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(54) Title: POULTRY SHRINK BAGS WITH ANTIBLOCK ADDITIVES

(57) Abstract: A multiple layer polymeric film comprising three layers wherein the first layer comprises a blend of ethylene vinyl acetate copolymer, linear low-density polyethylene, and a second ethylene vinyl acetate copolymer, the second layer comprises ethylene vinyl acetate copolymer; and the third layer comprises a blend of linear low-density polyethylene and low-density polyethylene said second layer being disposed between said first and third layer and wherein each a color concentrate, a slip additive and an antiblock additive may optionally and independently be present in layers one, two and three.

POULTRY SHRINK BAGS WITH ANTIBLOCK ADDITIVES

Background of the Invention

5 The present invention relates to multilayer polymeric film comprising three layers wherein an antiblock additive may be present in layers one, two and three. These film structures are useful in the packaging of meats and poultry.

 Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common
10 general knowledge in the field.

 Polymeric materials have many applications in packaging structures. They are used as films, sheets, lidstock, pouches, tubes and bags. These polymeric materials may be employed as a single layer or one or more layers in a structure. Unfortunately, there are countless polymeric materials available. Furthermore, resin suppliers frequently
15 have a tendency to claim many more applications for a product than the product is actually suitable for. In addition, in view of the specialized applications and processing problems that are encountered despite the suppliers claims, one skilled in the art can not tell whether a particular resin will be suitable for an application unless tested. However, for various reasons there are frequently drawbacks to the use of many of these polymeric
20 materials. For example, ethylene vinyl alcohol is an excellent oxygen barrier material for use in packaging food products. However, this polymeric material can be affected by moisture that is present in the atmosphere or the packaged product. As a result, it is frequently found that some polymeric materials are better for certain applications than others.

One area where there is a need for suitable resins in film applications is in the area of heat shrinkable films. Heat shrinkable polymeric films are commonly used in packaging meats, particularly primal meat cuts and other large pieces of meat or poultry. While this description will detail the usage of films for packaging meat and meat by-products, it will be understood that these films are also suitable for packaging a myriad of other products, both including food products and non-food products.

Some of the films embodying the present invention are intended to be used by meat or poultry packers in the form of heat shrinkable bags with one opened end, which bags are closed and sealed after insertion of the meat or poultry. After the product is inserted, air is usually evacuated from the package and the open end of the bag is closed. Suitable methods of closing the bag include heat sealing, metal clips, adhesives etc. Heat is applied to the bag once sealing is completed to initiate shrinkage of the bag about the meat.

In subsequent processing of the meat, the bag may be opened and the meat removed for further cutting of the meat into user cuts, for example, for retail cuts or for institutional use.

Suitable shrink bags must satisfy a number of criteria. Many bag users seek a bag that is capable of surviving the physical process of filling, evacuating, sealing and heat shrinking. For example, during the shrinking process great stress can be placed on the film by the sharp edges of bone in the meat or poultry. The bag must also have sufficient strength to survive the material handling involved in moving the large cuts of meat or poultry, which may weigh twenty-five pounds or less, along the distribution system.

Because many food products including meat deteriorate in the presence of oxygen and/or water, it is desirable that the bags have a barrier to prevent the infusion of deleterious gases and/or the loss or addition of moisture.

Conventional packaging for many products has frequently been made of multiple layer films having at least three layers. These multiple layer films are usually provided with at least one core layer of either an oxygen barrier material such as a vinylidene chloride copolymer, ethylene vinyl alcohol, a nylon or a metal foil preferably aluminum. Heat shrinkable meat bags, for example, have generally used vinylidene chloride copolymers. The copolymer of the vinylidene chloride may, for example, be a copolymer with vinyl chloride or methyl acrylate. Collapsible dispensing tubes have generally used one or more foil layers. The foil layers in addition to supplying an oxygen barrier also provide the dispensing tube with "deadfold", i.e., the property of a collapsible dispensing tube when squeezed to remain in the squeezed position without bouncing back.

Outer layers of films used in packaging food products can be any suitable polymeric material such as linear low density polyethylene, low density polyethylene, ionomers including sodium and zinc ionomers, such as Surlyn®. In conventional shrink bags, the outer layers are generally linear low density polyethylene or blends thereof. Suitable outer layers for meat bags are taught by U.S. Patent No. 4,457,960 to Newsome, the disclosures of which are incorporated herein by reference.

United States Patent No. 4,894,107 to Tse et al. commonly assigned to American National Can discloses novel films and processes for making them. The films are characterized by having first and second layers whose compositions have a significant fraction of ethylene vinyl acetate (EVA). A third layer of vinylidene

chloride copolymer (VDC-CP) is disposed between the first and second layers. The composition of at least one of the first and second layers is a blend of 10% by weight to 90% by weight linear low density polyethylene (LLDPE) and 90% to 10% EVA. These polymeric films are useful as heat shrinkable polymeric films. The film may be
5 unoriented or oriented. Oriented films may be optionally cross-linked.

While conventional films have been suitable for many applications, it has been found that there is a need for films that are stronger and more easily processed than conventional films. In meat bags, there is a need for films and bags that have superior toughness and sealability and the ability to undergo cross-linking without undue
10 deterioration.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

It is an object of the present invention in a preferred form to provide improved structures, including single and multi-layer films, sheets, lidstock, pouches, tubes and
15 bags. In particular, structures for use in shrink bags wherein the shrink bags are capable of withstanding production stresses and the shrink process.

Summary of the Invention

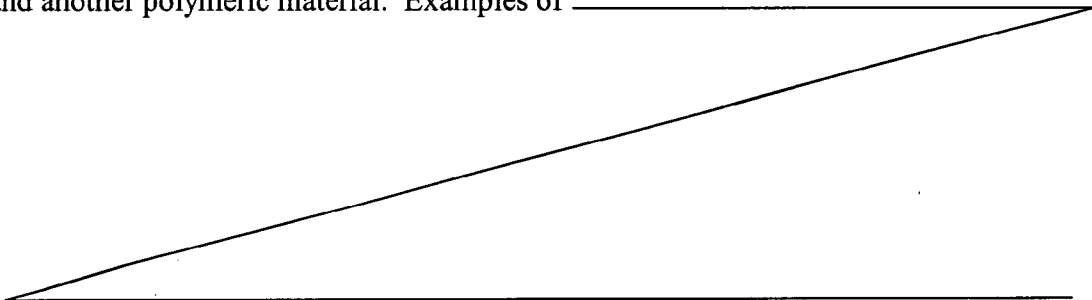
According to a first aspect of the present invention, there is provided a multiple layer polymeric film comprising three layers wherein the first layer comprises a blend of
20 ethylene vinyl acetate copolymer, linear low-density polyethylene, and a second ethylene vinyl acetate copolymer; the second layer comprises ethylene vinyl acetate copolymer; and the third layer comprises a blend of linear low-density polyethylene and low-density polyethylene said second layer being disposed between said first and third layer and

wherein each a color concentrate, a slip additive and an antiblock additive may optionally and independently be present in layers one, two and three.

