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(54) Title: PACKAGING FILM, PACKAGES AND METHODS FOR USING THEM**(57) Abstract**

The invention provides a film (1, 2, 3, 4) a package (5) and methods for employing the same. The film has a first layer of an elastomer (10) and a second layer of a polyethylene (20) such as a single site catalyst polyethylene. The film can have a third layer of a polyethylene (20') such that the second layer (20) is disposed between the first (10) and third layers (20'). The polyethylene of the third layer also can be single site catalyst polyethylene and, the elastomer of the first layer can be styrene butadiene copolymer. The film has an oxygen transmission rate of up to about 1000, such as 150-400 cc/100in²/24 hr., typically 260-400 cc/100in²/24 hr., with values of 300, 350-360, 400 cc/100in²/24 hr. and even higher exhibited by the film. The film is suitable for packages, for instance, packaging for cole slaw and leafy salad. The film also exhibits excellent clarity, durability, seal strength and machinability.



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PACKAGING FILM, PACKAGES AND METHODS FOR USING THEM**Field of the Invention**

The present invention relates to films and packages therefrom and to methods for using them. The
5 films have at least two layers including an elastomer layer such as butadiene styrene copolymer and a layer from a single site catalyst polyethylene.

Background of the Invention

Foods such as fresh, pre-cut vegetables as a
10 product in a package formed from film present unique problems. When living as part of a plant, vegetables absorb carbon dioxide from the atmosphere and release oxygen. However, when cut or picked from the plant, the vegetable tends to absorb oxygen and release carbon
15 dioxide (reverse photosynthesis). Thus, the nature of vegetables calls for packaging having certain permeability characteristics.

From health, safety and shelf-life perspectives, packaging for fresh, pre-cut vegetables must
20 have certain gas permeability characteristics. For instance, packaging for a leafy vegetable such as chopped cabbage without dressing (pre-cut cole slaw) must have an oxygen transmission rate (OTR) of about 300 to 400 cc/100in²/24hr. If pre-cut vegetables are in a package
25 which has low permeability to gases such as oxygen (OTR), bacteria growth inside the package can be stimulated, which can spoil the vegetables. The bacteria can also grow undetected without malodor or spoiling the food, and cause sickness. Further, this condition can lower the
30 shelf-life of the vegetables. An approach to obtaining desired carbon dioxide and oxygen transmission through a package is to provide the package with loose or open seals or, perforations. However, this approach literally leaves the food exposed to all possible contaminants,
35 including bacteria, lowers the shelf-life of the food, and, to some extent, defeats the purpose of employing packaging.

In addition, food such as fresh precut vegetables is an item which the consumer prefers to visually inspect prior to purchasing, for instance, to see if the vegetables have spoiled. If the packaging is cloudy or not sufficiently transparent or translucent, the food is not especially desirable to the consumer. Likewise, the packaging should not be too soft in order to provide adequate protection for the food. The packaging should also be able to be sealed, such as by heat-sealing, with a seal which is sufficiently strong so as to also provide adequate protection for the food. Further, the packaging should not be constructed from materials having high levels of extractables because these materials tend to impart unpleasant odors or tastes to the food.

To meet the unique situation of vegetable packaging, it has been proposed to use oriented polypropylene adhered by adhesive lamination to polyethylene. The polyethylene being heat-sealable allows the film to be formed into a package. Likewise, it has been proposed to coextrude unoriented polypropylene and very low density polyethylene (VLDPE) and adhesively laminate the multi-layer coextrusion at the VLDPE side to another layer of VLDPE. These types of structures however do not provide enhanced shelf life for vegetables with high respiration requirements; for instance, cole slaw, broccoli and cauliflower.

In particular, these packages do not exhibit sufficiently high or sufficiently consistently high OTR, or seal strength.

It has also been proposed to coextrude butadiene styrene as a core layer between two layers of polyethylene such as very low density polyethylene. However, this structure does not allow for resistant type crimp seals as typically used in the snack food industry. The VLDPE is the temperature-sensitive heat seal layer and, the butadiene styrene, which is more heat resistant,

is in the core. Thus, the high temperature heat sealing apparatus contacts the more temperature sensitive VLDPE rather than the butadiene styrene. Accordingly, the seal temperature must be sufficiently low so as to prevent
5 damage to the heat-sealable VLDPE layer contacting the heat-sealing apparatus resulting in a low seal strength seal. In addition, such a structure can only be printed upon its outer surface, rendering the printing exposed to scuffing. The package will therefore lose its label or
10 be visually unappealing. Likewise, polyethylene such as linear low density polyethylene has been used as a skin layer in an A/B/A film structure with another material such as a copolymer of ethylene and an ethylenically unsaturated comonomer, for instance ethylene vinyl
15 acetate (EVA), being the core layer. This type of film structure can suffer from the disadvantages of low seal strength because both outer layers are temperature sensitive heat seal layers, and unpleasant odor or taste from the EVA.

20 However, characteristics such as heat sealability are not the only criteria by which one evaluates a film structure for suitability to package food such as vegetables. Health and safety considerations are very important. Thus, to obtain the
25 desired OTR, certain films are adhered to a monolayer of polyethylene such as ultra linear low density polyethylene (ULDPE). However, films from these resins tend to be soft and cloudy, rendering the film unsuitable with respect to appearance and limiting its utility to
30 impulse seals and not resistant seals.

Typically, polyethylene resins employed in packaging are low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), VLDPE or ULDPE. These polyethylenes are
35 typically made with traditional Ziegler-type catalysts which contain different types of reaction sites which result in the polyethylene containing a broad range of

molecules. For instance, the typical polyethylene contains polymers having medium molecular weight with medium branching, low molecular weight with high branching, and high molecular weight with low branching.

