(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 July 2007 (12.07.2007)

PCT

(10) International Publication Number
WO 2007/078454 A2

(51) International Patent Classification:
B32B 27/14 (2006.01)

(21) International Application Number:
PCT/US2006/045179

(22) International Filing Date:
20 November 2006 (20.11.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/755,659 29 December 2005 (29.12.2005) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2007/078454 A2

(54) Title: CALCIUM CARBONATE BARRIER FILMS AND USES THEREOF

(57) Abstract: The present invention provides polyolefin films comprising calcium carbonate that have a reduced moisture vapor transmission rate, methods of making the films, and packaging materials comprising the films.

CALCIUM CARBONATE BARRIER FILMS AND USES THEREOF

CROSS REFERENCE TO RELATED APPLICATION

[1] This application claims the benefit of U.S. Provisional Patent Application No. 60/755,659, filed December 29, 2005, the content of which is hereby incorporated by reference.

FIELD OF THE INVENTION

[2] This invention is directed toward a film structure comprising polyolefin and calcium carbonate that has reduced moisture vapor transmission rate and is suitable for packaging moisture-sensitive materials such as dry foods, animal feed, and pharmaceutical products.

BACKGROUND OF THE INVENTION

[3] Throughout this application various publications are referred to in parenthesis. Full citations for these references may be found at the end of the specification immediately preceding the claims. The disclosures of these publications are hereby incorporated by reference in their entireties into the subject application to more fully describe the art to which the subject application pertains.

[4] For packaging of dry foods and other moisture sensitive materials, it is desirable to have a barrier package that prevents the ingress of moisture vapor and thus keeps the contents from becoming soggy. The packaging should allow the food material to be containerized into a paperboard box for shelf display and ease of handling.

[5] Polymer films have been developed with the objective of increasing, rather than decreasing, moisture vapor transmission through the film (e.g., PCT International Publication Nos. WO 02/10275 A2, 03/020513 A1 and WO 03/031134 A1). In contrast, reduced water vapor transmission rate (WVTR) has been achieved using a laminated paperboard substrate, which is suitable as a container for beverages (U.S. Patent Application Publication No. 2004/0105942). Reduced WVTRs have also been obtained by orientation of high density polyethylene (HDPE) films (U.S. Patent Nos. 4,183,893, 4,870,122, 6,391,411).

[6] While there are different technologies that provide a moisture vapor barrier in packaging films, there is a need for improved barrier films for packaging dry foods and other moisture-sensitive material where the film is both moisture resistant and economical.

SUMMARY OF THE INVENTION

[7] The present invention satisfies this need by using calcium carbonate ($CaCO_3$) to provide improved polyolefin barrier films. The barrier film affords good moisture vapor resistance, heat sealing and handling properties. The barrier structure is comprised of a calcium carbonate containing polyolefin film in a single or multiple layer film construction. In structures having a plurality of film barrier layers comprising $CaCO_3$, the $CaCO_3$ provides in each of the multiple barrier layers a reduced rate of moisture vapor transmission through the respective barrier layers. The films are especially useful in food packaging, animal feed packaging, pharmaceutical packaging, and packaging of other moisture-sensitive materials.

[8] Additional objects of the invention will be apparent from the description which follows.

DETAILED DESCRIPTION OF THE INVENTION

[9] The present invention is directed to films comprising polyolefin and calcium carbonate, where the films have a reduced moisture vapor transmission rate (MVTR).

[10] Polyolefins are a family of polymers made from olefin monomers. Examples include polyethylene (PE), polypropylene and polyisoprene. PE can be high density PE (HDPE, density ≥ 0.95 gm/cm^3), medium density PE (MDPE, density 0.934 to <0.95 gm/cm^3) and low density PE (LDPE, density <0.934 gm/cm^3). LDPE can be linear LDPE (LLDPE). HDPE is a preferred polyolefin. Medium molecular weight HDPE (MMW-HDPE) is a preferred HDPE.

[11] As used herein, medium molecular weight (MMW) polymers have the following weight distributions: number average molecular weight (Mn) of 6,000 to 13,000, weight average molecular weight (Mw) of 50,000 to 120,000, and Z average molecular weight (Mz) of 175,000 to 500,000. Preferably, the number

average molecular weight (Mn) is 8,000 to 11,000. Preferably, the weight average molecular weight (Mw) is 70,000 to 100,000. Preferably, the Z average molecular weight (Mz) is 250,000 to 400,000.

[12] A preferred film comprises a) a polyolefin base resin and b) a polyolefin carrier resin admixed with calcium carbonate ($CaCO_3$), wherein the $CaCO_3$ and the carrier resin are present in a ratio of 15/85 to 80/20 by weight. Preferably, the base resin and the carrier resin are different resins. The base resin and the carrier resin may differ, for example, in molecular weight, density, melt index, and/or polydispersity index. The polydispersity index is the weight average molecular weight (Mw) divided by the number average molecular weight (Mn). The carrier resin may have a Mw/Mn ratio of, e.g., 6.82 and the base resin may have a ratio of, e.g., 9.35. The carrier resin and base resin may differ in Z average molecular weight (Mz) where, e.g., the carrier resin has a Mz of 203,000 and the base resin has a Mz of 332,000.

[13] Another preferred film comprises polyolefin and calcium carbonate ($CaCO_3$), wherein the film comprises: a) a polyolefin base resin having a melt index of 0.05-2.0 dg/min and a density of 0.958-0.963 g/cm^3; b) a polyolefin carrier resin for $CaCO_3$, wherein the carrier resin has a melt index of 4-10 dg/min and a density of 0.958-0.963 g/cm^3; and c) $CaCO_3$; wherein $CaCO_3$ is present in the film in a total concentration of 5%-35% by weight.

[14] An additional preferred film comprises: a) a high density polyethylene (HDPE) base resin, wherein the HDPE base resin has a melt index of 0.05 - 2.0 dg/min and a density of 0.958-0.963 g/cm^3; b) a HDPE carrier resin for calcium carbonate ($CaCO_3$), wherein the HDPE carrier resin has a melt index of 4-10 dg/min and a density of 0.958-0.963 g/cm^3; and c) $CaCO_3$, wherein the $CaCO_3$ has a median particle size of 0.7-2.5 μm, a top cut d98 of 4-15 μm, a surface area of 3.3-10.0 m^2/g, and a total concentration in the film of 5-35% by weight, wherein the $CaCO_3$ has been treated with a surface treatment agent at a treatment level of 0.3-2.3% by weight, and wherein the $CaCO_3$ and the HDPE carrier resin are present in a ratio of 15/85 to 80/20 by weight. Preferably, the $CaCO_3$ has been treated with the surface treatment agent at a treatment level of 1.5-3 mg surface treatment agent/m^2 of $CaCO_3$. Preferably, the $CaCO_3$ has been wet ground and/or dry ground prior to incorporation of $CaCO_3$ in the film. Wet grinding can be carried out in the absence of a grinding aid or in the presence of a grinding aid comprising, e.g., a salt of polyacrylic acid and/or a salt of a copolymer of acrylic acid. Preferably, the calcium carbonate is dried after grinding. $CaCO_3$ can be treated with the surface treatment agent before and/or during and/or after grinding the $CaCO_3$.