According to a second aspect of the present invention, there is provided a molecularly oriented multiple layer polymeric film comprising three layers wherein the first layer comprises a blend of ethylene vinyl acetate copolymer, linear low-density polyethylene, a second ethylene vinyl acetate copolymer, slip additive and an antiblock additive; the second layer comprises ethylene vinyl acetate copolymer; and the third layer comprises a blend of linear low-density polyethylene and low-density polyethylene said second layer being disposed between said first and third layer and wherein a color concentrate may optionally and independently be present in layers one, two and three.

The structures of the present invention may be single or multilayer films, sheets, lidstock, pouches, containers, tubes and bags where at least one layer contains a polymer, usually a copolymer, formed by a polymerization reaction in the presence of a single site catalyst such as a metallocene. Examples of such a polymer are ethylene and propylene polymers and copolymers thereof. One preferred copolymer is a copolymer of ethylene and an alpha olefin where such alpha olefin has a carbon chain length of from C₃-C₂₀.

The structures of the present invention may also include blends of polymers and copolymers formed by a polymerization reaction with a single site catalyst or blends of a polymer and copolymer formed by a polymerization reaction with a single site catalyst and another polymeric material. Examples of _____



suitable polymers for blending include: high and medium density polyethylene (HDPE, MDPE), linear low density polyethylene (LLDPE), low density polyethylene (LDPE), ethylene vinyl acetate (EVA), ultra low density polyethylene (ULDPE or very low density polyethylene VLDPE), and ionomers such as Surlyn®. Polymers
5 made from single site catalyst, preferably metallocene catalysts, provide increased strength, particularly seal, burst, impact and puncture as well as improved optics and faster bag making/sealing speeds.

The present invention may also be a multilayer structure of at least three layers wherein the core layer is a barrier layer. In one embodiment of the present invention,
10 there may be a first outer layer of an ethylene or propylene polymer or copolymer formed by a polymerization reaction in the presence of a single site catalyst, a barrier layer and a second outer layer of a polymeric material. The second outer layer may be an ethylene or propylene polymer or copolymer formed by a polymerization reaction in the presence of a single site catalyst or a layer of another polymeric material such
15 as high density polyethylene, medium density polyethylene, linear low density polyethylene, ultra low density polyethylene, low density polyethylene, ethylene vinyl acetate, an ionomer or blends thereof. The first outer layer may also be a blend of the ethylene copolymer with another suitable polymeric material such as described above. A preferred polymer formed by a single site catalyst is a copolymer of ethylene and an
20 alpha olefin such as 1-octene. Additional layers such as adhesive layers or other polymeric layers may be interposed in the structure between one or both of the outer layers or on top of one or both of the outer layers. The structure of the present invention may be rendered oriented either uniaxially or biaxially and cross-linked by any suitable means, such as for example irradiation or chemical cross-linking.

Brief Description of the Drawings

Figure 1 is a side view of a three layer structure of the present invention.

Figure 2 is a side view of a five layer film of the present invention.

Figures 3-6 are examples of the structure of metallocene catalysts which could
5 be used in the polymerization of the polymer used in the structures of the present
invention.

Detailed Description of the Invention

The structures of the present invention include films, sheets, lidstock, pouches,
containers, tubes and bags. These structures may be a single layer or multi-layer
10 structure. The structures are comprised of polymers that have been polymerized in the
presence of a single site catalyst, such as a metallocene. A metallocene is a complex
organometallic molecule typically containing zirconium or titanium, with a pair of
cyclic alkyl molecules. More specifically, metallocene catalysts are usually
compounds with two cyclopentadiene rings fixed to the metal. These catalysts are
15 frequently used with aluminoxanes as a cocatalyst or an activator, one suitable
aluminozane is a methaluminoxane (MAO). Besides, titanium and zirconium,
hafnium may also be used as the metal to which the cyclopentadiene is bonded.
Alternative metallocenes may include Group IVA, VA and VIA transition metals with
two cyclopentadiene rings. Also mono-cyclopentadiene rings or silyl amides may
20 alternatively be in the metallocene instead of two cyclopentadienes. Other metals to
which the cyclopentadiene may be attached may include the metals in the lanthanide
series. Figures 3, 4, 5 and 6 show representative metallocenes that are suitable single
site catalysts.

While the reaction mechanism is not completely understood, it is believed that the metallocene, single site catalyst confines the copolymerization reaction to a single site over the polymer thus controlling comonomer placement and side chain length and branching. The copolymers formed from metallocene single site catalysts are highly stereo regular products with narrow molecular weight distribution. The metallocenes can be used to polymerize ethylene, propylene, ethylenic and acetylenic monomers, dienes and carbon monoxide. Comonomers with ethylene and propylene include styrene, substituted styrene and 1,4-hexadiene. The metallocene single site catalysts are capable of producing isotactic polymers and syndiotactic polymers, i.e., polymers in which the crystalline branches alternate regularly on both sides of the back bone of the polymer. There are two general types of single site catalyst reactions. The first are nonstereoselective catalysts reactions which have been developed by Exxon and Dow and which are used to make Exxon's Exact resins and Dow's constrained geometry catalyst technology (CGCT) resins. See Figs. 3 and 4. The second type of reactions are stereoselective catalysts developed by Hoechst and Fina for stereo specific polymerization particularly of polypropylene and other olefins such as 1-butene and 4-methyl-1-pentene. See, e.g., Figures 5 and 6.