5 This results in inconsistent properties.

With respect to packaging materials, ecological considerations as well as economic considerations make it desirable to have as few layers as possible with the most favorable combination of properties. In particular, it
10 would be desirable to have a two- or three- layered structure which has optimal clarity, optimal strength, can be readily heat sealed, has a strong heat seal, can be readily printed upon, has protection for the printing, and, provides the proper barrier properties for products
15 such as vegetables.

Objects and Summary of the Invention

It is an object of the present invention to provide a film which has an OTR of up to about 1000 such as about 150 to about 450, preferably about 260-400, more
20 preferably about 300-400 cc/100in²/24hr.

It is another object of the invention to provide a film which can be heat sealed and, which has a strong seal.

It is yet a further object of the invention to
25 provide a film which is sufficiently durable so as to be useful as a packaging material for food, particularly leafy vegetables such as cole slaw and salad mix.

It is also an object of the invention to provide a film which has sufficient clarity so as to be
30 useful as a packaging material for food.

It is additionally an object of the invention to provide a film which can be printed upon and, wherein the printing can be protected from scuffing.

It is yet another object of the invention to
35 provide a film having as few layers as possible to obtain the desired combination of properties.

It is also an object of the invention to provide a package from a film.

And, it is an object of the invention to provide a method for packaging a product.

5 It has been surprisingly found that polyethylenes from a catalyst having one type of catalytic site provide excellent properties with the respect to heat sealability and, oxygen and carbon dioxide transmission. It is further surprising that an
10 elastomer such as butadiene styrene copolymer can be employed as an outer layer over such a single site catalyst polyethylene to provide a film which can meet the needs of the food packaging industry.

Thus, the present invention provides a film
15 having oxygen permeability of up to about 1000, typically about 150-450 cc/100in²/24hr. The film comprises a first outer layer of an elastomer which is preferably heat resistant such as butadiene styrene copolymer and, a second layer of a single site catalyst polyethylene. The
20 film preferably has an oxygen permeability of about 260-400 and, more preferably about 300-400 cc/100in²/24hr.

The present invention also provides a coextruded film comprising a first outer layer of butadiene styrene copolymer and, a second layer of single
25 site catalyst polyethylene. In a preferred embodiment, the film includes a third layer of single site catalyst polyethylene which is adhesively laminated to the second layer. The three layer film can also include printing on the second or third layer.

30 The present invention also comprehends packages from the films of the invention wherein the second or third layer is heat sealed. The invention further includes a method for packaging a product such as food, preferably vegetables, more preferably, leafy vegetables
35 such as salad or cole slaw, comprising sealing the product in a package made from the film. In addition, the invention comprehends a method for preserving a

product comprising storing the food in a package of the invention.

Brief Description of Drawings

In the following detailed description reference
5 will be made to the accompanying drawings wherein:

Fig. 1 shows in cross-section a two layer film structure of the invention;

Fig. 2 shows in cross-section a three layer film structure of the present invention;

10 Fig. 3 shows in cross-section a three layer structure of the present invention with printing;

Fig. 4 shows in cross-section a three layer structure of the present invention with printing; and,

15 Fig. 5 shows a package of the present invention.

Detailed Description

Turning initially to the Figs., Figs. 1-4 show films 1-4 of the invention. The films are shown in cross-section and, the thickness of layers is arbitrary
20 and not to necessarily represent the actual thickness of layers of the inventive film.

Film 1 of Fig. 1 is a two-layer structure comprised of layers 10 and 20. Layer 10 is an elastomer such as butadiene styrene and, layer 20 is comprised of a
25 single site catalyst polyethylene, which is discussed in more detail below. Layers 10 and 20 can be joined by any suitable means. Co-extrusion is preferred.

Fig. 2 shows film 2 comprised of layers 10, 20 and 20' and, adhesive 25. Layers 10 and 20 are comprised
30 of the same materials as layers 10 and 20 of film 1 of Fig. 1 (hence the same numbering). Since layer 20' is also comprised of single site catalyst polyethylene but is a separate layer, it is numbered similarly to layer 20 of Figs. 1 and 2, but is given the prime designation
35 because it is a separate layer. In Fig. 2 layer 20 is between layers 10 and 20', with layer 20' having been

separately extruded and, adhesive 25 adhering layers 20 and 20' to each other.

Fig. 3 shows three-layered film 3 which is akin to film 2 of Fig. 2, except that printing 22 is on the inner surface of layer 20, between layer 20 and adhesive 25.

Film 4 of Fig. 4 is the same as film 3 of Fig. 3, except that the order of the printing and adhesive are reversed. That is, printing 22 is on the outer surface of layer 20', between layer 20' and adhesive 25.

Fig. 5 depicts package 5 of the invention wherein a sheet of film of the invention is heat sealed at the periphery. Typically, portions of the sheet are brought into face-to-face relationship with layers 20 or 20' on each portion facing the opposing portion. Heat seals 28 are then formed at or near the periphery to define an enclosed area. One side is left open, as shown, for insertion of the product to be packaged and, the filled package is then closed and heat sealed along the open side. Heat seals 28 can be heat resistant type seals as found in snack food packaging.

Alternatively, the film may be made into a package by means of a form, fill and seal apparatus. For instance, the film can be formed into a tube by forming a fin seal along opposing edges and, a transverse seal is also formed across the width of the tube (see, e.g., U.S. Patent No. 4,521,437, incorporated herein by reference). This process is suitable for vertical form, fill and seal machines.