[15] Another preferred film comprises a) a high density polyethylene (HDPE) having a density of 0.958-0.963 g/cm^3, and b) calcium carbonate ($CaCO_3$) having a median particle size of 0.7-2.5 μm, a top cut d98 of 4-15 μm, a surface area of 3.3-10.0 m^2/g, and a total concentration in the film of 5-35% by weight.

[16] $CaCO_3$ and carrier resin can be present in the films in a ratio of 15/85 to 80/20 by weight, for example 40/60 to 80/20 by weight. Preferred ranges of $CaCO_3$/carrier resin ratios are 15/85 to less than or equal to (≤) 60/40 by weight, for example 40/60 to ≤ 60/40 by weight and 45/55 to 55/45 by weight. In a most preferred film, $CaCO_3$ and carrier resin are present in a ratio of 50/50 by weight.

[17] $CaCO_3$ can be present in the films in a total concentration, for example, of 5%-35% by weight, preferably 20%-30% by weight, and more preferably 25% by weight. These concentrations apply both to single layer films and to multi layer films, where some layers may not contain any $CaCO_3$ or where different layers may contain different amounts of $CaCO_3$.

[18] The base resin of the present invention can have a melt index, for example, of 0.05-2.0 dg/min, preferably 1 dg/min. The base resin can have a density of 0.958-0.963 g/cm^3, preferably 0.962 g/cm^3. Preferably, the base resin is a high density polyethylene (HDPE). Preferably, the HDPE is a medium molecular weight high density polyethylene (MMW-HDPE). Base resins such as MMW-HDPE resins can be produced via Zigler-Natta catalyst chemistries and generally fall into the range of 0.85 to 1.5 dg/min melt index, and densities 0.9580 g/cm^3 and higher to the maximum limits for polyethylene manufactured without co-monomers. A preferred base resin is a resin having the properties of Resin A (see Table 1, below). In traditional applications, films can be made by extruding this material, or like material in its neat form (without any other additives or masterbatches). As used herein, this material is referred to as a "base resin."

[19] The carrier resin for $CaCO_3$ can have a melt index of 4-10 dg/min, preferably

6.5-8.0 dg/min, and most preferably 6.5 dg/min. The carrier resin can have a density, for example, of 0.958-0.963 g/cm^3, preferably 0.962 g/cm^3. Preferably, the carrier resin is a high density polyethylene (HDPE). Preferably, the HDPE is a medium molecular weight high density polyethylene (MMW-HDPE).

[20] The $CaCO_3$ in the films can have a median particle size of 0.7-2.5 μm, preferably 1.4-2.0 μm, and more preferably 1.4 μm. The $CaCO_3$ can have a top cut d98 of 4-15 μm, preferably 8-10 μm, and more preferably 8 μm. Top cut d98 refers to the average diameter of calcium carbonate particles in the 98th mass percentile. The $CaCO_3$ can have a surface area of 3.3-10.0 m^2/g, preferably 3.3-5.5 m^2/g, and more preferably 5.5 m^2/g.

[21] The calcium carbonate may be a natural ground calcium carbonate such as, for example, ground marble, limestone or chalk, and/or a precipitated calcium carbonate (e.g., aragonite, waterite or calcite). Preferably, the calcium carbonate is a natural ground calcium carbonate. Calcium carbonate can be dry ground and/or wet ground. Wet grinding refers to grinding the calcium carbonate in a liquid medium. Wet grinding may be carried out in the absence of a grinding aid or in the presence of a grinding aid. One or more grinding aid agents can be included, such as, e.g., sodium polyacrylate, a salt of polyacrylic acid, and/or a salt of a copolymer of acrylic acid. For example, calcium carbonate can be derived from marble, which is finely ground in a high solids aqueous media using dispersion aids to keep the particles suspended during the process. The material is then dewatered, dried, treated and deagglomerated to again finely divide the individual particles. Drying may take place using any suitable drying equipment and can, for example, include thermal drying and/or drying at reduced pressure using equipment such as an oven, a spray drier (such a spray drier sold by Niro and/or Nara), and/or a drying in a vacuum chamber. Drying may be batch wise and/or continuous.

[22] Surface treatment agents can be added to the $CaCO_3$ to facilitate dispersion of $CaCO_3$ in the resin. Surface treatment agents can be, for example, one or more fatty acids having 8 to 24 carbon atoms. These agents include, e.g., one or more of arachidic acid, behenic acid, capric acid, cerotic acid, isostearic acid, lauric acid, myristic acid, montanic acid, palmitic acid and stearic acid. Preferred treatment agents include stearic acid and a blend of stearic acid and palmitic acid. The fatty acid may be from a vegetable source. The fatty acid may be kosher. The $CaCO_3$ can be treated with the surface treatment agent at a treatment level of 0.3-2.3% by weight treatment agent and 97.7-99.7% by weight $CaCO_3$. Preferably, the treatment level is 0.8-1.1% by weight treatment agent (89.9%-99.2% by weight $CaCO_3$), and more preferably 1.1% by weight treatment agent (89.9% by weight $CaCO_3$). Preferably, the treatment level is 1.5-3.0 mg of surface treatment agent per m^2 of $CaCO_3$, more preferably 2-2.4 mg agent/m^2 $CaCO_3$. For ground $CaCO_3$, the $CaCO_3$ can be treated with the surface treatment agent before and/or during and/or after grinding the $CaCO_3$.

[23] Construction of moisture vapor barrier packaging films are either mono or multi layer. The present invention is also directed to multilayer films that comprise any of the polyolefin and calcium carbonate films disclosed herein. Multi layer films generally use an inner contact layer to promote sealing, where the inner contact layer comprises one or more of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), and ethylene acrylic acid (EAA). Vinyl acetate content in this contact layer resin is typically about 18% by weight. Depending upon the extruder configuration in a coextrusion process, there may be anywhere from 2 to 7 or more layers.

[24] A preferred multilayer film comprises an inner layer comprising one or more of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), and ethylene acrylic acid (EAA), a core layer comprising polyolefin and calcium carbonate ($CaCO_3$), and an outer layer comprising polyolefin and calcium carbonate ($CaCO_3$). As used herein, the terms "inner," "core" and "outer" are used to describe and clarify the relative position of various layers in a multiple layer film construction. The term "inner" refers to the surface of a packaging film that comes in contact with the contained product; whereas, the term "outer" refers to the outside of the packaging film that is in contact with the surrounding atmosphere. "Core" describes the layer effectively sandwiched between the inner and outer layers. The multilayer film can have a weight distribution by layer, for example, of 25-35% outer layer, 50-60% core layer, and 10-20% inner layer, e.g. 30% outer layer, 55% core layer, and 15% inner layer.

[25] The concentration of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), or ethylene acrylic acid (EAA) in the film layer containing EVA, EEA or EAA can be, for example, 15-20% by weight. The ethylene vinyl acetate (EVA) can have a density, for example, of 0.95 g/cm^3. The ethylene vinyl acetate (EVA) can have a melt index, for example, of 1.5 dg/min.

[26] Another multilayer film comprises at least a first layer containing one or more of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), and ethylene acrylic acid (EAA) and at least a second layer containing polyolefin and calcium carbonate ($CaCO_3$), wherein $CaCO_3$ is present in the multilayer film in a total concentration of 5%-35% by weight, preferably 20%-30% by weight, and more preferably 25% by weight.

