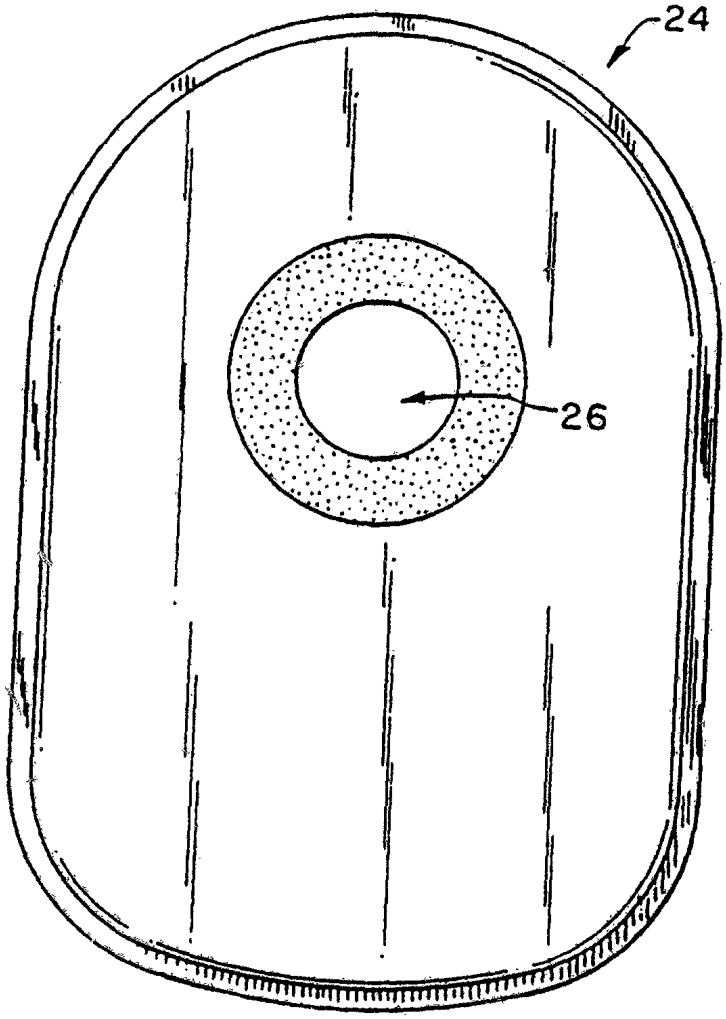


FIG-3

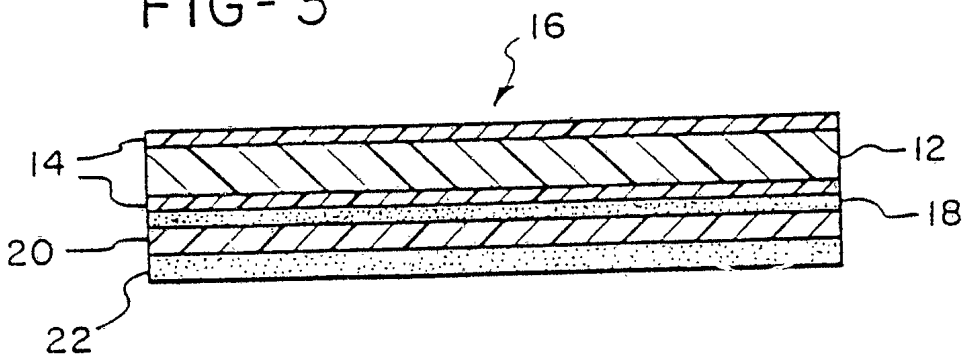
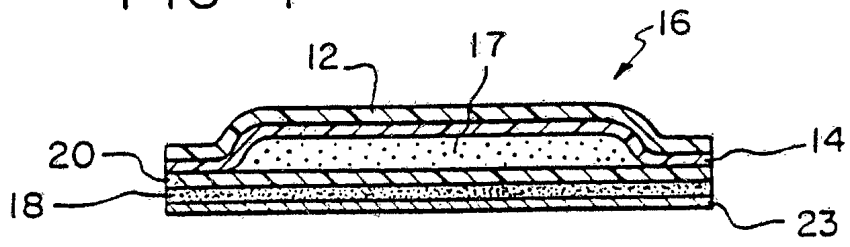


FIG-4



INTERNATIONAL SEARCH REPORT

Interr al Application No
PCT/US 94/09231

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/08 B65D65/40 A61F5/445

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B32B A61F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	EP,A,0 318 025 (W.R. GRACE & CO.) 31 May 1989 see column 1, line 1 - line 25 see column 1, line 40 - line 52 see column 2, line 7 - line 12 see column 2, line 42 - column 3, line 1 see column 3, line 7 - line 18 ---	1,3-5, 11,12,14 2
A	DATABASE WPI Week 8831, Derwent Publications Ltd., London, GB; AN 88-218087 see abstract & RESEARCH DISCLOSURE, RD290014, 6 October 1988, HAVANT GB ANONYMOUS 'STRETCHED SILANE CROSSLINK PLASTIC PRODUCT' --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 December 1994	23. 12. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	De Jonge, S

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INTERNATIONAL SEARCH REPORT

Intern. al Application No
PCT/US 94/09231

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO,A,93 11938 (MINNESOTA MINING AND MANUFACTURING) 24 June 1993 see claims 1-8,18,21,25 see page 4, line 36 - page 5, line 23 see page 6, line 17 - line 23 see page 7, line 9 - line 18 see page 14, line 4 - line 40 see page 15, line 1 - line 7 see page 15, line 28 - line 39 see page 16, line 18 - line 29	1,3,4, 11,12, 14-16
Y	EP,A,0 240 886 (WOLFF WALSRODE AKTIENGESELLSCHAFT) 14 October 1987 see claim 1	2
A	EP,A,0 524 775 (DOW CORNING CORPORATION) 27 January 1993 see claims 1-4	15,16

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Information on patent family members

Inter al Application No
PCT/US 94/09231

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		DE-T-	3884567	31-03-94
		ES-T-	2045069	16-01-94
		JP-A-	1170606	05-07-89
		US-A-	5043205	27-08-91
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		AU-B-	587541	17-08-89
		AU-A-	7146687	15-10-87
		JP-A-	62244635	26-10-87
		US-A-	4830918	16-05-89
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		US-A-	5352722	04-10-94