Package 5 of Fig. 5 can also contain resealing means positioned away from a peripheral heat seal. For instance, slot means can be provided on one interior face and tab means on the opposing interior face of the package such that after the heat seal is cut away, the consumer can reseal the package by mating the tab with the slot. Such resealing means or slot and tab means can be of the nature of the "zipper" or "zip-lock" type on

existing plastic bags such as Dow's ZIPLOC™ or Illinois Tool Works' ZIP PAK® food storage bags.

Turning to elastomer layer 10, this layer can be any suitable elastomeric polymer such as butadiene
5 styrene copolymer, polymethylpentene, polybutylene, polyisobutylene, ethylene propylene diene monomer terpolymer, styrene butadiene styrene copolymer, styrene ethylene butylene copolymer, styrene isoprene styrene copolymer, polybutene-1, isobutylene rubber, methyl
10 acrylate butadiene styrene copolymer, acrylonitrile butadiene styrene copolymer, acrylonitrile alkylacrylate butadiene styrene copolymer, methyl methacrylate alkyl acrylate styrene copolymer, methyl methacrylate alkyl acrylate butadiene styrene copolymer, and the like.
15 Considerations for selecting a material for layer 10 include sufficient heat resistance, OTR, strength and clarity.

Butadiene styrene copolymer is a presently preferred elastomer for layer 10. Preferred butadiene
20 styrene copolymers are those of the K-Resin® series from Phillips 66, e.g., KR03, KR04, KR05 and KR10. Of these, KR05 is preferred and, its normal physical properties are set forth below in Table 1.

TABLE 1 - NOMINAL PHYSICAL PROPERTIES OF KR05 SB COPOLYMER**

PROPERTY	ASTM	ENGLISH		SI	
		UNIT	VALUE	UNIT	VALUE
Density	D792	g/cc	1.01	g/cc	1.01
Flow Rate, Condition G	D1238	g/10 min	8.0	g/10 min	8.0
Tensile Yield Strength 2 in (50 mm) per min *	D638	%	160	%	160
Flexural Modulus *	D790	psi	205,000	MPa	1413
Flexural Yield Strength *	D790	psi	4900	MPa	34
Heat Deflection Temperature 264 psi (1.8 MPa) Fiber Stress	D638	°F	163	°C	73
Izod Impact Strength 1/8 in (3.2 mm) Specimen	D256	ft-lbf/in	0.75	J/m	41
Hardness, Shore D	D2240		65		65
Vicat Softening Point	D1525	°F	188	°C	87
Light Transmission	-	%	90	%	90
Moisture Absorption, 24 h	D570	%	0.09	%	0.09

* Specimen injection molded by ASTM Method D1897.

.. From Product Literature

Other elastomeric materials exhibiting substantially similar properties or suitable heat resistance, OTR, strength and clarity characteristics can be employed for layer 10 and, one can sacrifice clarity if visual appearance and inspection of the packaged product is not a major consideration.

As to layers 20 and 20', metallocene catalyst systems are utilized for producing polyethylenes such as those described in U.S. Patent Nos. 4,808,561, 4,871,705, 4,871,523, 4,897,455, 4,925,821, 4,935,397, 4,937,301, 4,952,714, 5,001,205, 5,001,244, 5,006,500, 5,013,803, 5,017,655, 5,026,798, 5,032,652, 5,077,255, 5,079,205, 5,084,534, 5,124,418, and 5,183,867, each of which is hereby incorporated herein by reference. Metallocene catalysts tend to have one type of reaction site, as opposed to traditional Zeigler-type catalysts which have different types of reaction sites. Polyethylenes from Zeigler-type catalysts are polymers containing a broad range of molecules. Polyethylenes from catalysts having one type of reaction site have been found to be more consistent and exhibit superior properties over conventional polyethylenes. Polyethylene polymers from a catalyst having one type of reaction site are herein termed "single site catalyst polyethylene" and, are commercially available from Exxon Chemical as "EXACT" products such as EXACT™ 2009, 2010, 3001, 3006, 3016, 3025, 3026, 3027, 3028 and, 4011. Presently EXACT™ 3025 and EXACT™ 3028 are preferred single site catalyst polyethylenes. Typical properties for the single site catalyst polyethylenes EXACT™ 3025 and EXACT™ 3028 (from Exxon Chemical Product Literature) are set forth in Tables 2 and 3, below.

TABLE 2 - EXACT™ 3025 (LINEAR ETHYLENE-BASED COPOLYMER)

POLYMER PROPERTIES	ASTM METHOD	UNITS	TYPICAL VALUE
Melt Index	D-1238 (E)	dg/min	1.2
Density	D-792	g/cm	0.910
DSC Peak Melting Point	Exxon Method	°C	103
Film Properties ^{1,2}			
1% Secant Modulus	D-882	psi (MPa)	
MD			16900 (117)
TD			18000 (124)
Tensile Strength @ Yield	D-882	psi (MPa)	
MD			980 (6.8)
TD			930 (6.4)
Tensile Strength @ Break	D-882	psi (MPa)	
MD			8140 (56)
TD			5680 (39)
Elongation @ Break	D-882	%	
MD			640
TD			660
Elmendorf Tear Strength	D-1922	g/mil	
MD			111
TD			237
Dart Drop Impact, F ₅₀	D-1709	g/mil	> 1050
Puncture, Force	Exxon Method	lbs/mil	5.9
Energy		in-lbs/mil	14.3
Total Energy Impact	D-4272	ft-lbs	
@ 23°C			2.1
@ -29°C			1.7
Haze	D-1003	%	3.7
Gloss	D-2457	%	79

- 1 1.25 mil film produced on a 2.5' blown film line with 2:1 BUR, melt temperature between 380-415 F, and throughout of 8 lbs/hr/in die.
- 2 Films contain 500 PPM slip and 2000PPM antiblock.