[27] The invention also provides methods of making masterbatch compositions for preparing the films, where the methods comprise mixing any of the $CaCO_3$ and polyolefin carrier resins disclosed herein. By itself, calcium carbonate is a finely divided powder and can be a difficult to handle, meter and feed to an extrusion system. To facilitate the introduction of finely ground mineral to the extrusion process, a pellet masterbatch can be produced from select polyolefin (e.g., polyethylene) resin(s) and calcium carbonate(s). Pellet masterbatches contain calcium carbonate and the "carrier resin" to bind the pellet. A small amount of antioxidant is typically added to prevent polymer degradation.

[28] A preferred method comprises mixing $CaCO_3$ with a polyolefin carrier resin, wherein the $CaCO_3$ and the carrier resin are present in a ratio of 15/85 to 80/20 by weight, more preferably 15/85 to ≤ 60/40 by weight. Another preferred method comprises mixing $CaCO_3$ with a HDPE carrier resin, wherein the $CaCO_3$ and the HDPE carrier resin are present in a ratio of 15/85 to 80/20 by weight, more preferably 15/85 to ≤ 60/40 by weight. The methods can include forming the masterbatch compositions into pellets.

[29] The invention provides masterbatch compositions prepared by any of the methods disclosed herein. A preferred masterbatch composition, for example, comprises 50% by weight calcium carbonate of 1.4 μm median diameter particle size, a top cut particle size d98 of 8.0 μm, with a 1.1% by weight stearic acid surface treatment, in a 50% by weight high density polyethylene (HDPE) carrier resin of 0.962g/cm^3 density and 6.5 dg/min melt index. A treatment level of 1.1% by weight stearic acid means 1.1% by weight stearic acid and 98.9% by weight calcium carbonate.

[30] The invention further provides methods of making a film comprising polyolefin and calcium carbonate ($CaCO_3$), wherein the method comprises blending any of the masterbatch composition disclosed herein with any of the polyolefin base resins disclosed herein. The masterbatch composition and the base resin can each be in the form of pellets, which can be blended in a desired ratio. The blended pellets are melted and then extruded or stretched into an intermediate film, which can then stretched to form a final film.

[31] Selection of the carrier resin is critical in determining the resultant physical properties of the film, especially at higher $CaCO_3$ loading levels. As disclosed in the present invention, it is advantageous to use a carrier resin that is different than the base resin in order to obtain either better production efficiencies or quality of the masterbatch, and/or desired physical properties of the resultant extrudates. Preferred carrier resins are polyethylenes of higher melt index (lower molecular weight), which work to improve MVTR barrier properties. A preferred carrier resin is one having the properties of Resin B (see Table 1, below).

[32] An alternative to using a pellet masterbatch system to deliver calcium is using a fully formulated resin. In this case, a resin would be compounded with the desired amount of calcium carbonate and pelleted. The pellets would then be directly added to an extruder to produce an extrudate of the desired type.

[33] The film making methods can include coextruding a film layer comprising polyolefin and calcium carbonate with a film layer comprising one or more of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), and ethylene acrylic acid (EAA). For example, an inner film layer comprising one or more of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), and ethylene acrylic acid (EAA) is coextruded with a core film layer comprising polyolefin and calcium carbonate ($CaCO_3$) and an outer film layer comprising polyolefin and calcium carbonate ($CaCO_3$).

[34] Coextrusion as a polymer materials processing technique uses multiple extruders to feed a die block to combine multiple polymer flow streams prior to shaping the combined melt in a die. The advantage of using coextrusion is the ability to form well bonded structures from multiple materials of varying properties in a single step. The method of production by coextrusion according to this invention may, for example, be carried out by leading two or more kinds of olefin resins, plasticized by means of two or more extruders, into a common die and causing them to come into contact inside or at the opening of the die to thereby form in the first step a film with two or more layers.

[35] Preferably, the film is processed at a blow up ratio (BUR) of from 1.6:1 to 2.2:1, more preferably 1.6:1. Preferably, the film is processed at a mil gauge of 2.0 - 3.0, more preferably 2.0-2.5.

[36] The invention provides films made by any of the methods disclosed herein.

[37] Preferred calcium carbonate - polyolefin films of the present invention have a reduced moisture vapor transmission rate (MVTR) in comparison to the film in the absence of $CaCO_3$. As used herein, moisture vapor transmission rate (MVTR) and water vapor transmission rate (WVTR) are used interchangeably. Preferably, the MVTR is reduced by 10-30% compared to the MVTR of the film in the absence of $CaCO_3$. More preferably, the MVTR is reduced by 20-30% compared to the MVTR of the film in the absence of $CaCO_3$. Even more preferably, the MVTR is reduced by 25-30% compared to the MVTR of the film in the absence of $CaCO_3$.

[38] The films can have a moisture vapor transmission rate (MVTR) of, for example, 0.213-0.230 g water vapor-mil/100 in^2 of film/day, more preferably 0.213 g water vapor-mil/100 in^2 of film/day, at 37.5 °C and 100% relative humidity. As used herein for values for MVTR, the term "mil" refers to the thickness of the film, where 1 mil = 1/1,000 of an inch of film thickness.

[39] The invention provides packaging films comprising any of the films disclosed herein. The films are especially useful in food packaging, animal feed packaging, pharmaceutical packaging, and packaging of other moisture-sensitive materials. The food products can be dry food products, such as cereal or crackers. The reduced MVTR of the films disclosed herein helps prevent the ingress of moisture vapor and thus keeps the food contents from becoming soggy. The film packaging allows the food material to be containerized into a paperboard box for shelf display and ease of handling. The films will enable an extended product shelf life in a cost effective package that meets multiple performance needs. The films described herein can serve as free standing films, which are not laminated to a support such as a

paperboard substrate or other rigid support.

[40] The present invention is illustrated in the following Experimental Details section, which is set forth to aid in the understanding of the invention, and should not be construed to limit in any way the scope of the invention as defined in the claims that follow thereafter.

EXPERIMENTAL DETAILS

Overview

[41] To illustrate the properties of a polyolefin film having a calcium carbonate additive, a comparative study of an extruded 3 layer MMW-HDPE film was compared to that of one with similar construction incorporating 20-30% by weight calcium carbonate in the total film construction. Calcium carbonate was contained in only the outer and core layers and not in the inner layer. The calcium carbonate was incorporated as a calcium carbonate masterbatch.

[42] A three layer film was coextruded using a MMW-HDPE base resin (Resin A in Table 1) having a density of 0.962 g/cm^3 and a 1.0 dg/min melt index for the outer and core layers, with an inner layer of ethylene vinyl acetate (EVA) (Dupont Evlax® 3169Z) with a density of 0.95 g/cm^3, 1.5 dg/min melt index and 18% by weight vinyl acetate co-monomer. The purpose of the inner EVA layer is to provide enhanced seal performance by allowing lower seal initiation temperatures, and shorter seal dwell time in the bag making process.