The ethylene alpha olefins polymerized by a single site catalyst can have low crystallinity and a density that ranges from 0.854 to 0.97 gm/cc. Although this density range is similar to conventional ethylene polymers, i.e., LDPE, LLDPE and ULDPE, the polymers in the structures of the present invention have a narrow molecular weight distribution and homogeneous branching. The molecular weight distribution of the preferred polymers may be represented by the formula

$$\text{MWD} = M_w/M_n = <2.5$$

In addition, the melt processability of these polymers (I_{10}/I_2) has a range of about 5.5 to about 12 while conventional homogenous polymers are generally less than 6.5 at an MWD of 2. The melt tension of these polymers is in the range of about 1.5 to 3.5 grams.

5 The MWD of these polymers may be determined using a Waters 150 GPC at 140°C with linear columns (103₆ A-10₆ A₀) from Polymer Labs and a differential refractometer detector. Comparison of the MWD of a 1MI, 0.920 density CGCT polymer with that of 1MI, 0.920 density conventional LLDPE illustrates the very narrow MWD of the CGCT polymers which usually have a M_w/M_n of approximately
10 2 compared to 3 or greater for LLDPE.

A preferred ethylene copolymer is a copolymer of ethylene and a C₃ to C₂₀ alpha olefin. A preferred copolymer is a low modulus ethylene octene copolymer sold by Dow. This copolymer is formed by Dow's constrained-geometry catalyst technology which uses a single site catalyst such as cyclopentadienyl titanium
15 complexes. As best understood, Dow's constrained geometry catalysts are based on group IV transition metals that are covalently bonded to a monocyclopentadienyl group bridged with a heteroatom. The bond angle between the monocyclopentadienyl group, the titanium center and the heteroatom is less than 115°. When the alpha olefin is present in the copolymer in the range of about 10 to 20% by weight these
20 copolymers are referred to as plastomers. When the percent alpha olefin is greater than 20% these copolymers are called elastomers. The preferred ethylene octene copolymer has the octene comonomer present in an amount less than 25%. Examples of Dow ethylene octene copolymers have the following physical properties.

	DENSITY <u>g/cc</u>	MOLECULAR <u>WEIGHT DISTRIBUTION</u> <u>STRENGTH</u>	MELT <u>INDEX</u>	MELT <u>FLOW RATIO</u>	MELT
5	0.920	1.97 1.89	1.0	9.5	
	0.910	1.90 1.68	1.0	7.9	
10	0.902	2.10 1.68	1.0	7.6	

Molecular weight distribution is defined as the ratio of weight average molecular weight to number average molecular weight. The lower the figure, the narrower the molecular weight distribution. Melt flow ratio is defined as the ratio of melt index, as tested with a 10-kg load to the melt index with a 2.168-kg load. The higher the ratio, the more processable the material. Melt flow ratio is defined as melt tension measured in grams. The higher the number the greater the melt strength. Other suitable resins are the Exact resins sold by Exxon, these resins have the following characteristics:

20

TYPICAL PROPERTIES OF EXACT
MEDICAL GRADE POLYETHYLENES

PROPERTY	VALUE BY GRADE					
	4028	4022	4021	4023	4024	4027
Melt index (D1238)*	10	6	22	35	3.8	4
Density, g./cc. (D-1505)	0.880	0.890	0.885	0.882	0.885	0.895
Hardness (D-2240)						
Shore A	78	84	84	80	83	89
Shore D	29	35	36	27	35	39
Tensile strength at break, p.s.i. (D-638)	2220	1700	3260	620	2840	2200
Tensile elongation at break, % (D-638)	>800	>800	>800	>800	>800	>800

PROPERTY	VALUE BY GRADE					
	4028	4022	4021	4023	4024	4027
Tensile impact, ft.-lb./sq. in. (D-1822)	145	130	350	280	300	340
Flexural modulus, p.s.i. (D-790)	5040	4930	3980	3100	4180	7230
Vicat softening point °F. (D-1525)	138	168	158	138	158	181

The structure of the present invention is comprised of an ethylene, propylene, or styrene polymer or copolymer formed by a polymerization reaction in the presence of a single site catalyst preferably a metallocene. Ethylene may be copolymerized with any suitable monomer such as C₃ - C₂₀ alpha olefin including propylene butene-1, 4-methy-1-pentene, 1-hexene and 1-octene. A preferred comonomer is 1-octene. The preferred ethylene alpha olefin copolymer of the present invention has a density in the range of .880 gm/cc to about .920 gm/cc, a more preferred range of .890 gm/cc to about .915 gm/cc and a most preferred range of about .900 gm/cc to about .912 gm/cc.

Figure 1 shows a cross section of a three layer coextruded structure. Layer 14 is the core layer which may be a barrier layer that minimizes the transmission of oxygen through the structure. Preferred barrier materials are polyvinylidene chloride copolymers such as copolymers of vinylidene chloride and vinyl chloride or an alkyl acrylate such as methyl acrylate. Other preferred barrier materials include, ethylene vinyl alcohol, nylon or a metal foil such as aluminum. Layer 14 may also be a copolymer of ethylene and styrene formed using a single site catalyst in the polymerization reaction. In addition, layer 14 may also be a polystyrene formed by a

polymerization reaction in the presence of a single site catalyst. One such polystyrene is the crystalline syndiotactic polystyrene sold by Idemitsu Petro-Chemical Co., Tokyo, Japan.

On opposite sides of the core layer 14 of Figure 1 are layers 12 and 16. At
5 least one of these layers 12 is a polymer formed by a polymerization reaction in the presence of a single site catalyst. The remaining layer 16 may be any suitable polymeric material or blends of material such as a polyester, co-polyester, polyamide, polycarbonate, polypropylene, propylene-ethylene copolymer, ethylene-propylene copolymer, combinations of polypropylene and ethylene vinyl acetate copolymer,
10 ultra low density polyethylene, low density polyethylene, medium density polyethylene, high density polyethylene, linear low density polyethylene copolymers, linear medium density polyethylene copolymer, linear high density polyethylene copolymer, ionomer, ethylene acrylic acid copolymer, ethylene ethyl acrylate copolymer, ethylene methyl acrylate copolymer, or ethylene methacrylic acid
15 copolymer.

In an alternate embodiment, the layer 12 may be a blend of a polymer formed by a polymerization reaction in the presence of a single site catalyst and a suitable polymeric material such as is identified in connection with the description of layer 16 above.

20 As seen in Figure 2, the structure may also include embodiments which have a fourth layer 28 over the first layer 22 and a fifth polymeric layer 30 over the third layer 26. The composition of the fourth layer 28 may be selected from the same group of materials from which the composition of the first layer 12 or third layer 16 is

selected, and the fifth layer 30 may also be the same composition as the first layer 22 or the third layer 26.