TABLE 3 - EXACT™ 3028 (LINEAR ETHYLENE-BASED COPOLYMER)

POLYMER PROPERTIES	ASTM METHOD	UNITS	TYPICAL VALUE
Melt Index	D-1238 (E)	dg/min	1.2
Density	D-792	g/cm	0.900
DSC Peak Melting Point	Exxon Method	°C	92
Film Properties ^{1,2}			
1% Secant Modulus	D-882	psi (MPa)	
MD			10600 (73)
TD			10800 (74)
Tensile Strength @ Yield	D-882	psi (MPa)	
MD			660 (4.6)
TD			610 (4.2)
Tensile Strength @ Break	D-882	psi (MPa)	
MD			8670 (60)
TD			7250 (50)
Elongation @ Break	D-882	%	
MD			590
TD			680
Elmendorf Tear Strength	D-1922	g/mil	
MD			123
TD			177
Dart Drop Impact, F ₅₀	D-1709	g/mil	> 1058
Puncture, Force	Exxon Method	lbs/mil	7
Energy		in-lbs/mil	21
Total Energy Impact	D-4272	ft-lbs	
@ 23°C			> 6.2
@ -29°C			2.2
Haze	D-1003	%	3.1
Gloss	D-2457	%	83

1 1.25 mil film produced on a 2.5' blown film line with 2:1 BUR, melt temperature between 380-415 F, and throughout of 8 lbs/hr/in die.

2 Films contain 500 PPM slip and 2000PPM antiblock.

The EXACT™ 3025 and 3028 are copolymers of ethylene and 1-butene and are linear ethylene polymers which are unique types of very low density polyethylenes. These single site polyethylenes have a narrow molecular weight distribution, typically greater than 1,000 and less than 100,000 and, a narrow range of single chain branching of about 12 or 12.5 to about 30 SCB/1000 carbons. Single site catalyst polyethylenes have an absence of low molecular weight, high comonomer content molecules, an absence of high molecular weight, low comonomer molecules, a narrow molecular weight distribution with slightly lower melt strength than traditional linear polymers and, a slightly flatter shear rate viscosity curve. Single site polyethylenes are a preferred material for a layer 20 or 20' of the film of the present invention. Other suitable materials can be employed for layer 20 or 20' if the material exhibits similar properties to the preferred single site catalyst polyethylene or, the resultant film displays the desired seal strength and OTR characteristics. For instance, other single site catalyst polyethylenes which can be used for layer 20 or 20' include Exxon's Exact™ and Exxpol™ resins as well as Dow's Insite™ resin. The use of single site catalyst polyethylene as a layer provides distinct advantages such as more consistency in OTR. For example, films including polypropylene have experienced wide swings in OTR: if the thickness of the polypropylene layer varies by 0.1 mil, then a 20% variation in OTR may be observed and, this is not a tolerable variation in the packaging industry.

Adhesive layer 25 can be any suitable adhesive to laminate the coextrusion comprising layers 10 and 20 to layer 20' such as solvent or liquid adhesive, e.g., water-based or urethane adhesive, or solid adhesive. The adhesive should not detract from the desired characteristics of the film. Preferred adhesives for layer 25 are solventless adhesives such as the TYCEL®

laminating adhesives available from the Lord Corporation, e.g., the TYCEL® 7975 Adhesive and TYCEL® 7276 curing agent.

Printing 22 can be imparted to the film by flexographic or rotogravure apparatus, with the ink employed preferably being suitable for food packaging. Referring to Fig. 1, printing can be placed upon the outer exposed or inner surface of layer 10 or, the surface of layer 20 which is in contact with layer 10.

The film of the invention can be any suitable thickness. Thickness can be varied depending upon the end use for the film. Typical thicknesses may range from about 3 microns to about 0.030 inches (0.25 mm) for a thin film to about 1 to 2 mm if a thick film is desired. With reference to Figs. 1-4, layer 10 is typically about 0.5 to 2.0 mils thick, preferably about 1.0 to 1.5 mils thick. Layers 20 and 20' are typically about 0.1 to about 1.5 mils thick. Accordingly, films 1 to 4 are typically about 0.6 to about 3.5 mils thick, preferably about 1 to 3 mils thick and, more preferably about 2 to 2.5 mils thick. The film can be supplied to users in a rollstock format for automatic form, fill and seal equipment or, it can be made into preformed bags or pouches (see Fig. 5).

The film of the invention is especially useful for packaging food such as precut produce, for instance, lettuce, cabbage, salad mixes, cole slaw mix, potatoes, onions and other vegetables and fruits, especially those which tend to respire. For washing and cooling produce and for determining and controlling the proper modified or unmodified packaging atmosphere for perishables such as produce, reference is made to U.S. Patent Nos. 4,996,071 and 4,962,777, incorporated herein by reference. However, the invention is not necessarily limited by the product contained within a package made from the inventive film as the film can suitably be used whenever a "breathable" package is desired. However, the

inventive film is especially useful for packaging food products which tend to oxidize because these foods require packaging having an OTR of about 260-400 cc/100in²/24hr. Indeed, in packaging from the inventive
5 film, cole slaw and leafy salads have an excellent shelf-life of about 4 to about 6 weeks. The inventive film exhibits OTRs of up to 1000 and from 150-450, typically 260-450, such as 300, 350 and 400 cc/100in²/24hr. Furthermore, the inventive film and packages therefrom
10 exhibit excellent clarity and seal strength. Thus, the inventive film and packages are suitable for the food service industry (e.g., hospitals, schools, restaurants, fast food, etc.) where appearance and seal strength are especially important and, long shelf-life may be
15 required.