[43] The coextrusion layer distribution consisted of 30% outer layer, 55% core layer and 15% inner EVA layer by weight. Total mineral load was targeted at 25% by weight of calcium carbonate in most of the films (see Table 4, below); therefore, 29.5% by weight calcium carbonate was necessary in the outer and core layers to compose the effective amount. Correspondingly, the additive feed system was targeted at 58.8% by weight concentrate masterbatch and 41.2% by weight MMW-HDPE (Resin A in Table 1) for the outer and core layer extruders to obtain the 29.5% necessary in these respective layers to hit the effective amount of 25% by weight in the films.

[44] The resultant films were evaluated for physical performance including moisture vapor transmission rate (MVTR) using a Mocon PERMATRAN-W® Model

3/33. Comparing standard films without calcium carbonate at 3.0 mil gauge extruded at 1.6 blow up ratio against the films extruded at lower gauge (2.5 mils) using 25% by weight calcium carbonate extruded at similar blow up ratios, resulted in improvements in MVTR as presented below.

[45] Having calcium carbonate present in the outer film layer contributes to a surface roughening effect, which effectively makes the films easier to handle in secondary operation bag making equipment, and allows for easier and improved printability and print register. Also, this surface modification by addition of calcium carbonate has been shown to lower the coefficient of friction.

[46] While a preferred embodiment is made in reference to a co-extruded polyolefin film having about 25% weight loading of calcium carbonate, it is recognized that other relative percentages of calcium carbonate in monolayer or various multi layer construction forms may be utilized. By way of example, changing the film construction layer distribution or the location of the calcium carbonate (calcium carbonate in the core layer only) would provide a structure having properties similar to the exemplary embodiment set forth.

Details of Experimental Work

[47] *Measurements of melt index, density and molecular weight:* Melt index was measured using ASTM standard method D1238-04, Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer. This standard can be found in the Annual Book of ASTM Standards 2005, Section Eight – Plastics Volume 8.01. Density was measured using ASTM standard method D1501-03, Standard Test Method for Density of Plastics by the Density-Gradient Technique. This standard can be found in the Annual Book of ASTM Standards 2005, Section Eight – Plastics Volume 8.01. Molecular weight was determined using a Waters gel permeation chromatograph. The pump used was a 150C operated at a flow rate of 1.00 mL/min on an injection volume of 250 μL at 135°C. The sample was prepared using 12mg of polyethylene sample dissolved in 4mL of 1,2,4-Trichlorobenzene. The columns used were Waters Styragel HT3, HT4, HT5 and HT6E. Number average molecular weight (Mn), weight average molecular weight (Mw) and Z average molecular weight (Mz) are calculated as follows.

[48] Number average molecular weight (Mn) is the total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in the sample. Mn is mathematically expressed as

$$Mn = \frac{\sum_{i=1}^{\infty} MiNi}{\sum_{i=1}^{\infty} Ni}$$

where Ni is equivalent to the particular number of molecules at a given molecular mass and Mi is mole weight of the respective molecules.

[49] Weight average molecular weight (Mw) is the next higher molecular weight mathematically expressed as

$$Mw = \frac{\sum_{i=1}^{\infty} NiMi^2}{\sum_{i=1}^{\infty} NiMi}$$

where each molecule contributes to Mw in proportion to the square of its respective mass.

[50] Z average molecular weight (Mz) is the next higher molecular weight to Mw and is mathematically expressed as

$$Mw = \frac{\sum_{i=1}^{\infty} NiMi^3}{\sum_{i=1}^{\infty} NiMi^2}$$

where each molecule contributes to Mz in proportion to the cube of its respective mass.

[51] *Measurement of Moisture Vapor Transmission Rate:* Evaluation of the moisture vapor transmission rate (MVTR) performance of the films was made on a Mocon Permatran-W Model 3/33. Samples were tested in accordance with ASTM standard, F1249-05 Standard Test Method for Water Vapor Transmission Rate Through Plastic Film and Sheeting Using a Modulated Infrared Sensor, operated at 37.8°C and 100% relative humidity. This standard can be found in the Annual Book of ASTM Standards 2005, Volume 15.09.

[52] *Measurement of Particle Size Distribution:* The evaluation of particle size distribution (PSD) was performed via x-ray sedimentation technique using a Sedigraph 5100, in accordance with ISO standards 13317-1 General Principles and

Guidelines, and 13317-3 X-Ray Gravitational techniques. Measurements using Sedigraph were made in the high speed analysis control mode using long flex life Tygon tubing. Sample were prepared in a 0.2% by weight sodium hexametaphosphate dispersant. A 5.0 gram sample was evaluated at 35°C using an internal fixed-position X-ray source/detector. Sample starting / end point diameters measure 50 – 0.5 μm, respectively.

[53] *Equipment*:

Extruder: Battenfeld Gloucester co-ex extrusion, 2" inside extruder, 3.5" core (middle) extruder, and a 2" outside extruder.

Layer Ratio: A (Inside)–30%, B (Core)–55%, and C (Outside)–15%

Screen Pack: 20/80/20 Mesh. Same pack configuration used in all three extruders

Die: 8" Battenfeld Gloucester w/ 80 mil die gap

Air Ring: Egan Davis-Standard dual-lip

[54] *Resins*:

Table 1. Resins

Resin	Density	MI	Mn	Mw	Mz
Resin A	0.962	1.0	8799	82314	331501
Resin B	0.962	6.5			
Resin C	0.962	8.0	9132	62247	203165
Resin D	0.962	8.0			

Density in g/cm^3, MI = melt index (dg/min), Mn = number average molecular weight, Mw = weight average molecular weight, Mz = z average molecular weight

[55] Resin D contains a fluoroelastomer polymer processing aid (a flow promoter) and showed poor response with respect to MVTR.

[56] *Calcium Carbonate Minerals*:

Table 2. Calcium Carbonate Minerals

Calcium Carbonate (CC) type	Description	Median Particle Size (μm)	Top Cut-d98 (μm)	Surface Area (m^2/g)	Treatment Level
CCA	Finely divided marble wet ground at 70% solids in presence of sodium polyacrylate dispersant and dried and surface treated	1.4	8	5.5	1.1% Wt. 2 mg/m^2
CCB	Finely divided marble wet ground in absence of a dispersant at 20% solids and dried and surface treated	2.0	10	3.3	0.8% Wt. 2.4mg/m^2

Top cut d98 refers to the average diameter of calcium carbonate particles in the 98th mass percentile. Treatment level refers to surface treatment of $CaCO_3$ with stearic acid/palmitic acid blend.

[57] *Process*:

Air Ring: Cooling temperature 52-54 °F with a 3.5 inch pressure (psig).

Frost Line: Height range – 18 to 19 inches

Output Rate: Constant at 250#/hr.

Conditions: Combinations of Blowup Ratio (BUR) and gauge (thickness measured in mils)

Table 3. Processing Conditions

Conditions	BUR	LAYFLAT	Gauge
1	1.60		2.00
2			2.50
3	2.20		2.00
4			2.50
5	1.60		3.00
6	2.2		3.00

BUR = Blow-Up Ratio.