In an alternate embodiment of Figure 2, the five layer structure may have a first layer 28 similar in composition to layer 12 of Figure 1, i.e., the film may have a
5 first layer of a polymer formed by the polymerization reaction with a single site catalyst or blends thereof with another suitable polymeric material. One or both of the second 22 and fourth 26 layers may be an adhesive layer.

The composition of adhesive layers 22 and 26 is selected for its capability to bond the core or barrier layer 24 to the surface layers 28 and 30. A variety of the well
10 known extrudable adhesive polymers adhere well to the core or barrier layer 24. Thus, if for example layer 30 is a polypropylene, an adhesive polymer based on polypropylene is desirably selected for layer 26. Examples of such adhesives are the extrudable polymers available under the trade designations Admer QF-500, QF550, of QF-551 from Mitsui Petrochemical Company, or Exxon 5610A2.

15 If the composition of layer 23 or 30 is an ethylene based polymer or copolymer, an adhesive polymer based on ethylene is preferably selected for layer 22, including ethylene homopolymer and copolymers. Such a preferred adhesive composition is an ethylene vinyl acetate copolymer (EVA) containing up to 25% to 30% by weight vinyl acetate. Other ethylene based homopolymer and copolymers,
20 modified to enhance adhesion properties are well known under the trade names of, for example, Bynel and Plexar. Typical base polymers for these extrudable adhesives are the polyethylene LLDPE and the ethylene vinyl acetate copolymers. Such adhesive polymers, including the polypropylene-based polymers, are typically modified with

carboxyl groups such as anhydride. Also acceptable as adhesives are ethylene methyl acrylate copolymers (EMA).

Additional layers may also be present in the structures of the present invention. For example, the present invention contemplates 4, 6, 7, 8, and higher
5 numbers of layers in the film of the present invention and different combinations of layer structures may also be present. For example, there may be more than one barrier layer, i.e., two layers of polyvinylidene chloride copolymers, two layers of foil or two layers of ethylene vinyl alcohol (EVOH) or nylon. Alternatively, this may be a layer of EVOH and a layer of a polyvinylidene chloride copolymer or a polyamide or a
10 polystyrene and other combinations of the core materials. The additional layers of the present invention also encompass more than one polymer formed by the polymerization reaction in the presence of a single site catalyst. The polymers may be in a layer alone or in the form of a blend. Suitable polymers for blending with an ethylene polymer formed in a polymerization reaction with a single site catalyst
15 include other ethylene polymers formed in a polymerization reaction with a single site catalyst, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), ultra low density polyethylene (ULDPE), EVA, ionomers, ethylene copolymers, ethylene methyl acrylate (EMA), ethylene acrylic acid (EAA), ethyl methyl acrylic acid (EMAA), polypropylene (PP), ethylene normal butyl acrylate (ENBA), ethylene
20 propylene copolymers (PPE). Suitable polymers for blending with a propylene polymers formed in a polymerization reaction with a single site catalyst include ethylene propylene copolymers.

Preferred blends using EVA's are those having a lower melt index as they tend to yield EVA layers having better hot strength. EVA's having higher VA content tend

to yield EVA layers having increased adhesion to for example, the vinylidene chloride copolymer layer. EVA's having virtually any amount of VA will have better adhesion to the vinylidene chloride copolymer layer than an ethylene homopolymer. However, good interlayer adhesion is considered desirable in the invention, and thus, steps are usually taken to enhance adhesion where no unacceptable negative effect is encountered. Thus, higher VA contents, in the range of 6% to 12% vinyl acetate are preferred, a melt index of less than 1 is also preferred. While blend amounts are shown herein in weight percent, VA contents are mole percent. Especially preferred EVA's have VA content of 7% to 9% and melt index of 0.2 to 0.8. Blends of EVA's to make up the EVA component of layers 16 and 18 are acceptable.

Other preferred structures of the invention are represented by a multiple layer polymeric film having three layers and not including a barrier layer.

In a preferred embodiment, the first outer layer comprises a blend of ethylene vinyl acetate copolymer (EVA) and linear low density polyethylene (LLDPE) wherein the LLDPE polymer is formed via a polymerization reaction in the presence of a single site catalyst. The core/middle layer comprises ethylene vinyl acetate (EVA). The second outer layer comprises a blend of LLDPE and low density polyethylene (LDPE) wherein the LLDPE polymer is formed via a polymerization reaction in the presence of a single site catalyst. The first outer layer, the core/middle layer and the second outer layer may independently contain a color concentrate such as titanium dioxide dispersed in a polymer carrier resin such as LDPE when a colored/pigmented film is desired.

In a preferred embodiment of the invention, the multiple layer polymer film comprises a first and second layer, the composition of said first layer comprising a

blend of ethylene vinyl acetate copolymer, linear low-density polyethylene and a second ethylene vinyl acetate copolymer and slip; the composition of said second layer comprising ethylene vinyl acetate copolymer; and a third layer comprising a blend of linear low-density polyethylene and low-density polyethylene said second
5 layer being disposed between said first and third layer. A color concentrate may optionally and independently be present in layers one, two and three.

In a further preferred embodiment of the invention, the first layer is a blend of 5% by weight to 100% by weight of ethylene vinyl acetate copolymer; 0% by weight to 50% by weight of linear low-density polyethylene, 0% by weight to 50% by weight
10 of a second ethylene vinyl acetate copolymer, 0% by weight to 2% by weight of slip, and 0% by weight to 25% by weight of a color concentrate said second layer is 25% by weight to 100% by weight of ethylene vinyl acetate copolymer and 0% by weight to 25% by weight of a color concentrate said third layer is a blend of 45% by weight to 100% by weight of linear low density polyethylene, 0% by weight to 30% by
15 weight of low density polyethylene and 0% by weight to 25% by weight of a color concentrate.

In further preferred embodiments of the invention, layers one, two and three may independently contain a color concentrate. The color concentrate is defined as a pigment dispersed in a polymer. When a white pigmented layer is desired, the color
20 concentrate is titanium dioxide dispersed in a polymer carrier resin such as LDPE. This particular color concentrate is exemplified by CM64224, CM64226 and CM82143 made by Equistar.