While coextrusion is preferred for forming film 1 (Fig. 1) and, adhesive lamination is preferred for adhering layer 20' to layer 20 (films 2-4; Figs. 2-4), the films of the present invention can be manufactured by
20 any suitable means. With reference to Figs. 1-4, layers 10, 20 and 20' may be joined by coextrusion, lamination, extrusion lamination and the like.

Further, while the invention has been illustrated with respect to two- and three- layer films, additional layers may be present. However, it is
25 desirable that the films exhibit the permeability (OTR values) of the illustrated and exemplified two- and three-layer films. Likewise, if additional layers are present, the outer layer (layer 10 in Figs. 1-4) should
30 be from a heat resistant elastomer and, the innermost layer should be a heat sealable polymer, preferably a polyethylene and, most preferably a single site catalyst polyethylene. Thus, between layers 10 and 20, between layers 20 and 20' or between both layers 10 and 20 and
35 layers 20 and 20' can be an additional layer or layers from any suitable material such as polyethylene, LDPE, LLDPE, ULDPE, VLDPE, HDPE, polypropylene, oriented

polypropylene, single site catalyst polyethylene, an elastomer (such as those mentioned above for layer 10 or other commercially available materials such as ethylene-propylene and ethylene-butene copolymer elastomers), or
5 blends thereof. However, given the excellent performance of the two- and three-layer films of the invention and economic and ecological considerations, additional layers are not considered necessary.

The following non-limiting Examples are given
10 by way of illustration only and are not to be considered a limitation of this invention.

EXAMPLES

EXAMPLE 1: THREE-PLY FILM

A three-ply A/B/B film according to the
15 invention was made by coextruding the A/B layers (A = butadiene styrene, KR05; B = EXACT™ 3025 single site catalyst polyethylene) and, adhesively laminating the coextruded structure to the separately extruded third "B" layer (Adhesive laminate = TYCEL® 7925 and 7276). The
20 coextruded structure had a 1.3 mil total thickness comprised of 1 mil butadiene styrene and 0.3 mil single site catalyst polyethylene. The inner film had a 1.2 mil thickness. The total structure 2.5 mil had a thickness and had an oxygen transmission rate of 160 cubic
25 centimeters per one hundred square inches in a twenty four hour period.

EXAMPLE 2: THREE-PLY FILM

A three-ply A/B/B film according to the
invention was made by coextruding the A/B layers
30 (A=butadiene styrene, KR05; B = EXACT™ 3028 single site catalyst polyethylene) and, adhesively laminating the coextruded structure to the separately extruded third "B" layer (Adhesive laminate = TYCEL® 7975 and 7276). The coextruded structure had about a 1 mil thickness
35 comprised of 0.7 mil butadiene styrene and about 0.2 mil single site catalyst polyethylene. The innermost "B" film had a 1 mil thickness. The total structure had a 2

mils thickness and had an oxygen transmission rate of 360 cubic centimeters per one hundred square inches in a twenty-four hour period.

EXAMPLE 3: THREE-PLY FILM

5 A three-ply A/B/B film according to the invention was made by coextruding the A/B layers (A=butadiene styrene, KR05; B = EXACT™ 3025 single site catalyst polyethylene) and, adhesively laminating the coextruded structure to the separately extruded third "B"
10 layer (Adhesive laminate = TYCEL® 7975 and 7276). The coextruded structure had about a 1 mil thickness comprised of 0.7 mil butadiene styrene and about 0.3 mil single site catalyst polyethylene. The innermost "B" film had a 1.2 mil thickness. The total structure had a
15 2.2 mils thickness and had an oxygen transmission rate of 250 cubic centimeters per one hundred square inches in a twenty-four hour period.

Each of Examples 1-3 utilized butadiene styrene and single site catalyst polyethylene, but, the
20 polyethylenes varied in density, effecting the oxygen transmission rates. By further varying the density of the single site catalyst polyethylene and/or changing the heat resistant layer (layer 10 in Figs. 1-4), for instance to polymethylpentene, the films of the invention
25 can achieve OTR values up to 1000, for instance, in the 800-1000 cc/100in²/24hr range for products such as broccoli, cauliflower and the like and, in the 600-700 cc/100in²/24hr range for packaging of product such as baby carrots (see Example 5).

EXAMPLE 4: TWO-PLY FILM

A two-ply A/B film according to the invention was made by coextruding the A/B layers (A=butadiene styrene, KR05; B = EXACT™ 3028). Each layer was about 1.0 mil thick and, the film had a total thickness of about 2.0 mil. The film had an oxygen transmission rate of about 340 cubic centimeters per one hundred square inches in a twenty-four hour period.

EXAMPLE 5: HIGH OTR TWO-PLY FILM

A two-ply A/B film according to the invention is made by coextruding polymethylpentene (as the A layer) and single site catalyst polyethylene (as the B layer). The film is about 1.25 mil thick and, respire in the 1000 cc/100in²/24hr range.

EXAMPLE 6: PACKAGING UTILITY

Film as per Example 2 was formed into packages with form, fill and seal apparatus and, a comparative film having an A/B/B structure (wherein the A/B layers were a coextrusion and the third "B" layer was adhesively laminated to the second "B" layer (A = unoriented polypropylene; B = VLDPE)) was also formed into packages with form, fill and seal apparatus. The comparative film was also about 2 mil total thickness with the third "B" layer about 1 mil thick and, the A/B coextrusion was about 1 mil thick (A = 0.3; B = 0.7 mil).