[58] *Samples:*

Table 4. Samples

Sample	Target % by weight $CaCO_3$ in film	$CaCO_3$ Masterbatch $CaCO_3$/Resin	Masterbatch Ratio Mineral/Resin
Control	0	-	-
Sample A	20	CCA/Resin B	50 / 50
Sample B	25	CCA/Resin B	50 / 50
Sample C	30	CCA/Resin B	50 / 50
Sample D	25	CCB/Resin C	50 / 50
Sample E	25	CCA/Resin C	50 / 50
Sample F	25	CCA/Resin D	60 / 40
Sample G	25	CCA/Resin B	50 / 50
Sample H	25	CCA/Resin B	75 / 25

Description of Resin types and Calcium carbonate (CC) types in Masterbatch are found in Tables 1 and 2, respectively.

[59] *Trial Notes:* Nine samples including a control and five different calcium carbonate masterbatches were extruded on a Gloucester Battenfeld coextrusion blown film line. Except for samples A and C, each of these samples was extruded at the four different conditions (2.0 and 2.5 gauge, and 1.6 and 2.2 blow up ratio). Samples A & C were processed only at the 2.5 mil gauge with the 1.6 and 2.2 blow up ratio, respectively. Conditions 5 and 6 (Table 3) were used for the controls only.

Results and Discussion

[60] The evaluation objective was to determine which set of extrusion and calcium carbonate concentrate material combinations provided the highest resistance to moisture vapor transmission rate. It was demonstrated that a film constructed from Resin A with 25% by weight calcium carbonate incorporated via a 50/50 masterbatch of either Resin B or C (Table 1) with Calcium Carbonate (CC) type A (Table 2) provided the best improvements to MVTR when processed at the 1.6 blow up ratio and 2.5 mil gauge. Table 5A-C summarizes the film performance, including the moisture vapor transmission rate (MVTR) response. The codes in Table 5A-C for the Samples and Process Conditions are found in Tables 3 and 4.

[61] The films described herein provide a cost efficient means, compared for example to the use of metallized films, of providing films with reduced MVTRs that can be used for packaging moisture-sensitive products such as dry foods.

Table 5A. Results of Film Performance (continued in Table 5B & 5C)

SAMPLE & PROCESS CONDITION		$CaCO_3$ MB Loading	Resin Base for MB	$CaCO_3$ (CC) Type	$CaCO_3$ in Film	$CaCO_3$ in Film by Ash	BUR	Film Gauge		
								Target	Measured	Basis Wt
		% Wt			% Wt			mils	mils	mils
Control	1				0	0.19	1.6	2	2.01	1.46
Control	2				0	0.16	1.6	2.5	2.63	2.15
Control	3				0	0.15	2.2	2	1.97	1.6
Control	4				0	0.15	2.2	2.5	2.47	2.11
Control	5				0	0.03	1.6	3	3.11	2.31
Control	6				0	0.12	2.2	3	3.06	2.54
A	2	50	B	CCA	20	20.20	1.6	2.5	2.57	2.67
A	4	50	B	CCA	20	19.45	2.2	2.5	2.46	2.51
B	1	50	B	CCA	25	24.19	1.6	2	1.96	2.11
B	2	50	B	CCA	25	23.70	1.6	2.5	2.43	2.77
B	3	50	B	CCA	25	25.70	2.2	2	2.03	2.26
B	4	50	B	CCA	25	24.43	2.2	2.5	2.45	2.79
C	2	50	B	CCA	30	28.52	1.6	2.5	2.58	2.87
C	4	50	B	CCA	30	28.62	2.2	2.5	2.57	2.78
D	1	50	C	CCB	25	26.58	1.6	2	2.02	2.18
D	2	50	C	CCB	25	25.20	1.6	2.5	2.56	2.7
D	3	50	C	CCB	25	24.71	2.2	2	2.03	2.17
D	4	50	C	CCB	25	25.64	2.2	2.5	2.53	2.75
E	1	50	C	CCA	25	23.90	1.6	2	2.04	2.19
E	2	50	C	CCA	25	24.23	1.6	2.5	2.57	2.72
E	3	50	C	CCA	25	23.83	2.2	2	2.04	2.21
E	4	50	C	CCA	25	24.28	2.2	2.5	2.51	2.6
F	1	60	D	CCA	25	21.60	1.6	2	1.99	2.23
F	2	60	D	CCA	25	21.78	1.6	2.5	2.54	2.8
F	3	60	D	CCA	25	26.27	2.2	2	1.97	2.2
F	4	60	D	CCA	25	23.98	2.2	2.5	2.46	2.63
G	1	50	B	CCA	25	25.62	1.6	2	1.91	2.23
G	2	50	B	CCA	25	27.20	1.6	2.5	2.4	2.85
G	3	50	B	CCA	25	24.70	2.2	2	1.93	2.24
G	4	50	B	CCA	25	26.02	2.2	2.5	2.55	2.86
H	1	75	B	CCA	25	22.82	1.6	2	1.97	1.91
H	2	75	B	CCA	25	26.70	1.6	2.5	2.52	2.83
H	3	75	B	CCA	25	25.24	2.2	2	2.07	2.19
H	4	75	B	CCA	25	30.25	2.2	2.5	2.54	2.83

Table 5B. Results of Film Performance (continuation of Table 5A)

SAMPLE & PROCESS CONDITION		MVTR	nMVTR	nMVTR (2)	Effect of $CaCO_3$	Effect of BUR
			Measured	Target	nMVTR	nMVTR
		g/100 in^2/d	g-mil/100 in^2/d	g-mil/100 in^2/d	% Improvement	% Improvement
Control	1	0.177	0.356	0.354		
Control	2	0.108	0.284	0.270		
Control	3	0.132	0.260	0.264		26.91
Control	4	0.097	0.240	0.243		8.45
Control	5	0.094	0.292	0.282		
Control	6	0.075	0.230	0.225		
A	2	0.1	0.257	0.250	9.52	
A	4	0.092	0.226	0.230	12.97	11.94
B	1	0.135	0.265	0.270	25.63	
B	2	0.091	0.221	0.228	22.15	
B	3	0.107	0.217	0.214	16.47	17.91
B	4	0.087	0.213	0.218	18.03	3.61
C	2	0.095	0.245	0.238	13.71	
C	4	0.097	0.249	0.243	4.13	-1.71
D	1	0.123	0.248	0.246	30.16	
D	2	0.095	0.243	0.238	14.38	
D	3	0.115	0.233	0.230	10.23	6.04
D	4	0.092	0.233	0.230	10.49	4.29
E	1	0.139	0.284	0.278	20.30	
E	2	0.096	0.247	0.240	13.14	
E	3	0.118	0.241	0.236	7.43	15.11
E	4	0.097	0.243	0.243	6.37	1.32
F	1	0.161	0.320	0.322	9.94	
F	2	0.115	0.292	0.288	-2.84	
F	3	0.134	0.264	0.268	-1.52	17.61
F	4	0.104	0.256	0.260	1.62	12.41
G	1	0.135	0.258	0.270	27.52	
G	2	0.095	0.228	0.238	19.73	
G	3	0.115	0.222	0.230	14.65	13.92
G	4	0.089	0.227	0.223	12.72	0.46
H	1	0.195	0.384	0.390	-7.98	
H	2	0.121	0.305	0.303	-7.35	
H	3	0.129	0.267	0.258	-2.69	30.49
H	4	0.091	0.231	0.228	11.11	24.20

Table 5C. Results of Film Performance (continuation of Table 5A&5B)