In a still further preferred embodiment of the invention, the first layer is a blend of 25% by weight to 90% by weight of ethylene vinyl acetate copolymer, 5% by

weight to 25% by weight of linear low density polyethylene and 5% by weight to 25%
by weight of a second ethylene vinyl acetate copolymer 0% to 1% by weight of slip
and 0% by weight to 25% by weight of a color concentrate. The second layer is a
blend of 25% to 100% by weight of ethylene vinyl acetate and 0% to 25% by weight
5 of a color concentrate and the third layer is a blend of 55% to 100% by weight linear
low density polyethylene 0% to 20% by weight of low density polyethylene and 0%
by weight to 25% by weight of a color concentrate wherein said second layer is
disposed between said first and third layers.

In a still further preferred embodiment of the invention, the first layer is a
10 blend of 80% by weight of ethylene vinyl acetate copolymer, 10% by weight of linear
low density polyethylene and 9.65% by weight of a second ethylene vinyl acetate
copolymer and 0.35% by weight of slip additive; the second layer is 100% by weight
of ethylene vinyl acetate; and a third layer is a blend of 82% by weight of linear low
density polyethylene and 18% by weight of a color concentrate and 0% by weight of
15 low density polyethylene wherein said second layer is disposed between said first and
third layers.

In a still further preferred embodiment of the invention, the composition of the
first layer is 80% by weight of ethylene vinyl acetate copolymer, 10% by weight of
linear low density polyethylene, 9.65% by weight of a second ethylene vinyl acetate
20 copolymer and 0.35% of slip; the second layer is 100% by weight of ethylene vinyl
acetate; and the third layer is a blend of 90% by weight of linear low density
polyethylene and 10% by weight of low density polyethylene.

In a preferred embodiment of the present invention, the film structure
comprises three layers; the first layer comprises a blend of ethylene vinyl acetate

copolymer, linear low-density polyethylene, and a second ethylene vinyl acetate copolymer, a second layer comprises an ethylene vinyl acetate copolymer and a third layer comprises a blend of linear low-density polyethylene and low-density polyethylene with said second layer being disposed between said first and second
5 layer. A color concentrate, a slip additive and an antiblock additive may optionally and independently be present in layers one, two and three.

In a further preferred embodiment of the present invention, the film structure comprises three layers; the first layer comprises a blend of ethylene vinyl acetate copolymer, linear low-density polyethylene, a second ethylene vinyl acetate
10 copolymer, a slip additive and an anti-block additive; a second layer comprises an ethylene vinyl acetate copolymer and a third layer comprises a blend of linear low-density polyethylene and low-density polyethylene with said second layer being disposed between said first and second layer. A color concentrate may optionally and independently be present in layers one, two and three.

In a still further preferred embodiment of the present invention, the first layer
15 is a blend of about 5% by weight to about 100% by weight of ethylene vinyl acetate copolymer; about 0% by weight to about 50% by weight of linear low-density polyethylene, about 0% by weight to about 50% by weight of a second ethylene vinyl acetate copolymer, about 0% by weight to about 2% by weight of slip additive about
20 0% by weight to about 10% by weight of antiblock additive said second layer is about 25% by weight to about 100% by weight of ethylene vinyl acetate copolymer and about 0% by weight to about 2% by weight of a slip additive said third layer is a blend of about 45% by weight to about 100% by weight of linear low density polyethylene,

about 0% by weight to about 30% by weight of low density with said second layer being disposed between said first and second layer.

In the preferred embodiment of the present invention the antiblock additive is selected from Ampacet 7012124 or Ampacet 10579 both additives are products of Ampacet Corporation of Mount Vernon, New York. The antiblock additive may be present in the film structure as a single antiblock additive or as a blend of antiblock additive. A preferred range of antiblock additive for the film structures of the present invention is about 0% by weight to about 10% by weight of the layer; a further preferred range of antiblock additive is about 2% by weight to about 5% by weight of the layer; and a most preferred percentage of antiblock additive is about 3% by weight of the layer.

Ethylene vinyl acetate resins suitable for the practice of this invention are exemplified by ESCORENE® (LD-318) and ESCORENE® (LD-712) from Exxon Chemical.

EXCORENE® LD-318 is a 9.0% vinyl acetate copolymer film resin. This resin has the following properties:

Resin Properties	ASTM Method	Units (SI)	Typical Value ²
Melt Index	Exxon Method	g/10 min.	2.0
Density	Exxon Method	g/cm ³	0.930
Vinyl Acetate	Exxon Method	% by wt.	9.0
Melting Point	Exxon Method	°F(°C)	210 (99)

ESCORENE® LD-712 is a 10.0% vinyl acetate copolymer film resin. This resin has the following properties:

Resin Properties	ASTM Method	Units (SI)	Typical Value ³
Melt Index	Exxon Method	g/10 min.	0.35
Density	Exxon Method	g/cm ³	0.931
Vinyl Acetate	Exxon Method	% by wt.	10
Melting Point	Exxon Method	°F(°C)	207 (97)

ESCORENE® LD-318 is suitable for the 9.65% of EVA of layers one and four and ESCORENE® LD-712 is suitable for the remaining ethylene vinyl acetate of layers one and two.

Linear low density polyethylene resin suitable for the practice of this invention is exemplified by DOWLEX® 2267A and DOWLEX® 2247A from Dow Chemical Company.

DOWLEX® 2267A has the following properties:

Physical Properties	ASTM Method	Values ⁽¹⁾ :English (SI)
Resin Properties		
Melt Index, gm/10 min	D 1238	0.85
Density, gm/cc	D 792	0.917
Vicat Softening Point, °F (°C)	D 1525	208 (98)

DOWLEX® 2247A has the following properties:

Physical Properties	ASTM Method	Values ⁽¹⁾ :English (SI)
Resin Properties		
Melt Index, gm/10 min	D 1238	2.3
Density, gm/cc	D 792	0.917
Vicat Softening Point, °F (°C)	D 1525	210 (99)

Alternatively, Exxon's EXCEED® 363C32 linear low density polyethylene resin may also be used in the structure of the present invention. EXCEED® 363C32 has the following properties:

Resin Properties ¹	Units (SI)	Typical Value ³
Melt Index	g/10 min.	2.5
Density	g/cm ³	0.917
Melting Point	°F (°C)	239 (115)

In the preferred embodiment of the present invention, the low density polyethylene resin suitable for the practice of this invention is exemplified by

PETROTHENE® NA204-000 from Equistar Chemical, L.P. PETROTHENE® has the following properties:

	Value	Units	ASTM Test Method
Density	0.918	g/cm ³	D1505
Melt Index	7.0	g/10 min.	D 1238
Melting Point	106.5	°C	

Slip additive is a coefficient of friction additive which is selected from erucamide and other fatty acid amides.