The packages were filled with one pound shredded cabbage or, 8 ounces of: broccoli florets; or cauliflower florets; or vegetable blends. The comparative film and the packages therefrom had an OTR of about 220 cc/100in²/24hr whereas the inventive film and packages therefrom exhibited OTR approximately in accordance with Example 2 (about 350-360 cc/100in²/24hr). The packages from the inventive film and cabbage, broccoli, cauliflower and vegetable blends therein were acceptable: the cabbage, broccoli, cauliflower and vegetable blends exhibited satisfactory characteristics

associated with sufficient oxygen transmission, e.g., no foul odor.

The cabbage, broccoli, cauliflower and vegetable blends packaged in the package from the comparative film exhibited unsatisfactory quality characteristics associated with low package oxygen levels, e.g., foul odor. Thus, the ultimate product (packaged cabbage, broccoli, cauliflower, vegetable blend or vegetables in general) was not acceptable; and accordingly, the comparative film was not acceptable for this utility. The ultimate product and its acceptability depended directly on the OTR characteristics of the film of the package.

Indeed, produce such as broccoli requires a package having an OTR of at least 300 cc/100in²/24hr. The approximately 39% lower OTR of the competitive film (.39 x 360 = 220) was unsuitable and unacceptable as were packages and ultimate products (the cabbage, broccoli, cauliflower and vegetables) therefrom. The high OTR of the inventive film allows it to be used for packaging products requiring high respiration requirements such as certain vegetables, e.g., broccoli, cauliflower, cole slaw and the like and, it can also be used for lower transmission products like Romaine lettuce.

For fresh produce items having high respiration requirement, such as cabbage, broccoli and cauliflower, and various blends of such vegetables, the packages from the inventive film as per Example 2 demonstrated OTR characteristics which provided an acceptable ultimate product, i.e., without causing the critical odor quality defects associated with insufficient oxygen in the package. As the produce item respired in the package, oxygen was consumed; the film OTR of the inventive film was the package characteristic which permitted new oxygen into the package at a rate sufficient to maintain the equilibrium oxygen level required for a good quality product inside the package. The inventive film exhibited

sufficiently high OTR to prevent production of the foul odors associated with anaerobic respiration. The comparative film failed to achieve an acceptable ultimate product (one without foul odor). Thus, the inventive
 5 film provided a package and an ultimate product therein which was acceptable and of good quality whereas the competitive film failed to achieve such.

EXAMPLE 7: MACHINABILITY

A film as per Example 2 was formed into a
 10 package with form, fill and seal apparatus. The package contained 1 lb. cole slaw mix. The jaw seal was resistance type and, the seam seal was fin type. The web width was 17 3/8 inches. The film and package were tested on a scale of "poor", "fair", "good", "very good"
 15 and "excellent" for the following characteristics (with rating also provided):

	CHARACTERISTIC	RATING
	End Seal - Heat & Dwell Range	Excellent
20	End Seal Integrity	Excellent
	Seam Seal - Heat & Dwell Range	Excellent
	Seam Seal Integrity	Excellent
	Bottom End Seal Speed 50 bpm	Excellent
	Seal Thru Wrinkles - End Seam	Excellent
25	Seal Thru Wrinkles - Seam Seal	Excellent

The package was also leak tested (evaluated for seal integrity, seal strength and stress handling) by submerging it in a vacuum chamber, and was "ok" (no leak) at 15", 20" and 23" vacuum (the latter being the
 5 maximum of the chamber). The film was overall rated as excellent, very user friendly, with no wrinkles in the side seam, very minor wrinkles in the end seals, nice clarity and, excellent sealability. The inventive film is very machinable and, can overcome prior art seal

problems, while providing a package having desired OTR, strength and appearance characteristics.

A utility of the inventive film is packaging for produce items with high oxygen requirements, especially on form, fill and seal apparatus such as high speed form-fill seal (FFS) equipment. Key characteristics of the inventive film which make it uniquely capable of achieving this utility (objective) are related to the multilayer laminate film structure combined with the high oxygen transmission rate (OTR) of the film.

The laminated construction of the inventive film provides FFS machine characteristics which permitted high operating speeds along with bag seals of high strength and integrity (resistance seals). Thus, the ultimate product e.g., packaged vegetables, can be produced at cost effective line speeds with a very low incidence of package seal failure. The inventive film was tested and found to be the only laminate film which can be resistance sealed in this manner and supply the necessary OTR required for ultimate products, e.g., packaged vegetables, of quality (see Example 6). The inventive film therefore provides the fresh produce industry with the ability to economically produce packaged vegetables, especially vegetables with high oxygen transmission requirements, in packages with resistance seals.

Having thus described in detail preferred embodiments of the present invention, it is to be understood that the invention defined by the appended claims is not to be limited by particular details set forth in the above description as many apparent variations thereof are possible without departing from the spirit or scope thereof.

WHAT IS CLAIMED IS:

1. A film having an oxygen permeability of about 150-450 cc/100in²/24hr., said film comprising a first outer layer of an elastomer and,
5 a second layer of a single site catalyst polyethylene.
2. The film of claim 1 having an oxygen permeability of about 260-400 cc/100in²/24hr.
3. The film of claim 2 having an oxygen
10 permeability of about 300 cc/100in²/24hr.
4. The film of claim 2 having an oxygen permeability of about 350-360 cc/100in²/24hr.
5. The film of claim 2 having an oxygen permeability of about 400 cc/100in²/24hr.
- 15 6. A film comprising a first, outer layer of styrene-butadiene copolymer and, a second layer of single site catalyst polyethylene.
- 20 7. The film of claim 6 wherein the first and second layers are in intimate contact with each other.
8. The film of claim 6 wherein the first and second layers are coextruded.
9. The film of claim 8 wherein the first and
25 second layers are in intimate contact with each other.
10. The film of claim 6 further comprising a third layer of single site catalyst polyethylene wherein said second layer is disposed between the first and the third layers.
- 30 11. The film of claim 10 wherein the first and second layers are coextruded and, the third layer is adhesively laminated to the second layer.
12. The film of claim 11 wherein the first and second layers are in intimate contact with each other.
- 35 13. The film of claim 11 further comprising printing on the second or third layer.