SAMPLE&PROCESS CONDITION		2.5 mil $CACO_3$ Containing HDPE film vs.3.0 HDPE Film	Average nMVTR Improvement	Average nMVTR Improvement
		nMVTR		
		% Improvement	% Improvement	% Improvement
Control	1			
Control	2			
Control	3			
Control	4			
Control	5			
Control	6			
A	2			11.24
A	4			
B	1		23.89	20.57
B	2	24.36		
B	3		17.25	
B	4	7.12		
C	2	16.16		8.92
C	4	-8.62		
D	1		22.27	16.31
D	2	16.81		
D	3		10.36	
D	4	-1.42		
E	1		16.72	11.81
E	2	15.61		
E	3		6.90	
E	4	-6.09		
F	1		3.55	1.80
F	2	0.08		
F	3		0.05	
F	4	-11.48		
G	1		23.63	18.66
G	2	22.01		
G	3		13.69	
G	4	1.11		
H	1		-7.66	-1.73
H	2	-4.30		
H	3		4.21	
H	4	-0.71		

[62] Notes to Table 5B: "MVTR" is the raw MVTR. "nMVTR" is the MVTR corrected using measured gauge. "nMVTR(2)" is the MVTR corrected using target gauge. "Effect of $CaCO_3$" shows improvement in MVTR (measured gauge corrected) versus control film at same gauge and film orientation (BUR). "Effect of BUR" shows improvement in MVTR resulting from BUR at equivalent $CaCO_3$ loading and gauge. Positive numbers indicates an improvement (i.e., reduced MVTR); negative number indicates a deficiency.

[63] Notes to Table 5C: Comparison in Column 3 is between a 2.5 mil film containing $CaCO_3$ versus a straight 3.0 mil HDPE at equivalent BUR. "Average nMVTR Improvement" in Column 4 is the average improvement in MVTR of $CaCO_3$ containing samples versus control at a given BUR. "Average nMVTR Improvement" in Column 5 is the average improvement in nMVTR of $CaCO_3$ containing samples versus the control across both gauges and BURs used. Positive numbers indicates an improvement (i.e., reduced MVTR); negative number indicates a deficiency.

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What is claimed is:

1. A film comprising:

a) a polyolefin base resin; and

b) a polyolefin carrier resin admixed with $CaCO_3$;

wherein the $CaCO_3$ and the carrier resin are present in a ratio of 15/85 to 80/20 by weight.

2. The film of Claim 1, wherein the base resin and the carrier resin are different resins.

3. The film of Claim 2, wherein the base resin and the carrier resin differ in molecular weight, density, melt index and/or polydispersity index.

4. The film of any of Claims 1-3, wherein the carrier resin has a melt index of 4-10 dg/min.

5. The film of any of Claims 1-4, wherein the carrier resin has a density of 0.958-0.963 g/cm^3.

6. The film of any of Claims 1-5, wherein the base resin has a melt index of 0.05-2.0 dg/min.

7. The film of any of Claims 1-6, wherein the base resin has a density of 0.958-0.963 g/cm^3.

8. The film of any of Claims 1-7, wherein $CaCO_3$ is present in the film in a total concentration of 5%-35% by weight.

9. A film comprising:

a) a polyolefin base resin having a melt index of 0.05-2.0 dg/min and a density of 0.958-0.963 g/cm^3;

b) a polyolefin carrier resin for $CaCO_3$, wherein the carrier resin has a melt index of 4-10 dg/min and a density of 0.958-0.963 g/cm^3; and

c) $CaCO_3$;

wherein $CaCO_3$ is present in the film in a total concentration of 5%-35% by weight.

10. The film of any of Claims 1-9, wherein the carrier resin has a melt index of 6.5-8.0 dg/min.

11. The film of Claim 10, wherein the carrier resin has a melt index of 6.5 dg/min.

12. The film of any of Claims 1-11, wherein the carrier resin has a density of 0.962 g/cm^3.

13. The film of any of Claims 1-12, wherein the base resin has a melt index of 1 dg/min.

14. The film of any of Claims 1-13, wherein the base resin has a density of 0.962 g/cm^3.

15. The film of any of Claims 1-14, wherein the concentration of $CaCO_3$ in the film is 20-30% by weight.

16. The film of Claim 15, wherein the concentration of $CaCO_3$ in the film is 25% by weight.

17. The film of any of Claims 9-16, wherein the $CaCO_3$ and the carrier resin are present in a ratio of 15/85 to 80/20 by weight.

18. The film of any of Claims 1-18, wherein the $CaCO_3$ and the carrier resin are present in a ratio of 40/60 to 80/20 by weight.

19. The film of Claim 18, wherein the $CaCO_3$ and the carrier resin are present in a ratio of 40/60 to ≤ 60/40 by weight.

20. The film of Claim 19, wherein the $CaCO_3$ and the carrier resin are present in a ratio of 45/55 to 55/45 by weight.

21. The film of Claim 20, wherein the $CaCO_3$/carrier resin ratio is 50/50 by weight.

22. The film of any of Claims 1-21, wherein the carrier resin is a polyethylene (PE), a polypropylene, or a polyisoprene.

23. The film of Claim 22, wherein the polyethylene is a high density polyethylene (HDPE) a medium density polyethylene (MDPE) a low density polyethylene (LDPE) or a linear LDPE (LLDPE).

24. The film of Claim 23, wherein the HDPE is a medium molecular weight high density polyethylene (MMW-HDPE).

25. The film of Claim 24, wherein the MMW-HDPE has a melt index of 0.85 to 1.5 dg/min.

26. The film of any of Claims 1-25, wherein the base resin is a polyethylene (PE), a polypropylene, or a polyisoprene.

27. The film of Claim 26, wherein the polyethylene is a high density polyethylene (HDPE) a medium density polyethylene (MDPE) a low density polyethylene (LDPE) or a linear LDPE (LLDPE).

28. The film of Claim 27, wherein the HDPE is a medium molecular weight high density polyethylene (MMW-HDPE).

29. The film of Claim 28, wherein the MMW-HDPE has a melt index of 0.85 to 1.5 dg/min.

30. A multilayer film comprising the film of any of Claims 1-29.

31. The multilayer film of Claim 30, which comprises an inner layer comprising one or more of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), and ethylene acrylic acid (EAA), a core layer comprising polyolefin and calcium carbonate ($CaCO_3$), and an outer layer comprising polyolefin and calcium carbonate ($CaCO_3$).

32. The multilayer film of Claim 31, wherein the concentration of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA) or ethylene acrylic acid (EAA) in the inner layer is 15-20% by weight.

33. The multilayer film of Claim 31 or 32, wherein the ethylene vinyl acetate (EVA) has a density of 0.95 g/cm^3.

34. The multilayer film of any of Claims 31-33, wherein the ethylene vinyl acetate (EVA) has a melt index of 1.5 dg/min.

35. The multilayer film of any of Claims 31-34, which has a weight distribution by layer of 25-35% outer layer, 50-60% core layer, and 10-20% inner layer.

36. The multilayer film of Claim 35, which has a weight distribution by layer of 30% outer layer, 55% core layer, and 15% inner layer.