The structure of the present invention may be formed by any conventional process. Such processes include extrusion, coextrusion, extrusion coating, extrusion lamination, adhesive lamination and the like, and combinations of processes. The specific process or processes for making a given film which is neither oriented nor cross-linked can be selected with average skill, once the desired structure and compositions have been determined.

When the structure of the present invention is a film, the film may also be oriented either uniaxially or biaxially. Orientation can also be done by any conventional process for forming multiple layer films. A preferred process includes the steps of coextrusion of the layers to be oriented, followed by orientation in one of the conventional processes such as blown tubular orientation or stretch orientation in the form of a continuous sheet; both being molecular orientation processes. The double bubble technique disclosure in Pahlke, U.S. Patent No. 3,456,044 is suitable for use in producing the film of this invention. The films may also be formed by a tubular water quench process. In this process the film may be extruded downwardly as a tube formed by an annular die, and carried into a water quench tank, generally

with a cascade of water on the outside surface providing initial cooling. The flattened tape is withdrawn from the quench bath, is reheated (normally in a second water bath) to its orientation temperature, is stretched in the machine direction between two sets of rolls that are so rotated as to establish a linear rate differential there between, and is
5 simultaneously oriented in the transverse, or cross-machine, direction as an inflated bubble trapped between the nips of the rolls. In accordance with conventional practice, the film will usually be cooled by air in the orientation zone.

The film of the present invention may also be oriented and/or cross-linked. The first step is the formation of a multiple layer film. The formation of the multiple
10 layer film, is usually most easily accomplished by coextrusion of the desired layers. Other formation processes are acceptable so long as the resulting oriented film at the conclusion of fabrication processing is a unitary structure.

The second step is orienting the multiple layer film. One method for accomplishing orientation is by heating the film to a temperature appropriate to
15 molecular orientation and molecularly orienting it. The film may then be optionally heat set by holding it at an elevated temperature while its dimensions are maintained. The orientation step is preferentially carried out in line with the first step, which is the film formation step of the process.

The third step is subjecting the formed and oriented multiple layer film, to
20 electron beam irradiation.

The amount of electron beam irradiation is adjusted, depending on the make-up of the specific film to be treated and the end use requirement. While virtually any amount of irradiation will induce some cross-linking, a minimum level of at least 1.0 megarads is usually preferred in order to achieve desired levels of enhancement of the

hot strength of the film and to expand the range of temperature at which satisfactory heat seals may be formed. While treatment up to about 50 megarads can be tolerated, there is usually no need to use more than 10 megarads, so this is a preferred upper level of treatment the most preferred dosage being 2 to 5 megarads.

5 The third step of subjecting the film to electron beam irradiation is performed only after the multiple layer film has been formed, and after molecular orientation, in those embodiments where the film is molecularly oriented. It should be noted that, in the irradiation step, all of the layers in the film are exposed simultaneously to the irradiation sources, such that irradiation of all the layers of the film takes place
10 simultaneously.

In one embodiment of the process, the second step of orientation may be omitted and the unoriented multiple layer film may be cross-linked by irradiation treatment to produce a cross-linked, unoriented, multiple layer film.

15

EXAMPLES

Multilayer films may be prepared according to the present invention. Biaxially stretched three layer films may be prepared by a "double bubble" process similar to that disclosed in U.S. Patent No. 3,456,044 by coextruding the following compositions through a multilayer die, biaxially stretching the coextruded primary
20 tube. The films may also be irradiated if desired.

EXAMPLE 1

Layer 1 - Copolymer of ethylene and an alpha olefin such as 1-Hexene or 1-Octene formed by the polymerization reaction in the presence of a single site catalyst or metallocene (hereinafter CEO)
25 Layer 2 - Vinylidene chloride - methyl acrylate (VDC-MA) copolymer
Layer 3 - Polyolefin. This film may be biaxially stretched and if necessary irradiated.

		<u>EXAMPLE 2</u>	<u>EXAMPLE 3</u>	<u>EXAMPLE 4</u>
5	Layer 1 Layer 2 Layer 3	CEO VDC-MA ULDPE-EVA Blend	CEO VDC-MA CEO	CEO-EVA Blend VDC-MA CEO-EVA Blend
10		<u>EXAMPLE 5</u>	<u>EXAMPLE 6</u>	<u>EXAMPLE 7</u>
	LAYER 1 LAYER 2 LAYER 3	CEO Nylon CEO	CEO Nylon ULDPE-EVA Blend	CEO-EVA Blend Nylon CEO-EVA Blend
15		<u>EXAMPLE 8</u>		<u>EXAMPLE 9</u>
	LAYER 1	Polyolefin		Polyolefin
20	LAYER 2	Styrene copolymer formed by the polymerization reaction with a single site catalyst		Propylene copolymer formed by the Polymerization reaction with a single site catalyst
25	LAYER 3	Polyolefin		Polyolefin
		<u>EXAMPLE 10</u>	<u>EXAMPLE 11</u>	<u>EXAMPLE 12</u>
30	LAYER 1 LAYER 2 LAYER 3	CEO CEO CEO	CEO EVOH ULDPE-EVA Blend	CEO-EVA Blend EVOH CEO-EVA Blend
35		<u>EXAMPLE 13</u>	<u>EXAMPLE 14</u>	<u>EXAMPLE 15</u>
40	LAYER 1 LAYER 2 LAYER 3 LAYER 4 LAYER 5	CEO Tie PVDC Copolymer or EVOH Tie ULDPE-EVA Blend	CEO Tie PVDC Copolymer or EVOH Tie CEO	CEO-EVA Blend Tie PVDC Copolymer or EVOH Tie CEO-EVA Blend
45		<u>EXAMPLE 16</u>		
	LAYER 1 LAYER 2	EVA-ULDPE ULDPE or CEO		

LAYER 3 PVDC Copolymer or EVOH
 LAYER 4 EVA
 LAYER 5 CEO or blend of CEO and EVA

5 The following examples may also be prepared in accordance with the present invention:

EXAMPLE 17

10 Meat Film – Forming Web
 Formed by TWQ Process
 (Tubular Water Quench Process)

15 LAYER 1 Nylon
 LAYER 2 Tie
 LAYER 3 EVOH
 LAYER 4 Tie
 LAYER 5 CEH or CEO

20 CEH is a copolymer of ethylene and 1-Hexene formed by the polymerization reaction in the presence of a single site catalyst or a metallocene. Other alpha olefins can be polymerized with the ethylene also.