14. A film consisting essentially of
a first, outer layer of styrene-butadiene
copolymer and,
a second layer of single site catalyst
polyethylene, said film having an oxygen permeability of
about 150-450 cc/100in²/24hr.
15. The film of claim 14 further consisting
essentially of
a third layer of single site catalyst
polyethylene, said second layer being disposed between
said first and third layers.
16. The film of claim 14 wherein the first and
second layers are in intimate contact.
17. The film of claim 15 wherein the first and
second layers are in intimate contact.
18. The film of claim 16 wherein the first and
second layers are coextruded.
19. The film of claim 17 wherein the first and
second layers are coextruded and, the third layer is
adhesively laminated to the second layer.
20. The film of claim 15 having an oxygen
permeability of about 260-400 cc/100in²/24hr.
21. The film of claim 20 having an oxygen
permeability of about 300-400 cc/100in²/24hr.
22. A package comprised of a film of any one
of claims 1, 6 or 14 wherein the second layer is heat
sealed.
23. A package comprised of a film of any one
of claims 10 or 15 wherein the third layer is heat
sealed.
24. A method for using a film as claimed in
claim 10 or 15 for packaging a product comprising forming
a package from the film by heat sealing said film.
25. The method as claimed in claim 24 further
comprising storing a product in said package and sealing
said package closed.

26. The method as claimed in claim 25 wherein said product is a leafy vegetable.

27. The method as claimed in claim 26 wherein said product is lettuce or cabbage.

5 28. A method for preserving a food product comprising storing said food product in a package as claimed in claim 22.

 29. A method for preserving a product comprising storing said food product in a package as
10 claimed in claim 23.

 30. The method of claim 29 wherein the food product is selected from the group consisting of cabbage and lettuce.

 31. The method of claim 30 wherein the food
15 product is cabbage in the form of cole slaw mix.

25
AMENDED CLAIMS

[received by the International Bureau on 29 September 1994 (29.09.94);
original claims 1-31 replaced by amended claims 1-36 (4 pages)]

1. A film having an oxygen permeability of about 150-450 or greater up to about 1000 cc/100in²/24hr., said film comprising
 - 5 a first outer layer of an elastomer and,
a second layer of a single site catalyst polyethylene.
2. A film having an oxygen permeability of about 150-450 or greater up to about 1000
10 cc/100in²/24hr., said film consisting essentially of
 - a first outer layer of an elastomer and,
a second layer of a single site catalyst polyethylene.
3. A film consisting of
 - 15 a first, outer layer of an elastomer and,
a second layer of single site catalyst polyethylene, said film having an oxygen permeability of about 150-450 or greater up to about 1000 cc/100in²/24hr.
4. The film of any one of claims 1, 2 or 3
20 having an oxygen permeability of about 260-400 cc/100in²/24hr.
5. The film of any one of claims 1, 2 or 3 having an oxygen permeability of about 300 cc/100in²/24hr.
- 25 6. The film of any one of claims 1, 2 or 3 having an oxygen permeability of about 350-360 cc/100in²/24hr.
7. The film of any one of claims 1, 2 or 3 having an oxygen permeability of about 400
30 cc/100in²/24hr.
8. The film of any one of claims 1 to 7 wherein the first, outer layer is selected from the group consisting of styrene-butadiene copolymer, polymethylpentene, polybutylene, polyisobutylene,
35 ethylene propylene diene monomer terpolymer, styrene butadiene styrene copolymer, styrene ethylene butylene copolymer, styrene isoprene styrene copolymer,

polybutene-1, isobutylene rubber, methyl acrylate
butadiene styrene copolymer, acrylonitrile butadiene
styrene copolymer, acrylonitrile alkylacrylate butadiene
styrene copolymer, methyl methacrylate alkyl acrylate
5 styrene copolymer, and methyl methacrylate alkyl acrylate
butadiene styrene copolymer.

9. The film of any one of claims 1 to 8
wherein the first layer is of styrene-butadiene
copolymer.

10 10. The film of any one of claims 1 to 8
wherein the first layer is of polymethylpentene.

11. The film of any one of claims 1 or 4 to 10
further comprising a third layer of single site catalyst
polyethylene, said second layer being disposed between
15 the first and the third layers.

12. The film of any one of claims 2 or 4 to 10
further consisting essentially of a third layer of single
site catalyst polyethylene, said second layer being
disposed between said first and third layers.

20 13. The film of any one of claim 3 to 10
further consisting of a thrid layer of single site
catalyst polyethylene, said second layer being disposed
between said first and third layers.

14. The film of any one of claims 1 to 10
25 wherein the first and second layers are coextruded or of
claims 11 to 13 wherein the first and second layers are
coextruded and, the third layer is adhesively laminated
to the second layer.

15. The film of claims 1 to 10 wherein the
30 first and second layers are adhesively laminated or of
claims 11 to 13 wherein the first and second layers are
adhesively laminated and, the third layer is adhesively
laminated to the second layer.

16. The film of any one of claims 14 or 15
35 wherein the layers are adhesively laminated with a
solventless adhesive.

17. The film of any one of claims 1 to 14 or 16 wherein the first and second layers are in intimate contact with each other.