37. A multilayer film, wherein at least a first layer of the multilayer film comprises one or more of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), and ethylene acrylic acid (EAA), and at least a second layer of the multilayer

film comprises polyolefin and calcium carbonate ($CaCO_3$), and wherein $CaCO_3$ is present in the multilayer film in a total concentration of 5%-35% by weight.

38. The multilayer film of Claim 37, wherein the concentration of $CaCO_3$ in the multilayer film is 20%-30% by weight.

39. The multilayer film of Claim 38, wherein the concentration of $CaCO_3$ in the multilayer film is 25% by weight.

40. The multilayer film of any of Claims 37-39, which comprises an inner layer comprising one or more of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), and ethylene acrylic acid (EAA), a core layer comprising polyolefin and calcium carbonate ($CaCO_3$), and an outer layer comprising polyolefin and calcium carbonate ($CaCO_3$).

41. The multilayer film of Claim 40, wherein the concentration of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA) or ethylene acrylic acid (EAA) in the inner layer is 15-20% by weight.

42. The multilayer film of any of Claims 37-41, wherein the ethylene vinyl acetate (EVA) has a density of 0.95 g/cm^3.

43. The multilayer film of any of Claims 37-42, wherein the ethylene vinyl acetate (EVA) has a melt index of 1.5 dg/min.

44. The multilayer film of any of Claims 40-43, which has a weight distribution by layer of 25-35% outer layer, 50-60% core layer, and 10-20% inner layer.

45. The multilayer film of any of Claim 44, which has a weight distribution by layer of 30% outer layer, 55% core layer, and 15% inner layer.

46. The multilayer film of any of Claims 37-45, wherein the film layers comprising polyolefin and calcium carbonate ($CaCO_3$) comprise a polyolefin carrier resin and wherein the $CaCO_3$ and the polyolefin carrier resin are present in a ratio of 15/85 to 80/20 by weight.

47. The multilayer film of Claim 46, wherein the $CaCO_3$ and the carrier resin are present in a ratio of 40/60 to 80/20 by weight.

48. The multilayer film of Claim 47, wherein the $CaCO_3$/polyolefin carrier resin ratio is 40/60 to ≤ 60/40 by weight.

49. The multilayer film of Claim 48, wherein the $CaCO_3$/polyolefin carrier resin ratio is 45/55 to 55/45 by weight.

50. The multilayer film of Claim 49, wherein the $CaCO_3$/polyolefin carrier resin ratio is 50/50 by weight.

51. The multilayer film of any of Claims 37-50, wherein the film layers comprising polyolefin and calcium carbonate ($CaCO_3$) comprise a polyolefin carrier resin having a melt index of 4-10 dg/min.

52. The multilayer film of Claim 51, wherein the carrier resin has a melt index of 6.5-8.0 dg/min.

53. The multilayer film of Claim 50, wherein the carrier resin has a melt index of 6.5 dg/min.

54. The multilayer film of any of Claims 37-53, wherein the carrier resin has a density of 0.958-0.963 g/cm^3.

55. The multilayer film of Claim 54, wherein the carrier resin has a density of 0.962 g/cm^3.

56. The multilayer film of any of Claims 37-55 comprising a carrier resin for $CaCO_3$, wherein the carrier resin is a polyethylene (PE), a polypropylene, or a polyisoprene.

57. The multilayer film of Claim 56, wherein the polyethylene is a high density polyethylene (HDPE) a medium density polyethylene (MDPE) a low density polyethylene (LDPE) or a linear LDPE (LLDPE).

58. The multilayer film of Claim 57, wherein the HDPE is a medium molecular weight high density polyethylene (MMW-HDPE).

59. The multilayer film of Claim 58, wherein the MMW-HDPE has a melt index of 0.85 to 1.5 dg/min.

60. The multilayer film of any of Claims 37-59 comprising a base resin, wherein the base resin is a polyethylene (PE), a polypropylene, or a polyisoprene.

61. The multilayer film of Claim 60, wherein the polyethylene is a high density polyethylene (HDPE) a medium density polyethylene (MDPE) a low density polyethylene (LDPE) or a linear LDPE (LLDPE).

62. The film of Claim 61, wherein the HDPE is a medium molecular weight high density polyethylene (MMW-HDPE).

63. The film of Claim 62, wherein the MMW-HDPE has a melt index of 0.85 to 1.5 dg/min.

64. The multilayer film of any of Claims 60-63, wherein the base resin has a melt index of 0.05 - 2.0 dg/min.

65. The multilayer film of Claim 64, wherein the base resin has a melt index of 1 dg/min.

66. The multilayer film of any of Claims 60-65, wherein the base resin has a density of 0.958-0.963 g/cm^3.

67. The multilayer film of Claim 66, wherein the base resin has a density of 0.962 g/cm^3.

68. A film comprising:

a) a high density polyethylene (HDPE) base resin, wherein the HDPE base resin has a melt index of 0.05 - 2.0 dg/min and a density of 0.958-0.963 g/cm^3;

b) a HDPE carrier resin for calcium carbonate ($CaCO_3$), wherein the HDPE carrier resin has a melt index of 4-10 dg/min and a density of 0.958-0.963 g/cm^3; and

c) $CaCO_3$, wherein the $CaCO_3$ has a median particle size of 0.7-2.5 μm, a top cut d98 of 4-15 μm, a surface area of 3.3-10.0 m^2/g, and a total concentration in the film of 5-35% by weight, wherein the $CaCO_3$ has been treated with a surface treatment agent at a treatment level of 0.3-2.3% by weight, and wherein the $CaCO_3$ and the HDPE carrier resin are present in a ratio of 15/85 to 80/20 by weight.

69. The film of Claim 68, wherein the $CaCO_3$ has been wet ground and/or dry ground prior to incorporation of $CaCO_3$ in the film.

70. The film of Claim 69, wherein the $CaCO_3$ has been wet ground in the presence or in the absence of a grinding aid.

71. The film of Claim 69 or 70, wherein the $CaCO_3$ has been wet ground in the presence of a grinding aid comprising a salt of polyacrylic acid and/or a salt of a copolymer of acrylic acid.

72. The film of any of Claims 69-71, wherein the calcium carbonate is dried after grinding.

73. The film of any of Claims 68-72, wherein the $CaCO_3$ has treated with the surface treatment agent before and/or during and/or after grinding the $CaCO_3$.

74. The film of any of Claims 68-73, wherein the $CaCO_3$ has been treated with the surface treatment agent at a treatment level of 1.5-3 mg surface treatment agent/m^2 $CaCO_3$.

75. The film of any of Claims 68-74, wherein the HDPE base resin is a medium molecular weight HDPE (MMW-HDPE) base resin.

76. The film of Claim 75, wherein the MMW-HDPE has a melt index of 0.85 to 1.5 dg/min.

77. The film of any of Claims 68-76, wherein the HDPE carrier resin is a medium molecular weight HDPE (MMW-HDPE) carrier resin.