EXAMPLES 18-20

 Innerliner Films - These films can be formed either on a blown film line or by using a tubular water quench.

25 LAYER 1 HDPE
 LAYER 2 Blend of CEH or CEO and EVA and polybutylene

30 LAYER 1 HDPE
 LAYER 2 CEH or CEO and polybutylene

 LAYER 1 HDPE
 LAYER 2 CEH or CEO

EXAMPLES 21 and 22

Meat - Non Forming Top Web film

- 5 LAYER 1 PVDC coated PET
 LAYER 2 Adhesive (lamination)
 LAYER 3 CEO or CEH

This film may be produced by adhesive laminating a film formed of a
 10 copolymer of ethylene and an alpha olefin with the PVDC coated PET film.

- LAYER 1 PVDC coated PET
 LAYER 2 LDPE - extrusion laminated
 LAYER 3 LDPE/CEH or CEO coextrusion

15 This film can be formed by extrusion laminating a film of PVDC coated PET
 or LDPE.

EXAMPLE 23

- 20 Layer 1 - Blend of two or more copolymers of ethylene and an alpha olefin
 polymerized in the presence of a single site catalyst or metallocene such
 as CEO with either CEH or CEB. CEB is a copolymer of ethylene and
 butene-1 formed by a polymerization reaction in the presence of a single
 site catalyst or a metallocene.

25

EXAMPLE 24

- 30 Layer 1 - Blend of a copolymer of ethylene and an alpha olefin formed by a
 polymerization reaction in the presence of a single site catalyst or a
 metallocene with polyethylene or other polyolefin such as EVA, EMA,
 FAA, EMAA, ionomers, ENBA, PP or PPE.

The films of example 23 and 24 can either be single layer films or multi layer
 films where additional layers are present on layer 1.

35 EXAMPLE 25

A three layer film was coextruded at a total caliper of 2.3 or 2.75 mil.
 depending upon the end user requirements. The outer layer of the film is a blend of
 EVA, LLDPE and slip additive. The 80% EVA was Exxon LD 712.06; the 9.65%

EVA was Exxon LD 318.92; the 10% LLDPE was Dow 2267 A-1 and the 0.35% slip Reed Spectrum 1080823 U slip. The core layer, which was positioned between the outer layer and the inner (sealant) layer, was 100% Exxon EVA LD 712.06. The inner (sealant) layer was a blend of approximately 82% Exxon Exceed 363C32 and 18% color concentrate. The color concentrate was Equistar white CM 82143 or Equistar cream CM 64224. Alternatively, if a clear film is desired, the inner (sealant) layer is a blend of 90% Exxon Exceed 363C32 and 10% Equistar LDPE NA204-000. The color concentrate was fed into the inner layer via a calibrated color auger. The, thus, coextruded film was cooled and reheated to orientation temperature via a hot water bath (98°C) and biaxially oriented at a stretch ratio of 3.8 X 2.7/1. After orientation, the film was treated with 5.3 megarads of electron beam irradiation and fabricated into bags for the use in the packaging of various fresh and frozen poultry products. The bags were clip sealed on a Rota-Matic 1 rotary vacuum packaging machine available from Tipper Tie, a division of Dover Industries Company. The bags can also be heat sealed on commercial 8300 and 8600 rotary evacuator-sealer equipment available from the Cryovac division of W.R. Grace and Company.

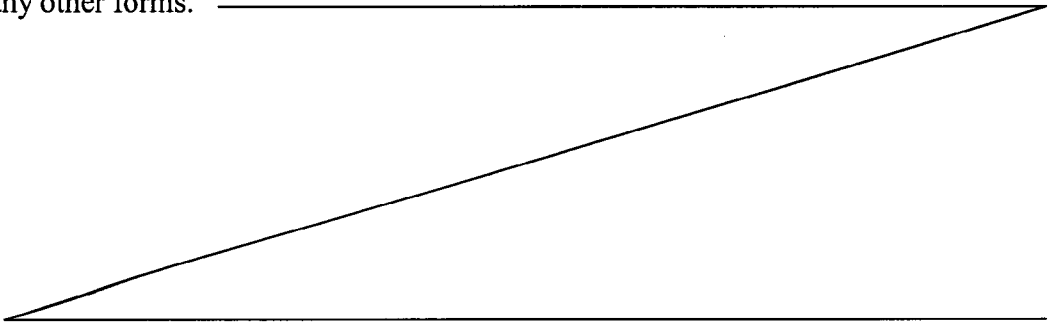
EXAMPLE 26

A three layer film was coextruded at a total caliper of 2.75 mil. depending upon the end user requirements. The outer layer of the film is a blend of EVA, LLDPE antiblock additive and slip additive. The 77.60% EVA was Exxon LD 712.06; the 9.36% EVA was Exxon LD 318.92; the 9.7% LLDPE was Dow 2267 A-1; the 0.34% slip was Reed Spectrum 1080823 U slip; and the 3.00% antiblock was Ampacet 7012124. The core layer, which was positioned between the outer layer and the inner (sealant) layer, was 100% Exxon EVA LD 712.06. The inner (sealant) layer

was a blend of approximately 84% Exxon Exceed 363C32 and 16% color concentrate. The color concentrate was Equistar white CM 82143 or Equistar cream CM 64224. Alternatively, if a clear film is desired, the inner (sealant) layer is a blend of 90% Exxon Exceed 363C32 and 10% Equistar LDPE NA204-000. The color concentrate was fed
5 into the inner layer via a calibrated color auger. The, thus, coextruded film was cooled and reheated to orientation temperature via a hot water bath (98°C) and biaxially oriented at a stretch ratio of 3.8 X 2.7/1. After orientation, the film was treated with 5.3 megarads of electron beam irradiation and fabricated into bags for the use in the packaging of various fresh and frozen poultry products. The bags were clip sealed on a
10 Rota-Matic 1 rotary vacuum packaging machine available from Tipper Tie, a division of Dover Industries Company. The bags can also be heat sealed on commercial 8300 and 8600 rotary evacuator-sealer equipment available from the Cryovac division of W.R. Grace and Company.