18. The film of any one of claims 1 to 17
5 having printing.

19. The film of any one of claims 11 to 17 having printing on the second or third layer.

20. The film of any one of claim 11 to 17 having an oxygen permeability of about 260-400
10 cc/100in²/24hr.

21. The film of claim 20 having an oxygen permeability of about 300-400 cc/100in²/24hr.

22. A package comprised of a film of any one of claims 1 or 4 to 21 wherein the second layer is heat
15 sealed.

23. A package comprised of a film of any one of claims 11 or 14 to 21 wherein the third layer is heat sealed.

24. A package consisting essentially of a film
20 of any one of claims 2 or 4 to 21 wherein the second layer is heat sealed.

25. A package consisting essentially of a film of any one of claims 12 or 14 to 21 wherein the third layer is heat sealed.

25 26. A package consisting of a film of any one of claims 3 to 21 wherein the second layer is heat sealed.

27. A package consisting of a film of any one of claims 13 to 21 wherein the third layer is heat
30 sealed.

28. The package of any one of claims 22 to 27 wherein the layers are heat sealed with resistance seals.

29. A method for using a film as claimed in any one of claim 1 to 21 for packaging a product
35 comprising forming a package from the film by heat sealing said film.

30. The method as claimed in claim 29 further comprising storing a product in said package and sealing said package closed.

5 31. The method as claimed in any one of claims 29 or 30 wherein said product is a leafy vegetable.

32. The method as claimed in claim 31 wherein said product is lettuce, cabbage, broccoli, cauliflower or a vegetable blend.

10 33. The method of any one of claim 29 to 32 wherein the heat sealing is with resistance seals.

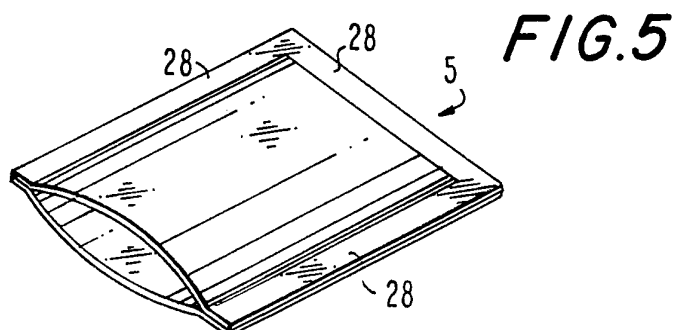
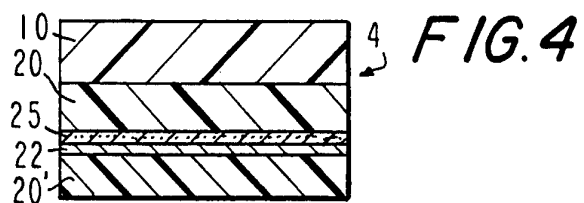
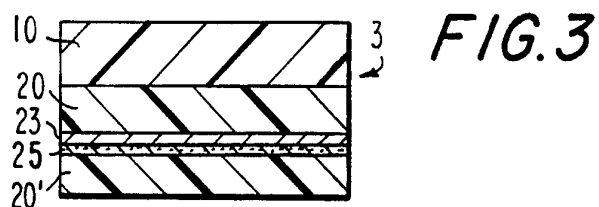
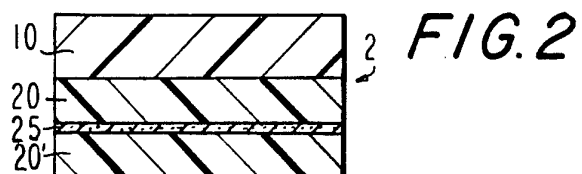
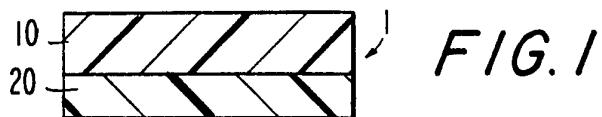
34. A method for preserving a food product comprising storing said food product in a package as claimed in any one of claim 22 to 28.

15 35. The method of claim 34 wherein the food product is cabbage, lettuce, broccoli, cauliflower or a vegetable blend.

36. The method of claim 35 wherein the food product is cabbage in the form of cole slaw mix.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/04655

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 27/08

US CL :428/35.7

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)

U.S. : 428/35.7, 35.9, 35.4, 36.7, 494, 516, 517, 519; 426/118, 127, 395, 415

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 practicable, 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.
Y	US, A, 5,158,836 (SCHIRMER ET AL) 27 October 1992, col. 1, line 9, Figure 1.	1-31
Y	US, A, 5,112,674 (GERMAN ET AL) 12 May 1992, col. 3, lines 52-62, Figure 1.	1-31
Y	JP, A, 54-153884 (IDEMITSU PETROCHEM KK) 04 December 1979, see Abstract.	1-31
Y	"EXACT POLYMERS FOR TARGETED PERFORMANCE IN FILM PACKAGING", Promotional material published by Exxon Chemical Company, 1992, entire document.	1-31
Y	"EXACT FACTS, EXXPOL TECHNOLOGY-EXXON CHEMICAL COMPANY, Vol. 1, No. 1, February 1992, see entire document.	1-31

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

"	Special categories of cited documents:	"T"	Inter 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
"A"	document defining the general state of the art which is not considered to be part of particular relevance		
"E"	earlier document published on or after the international filing date	"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
"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)	"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
"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	"&"	document member of the same patent family

Date of the actual completion of the international search 07 JUNE 1994	Date of mailing of the international search report 01 AUG. 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer CHARLES R. NOLD Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/04655

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	"EXXPOL TECHNOLOGY FOR TARGETED POLYMER PERFORMANCE", Promotional material published by the Exxon Chemical Company, (1991), see entire document.	1-31