Unless the context clearly requires otherwise, throughout the description and the
15 claims, the words 'comprise', 'comprising', and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

Although the invention has been described with reference to specific examples it will be appreciated by those skilled in the art that the invention may be embodied in
20 many other forms. _____



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A multiple layer polymeric film comprising three layers wherein the first layer comprises a blend of ethylene vinyl acetate copolymer, linear low-density polyethylene, and
5 a second ethylene vinyl acetate copolymer; the second layer comprises ethylene vinyl acetate copolymer; and the third layer comprises a blend of linear low-density polyethylene and low-density polyethylene said second layer being disposed between said first and third layer and wherein each a color concentrate, a slip additive and an antiblock additive may optionally and independently be present in layers one, two and three.
- 10 2. The multiple layer polymeric film according to claim 1 wherein the antiblock additive is a blend.
3. The multiple layer polymeric film according to claim 1 or claim 2 wherein the antiblock additive is present up to 10% based on the total weight of the layer.
4. The multiple layer polymeric film according to any one of the preceding claims
15 wherein a color concentrate is present in said second layer.
5. The multiple layer polymeric film according to any one of the preceding claims wherein a color concentrate is present in said third layer.
6. The multiple layer polymeric film according to any one of the preceding claims wherein a color concentrate is present in said second and third layer.
- 20 7. The multiple layer polymeric film according to any one of the preceding claims wherein an antiblock additive is present in said first layer.

8. The multiple layer polymeric film according to claim 7 wherein the antiblock additive is present from about 2% by weight to about 5% by weight of the layer.

9. A molecularly oriented multiple layer polymeric film comprising three layers wherein the first layer comprises a blend of ethylene vinyl acetate copolymer, linear low-
5 density polyethylene, a second ethylene vinyl acetate copolymer, slip additive and an antiblock additive; the second layer comprises ethylene vinyl acetate copolymer; and the third layer comprises a blend of linear low-density polyethylene and low-density polyethylene said second layer being disposed between said first and third layer and
10 wherein a color concentrate may optionally and independently be present in layers one, two and three.

10. The multiple layer polymeric film according to claim 1 wherein the composition of said first layer is a blend of about 5% by weight to about 100% by weight of ethylene vinyl acetate copolymer, about 0% by weight to about 50% by weight of linear low-density polyethylene, about 0% by weight to about 50% by weight of a second
15 ethylene vinyl acetate copolymer, about 0% by weight to about 2% by weight of slip; about 0% by weight to about 25% by weight of a color concentrate and about 0% by weight to about 10% by weight of antiblock; said second layer is about 75% by weight to about 100% by weight of ethylene vinyl acetate copolymer and about 0% by weight to about 25% by weight of a color concentrate said third layer is a blend of about 45% by
20 weight to about 100% by weight of linear low density polyethylene, and about 0% by weight to about 30% by weight of low density polyethylene and about 0% by weight to about 25% by weight of a color concentrate.

11. The multiple layer polymeric film according to claim 10 wherein the composition of said first layer is a blend of 77.6% by weight ethylene vinyl acetate copolymer, 9.7% by weight of linear low density polyethylene, 9.4% by weight of a second ethylene vinyl acetate copolymer, 3.0% by weight of antiblock additive and 0.34% by
5 weight of slip additive.

12. The molecularly oriented multiple layer polymer film according to claim 9 wherein the antiblock additive is a blend.

13. A bag made from the film of claim 1.

14. A bag made from the film of claim 10.

10 15. A bag made from the film of claim 9.

16. Use of a bag according to any one of claim 13 to claim 15 for the packaging of meat and/or poultry.

17. A multiple layer polymeric film, substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings
15 and/or examples.

18. A molecularly oriented multiple layer polymer film, substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.

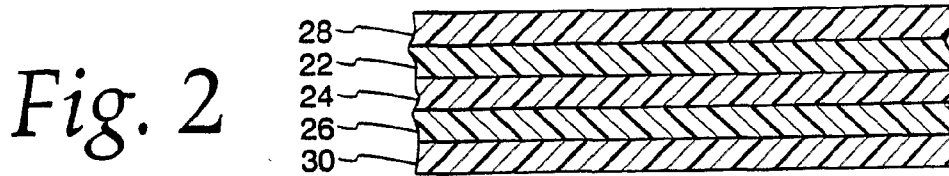
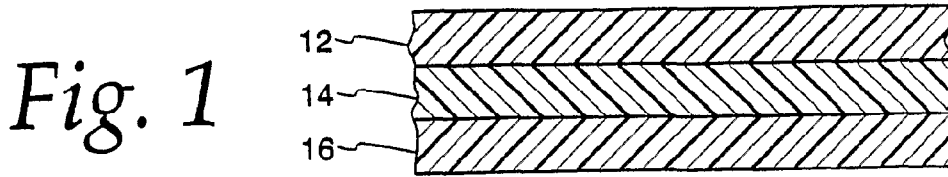
19. A bag, substantially as herein described with reference to any one of the
20 embodiments of the invention illustrated in the accompanying drawings and/or examples.

20. Use of a bag, substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.

DATED this 14th day of September 2004

5 Shelston IP

Attorneys for: Pechiney Emballage Flexible Europe



Primary Metallocene Catalysts

Fig. 3

NON-STERESELECTIVE

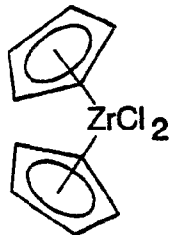


Fig. 4

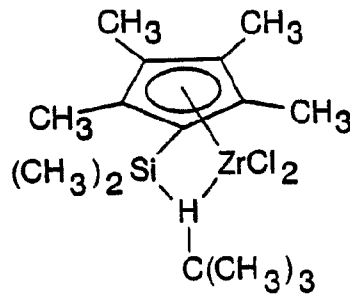


Fig. 5

STERESELECTIVE

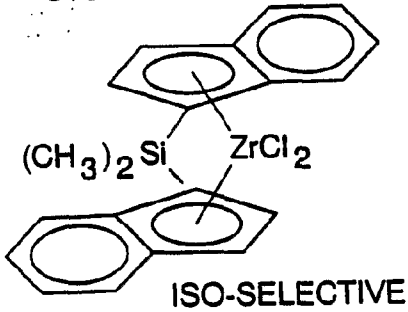


Fig. 6