78. The film of Claim 77, wherein the MMW-HDPE has a melt index of 0.85 to 1.5 dg/min.

79. The film of any of Claims 68-78, wherein the HDPE base resin has a melt index of 1.0 dg/min.

80. The film of any of Claims 68-79, wherein the HDPE carrier resin has a melt index of 6.5-8.0 dg/min.

81. The film of Claim 80, wherein the HDPE carrier resin has a melt index of 6.5 dg/min.

82. The film of any of Claims 68-81, wherein the HDPE base resin has a density of 0.962 g/cm^3.

83. The film of any of Claims 68-82, wherein the HDPE carrier resin has a density of 0.962 g/cm^3.

84. The film of any of Claims 68-83, wherein the concentration of calcium carbonate ($CaCO_3$) in the film is 20%-30%.

85. The film of Claim 84, wherein the concentration of calcium carbonate ($CaCO_3$) in the film is 25%.

86. The film of any of Claims 68-85, wherein the $CaCO_3$ and the HDPE carrier resin are present in a ratio of 40/60 to 80/20 by weight.

87. The film of Claim 86, wherein the $CaCO_3$ and the HDPE carrier resin are present in a ratio of 40/60 to ≤ 60/40 by weight.

88. The film of Claim 87, wherein the $CaCO_3$ and the HDPE carrier resin are present in a ratio of 45/55 to 55/45 by weight.

89. The film of Claim 88, wherein the $CaCO_3$ and the HDPE carrier resin are present in a ratio of 50/50 by weight.

90. A film comprising:

a) a high density polyethylene (HDPE) having a density of 0.958-0.963 g/cm^3, and

b) calcium carbonate ($CaCO_3$) having a median particle size of 0.7-2.5 μm, a top cut d98 of 4-15 μm, a surface area of 3.3-10.0 m^2/g, and a total concentration in the film of 5-35% by weight.

91. The film of Claim 90, wherein the HDPE is a medium molecular weight HDPE (MMW-HDPE).

92. The film of Claim 90 or 91, wherein the HDPE has a density of 0.962 g/cm^3.

93. The film of any of Claims 90-92, wherein the concentration of $CaCO_3$ in the film is 20-30% by weight.

94. The film of Claim 93, wherein the concentration of $CaCO_3$ in the film is 25% by weight.

95. The film of any of Claims 1-94, wherein the $CaCO_3$ has a median particle size of 0.7-2.5 μm.

96. The film of Claim 95, wherein the $CaCO_3$ has a median particle size of 1.4-2.0 μm.

97. The film of Claim 96, wherein the $CaCO_3$ has a median particle size of 1.4 μm.

98. The film of any of Claims 1-97, wherein the $CaCO_3$ has a top cut d98 of 4-15 μm.

99. The film of Claim 98, wherein the $CaCO_3$ has a top cut d98 of 8-10 μm.

100. The film of Claim 99, wherein the $CaCO_3$ has a top cut d98 of 8 μm.

101. The film of any of Claims 1-100, wherein the $CaCO_3$ has a surface area of 3.3-10.0 m^2/g.

102. The film of Claim 101, wherein the $CaCO_3$ has a surface area of 3.3-5.5 m^2/g.

103. The film of Claim 102, wherein the $CaCO_3$ has a surface area of 5.5 m^2/g.

104. The film of any of Claims 1-103, wherein the $CaCO_3$ has been treated with a surface treatment agent at a treatment level of 0.3-2.3% by weight.

105. The film of Claim 104, wherein the treatment level is 0.8-1.1% by weight.

106. The film of Claim 105, wherein the treatment level is 1.1% by weight.

107. The film of any of Claims 104-106, wherein the surface treatment agent is one or more fatty acids have 8 to 24 carbon atoms.

108. The film of Claim 107, wherein the surface treatment agent is one or more of arachidic acid, behenic acid, capric acid, cerotic acid, isostearic acid, lauric acid, myristic acid, montanic acid, palmitic acid and stearic acid.

109. The film of Claim 107, wherein the surface treatment agent comprises stearic acid.

110. A multilayer film comprising the film of any of Claims 68-109.

111. The multilayer film of Claim 110, which comprises an inner layer comprising one or more of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), and ethylene acrylic acid (EAA), a core layer comprising HDPE and calcium carbonate ($CaCO_3$), and an outer layer comprising HDPE and calcium carbonate ($CaCO_3$).

112. The multilayer film of Claim 111, wherein the concentration of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA) or ethylene acrylic acid (EAA) in the inner layer is 15-20% by weight.

113. The multilayer film of Claim 111 or 112, wherein the ethylene vinyl acetate (EVA) has a density of 0.95 g/cm^3.

114. The multilayer film of any of Claims 111-113, wherein the ethylene vinyl acetate (EVA) has a melt index of 1.5 dg/min.

115. The multilayer film of any of Claims 111-114, which has a weight distribution by layer of 25-35% outer layer, 50-60% core layer, and 10-20% inner layer.

116. The multilayer film of Claim 115, which has a weight distribution by layer of 30% outer layer, 55% core layer, and 15% inner layer.

117. A method of making a masterbatch composition of calcium carbonate ($CaCO_3$) and polyolefin for preparing a film, the method comprising mixing $CaCO_3$ with a polyolefin carrier resin, wherein the $CaCO_3$ and the carrier resin are present in a ratio of 15/85 to ≤ 60/40 by weight.

118. The method of Claim 117, wherein the polyolefin carrier resin is a high density polyethylene (HDPE).

119. A method of making a masterbatch composition of calcium carbonate ($CaCO_3$) and high density polyethylene (HDPE) for preparing a film, the method comprising mixing $CaCO_3$ with a HDPE carrier resin, wherein the $CaCO_3$ and the carrier resin are present in a ratio of 15/85 to 80/20 by weight.

120. The method of Claim 119, wherein the $CaCO_3$/carrier resin ratio is 40/60 to 80/20 by weight.

121. The method of Claim 119, wherein the $CaCO_3$/carrier resin ratio is 40/60 to ≤ 60/40 by weight.

122. The method of Claim 119, wherein the $CaCO_3$/carrier resin ratio is 45/55 to 55/45 by weight.

123. The method of Claim 119, wherein the $CaCO_3$/carrier resin ratio is 50/50 by weight.

124. The method of any of Claims 117-123, wherein the carrier resin has a melt index of 4-10 dg/min.

125. The method of Claim 124, wherein the carrier resin has a melt index of 6.5-8.0 dg/min.

126. The method of Claim 124, wherein the carrier resin has a melt index of 6.5 dg/min.

127. The method of any of Claims 117-126, wherein the carrier resin has a density of 0.958-0.963 g/cm^3.

128. The method of Claim 127, wherein the carrier resin has a density of 0.962 g/cm^3.

129. The method of any of Claims 118-128, wherein the HDPE is a medium molecular weight high density polyethylene (MMW-HDPE).

130. The method of Claim 129, wherein the MMW-HDPE has a melt index of 0.85 to 1.5 dg/min.

131. The method of any of Claims 117-130, wherein the $CaCO_3$ has a median particle size of 0.7-2.5 μm.

132. The method of Claim 131, wherein the $CaCO_3$ has a median particle size of 1.4-2.0 μm.

133. The method of Claim 131, wherein the $CaCO_3$ has a median particle size of 1.4 μm.

134. The method of any of Claims 117-133, wherein the $CaCO_3$ has a top cut d98 of 4-15 μm.

135. The method of Claim 134, wherein the $CaCO_3$ has a top cut d98 of 8-10 μm.

136. The method of Claim 134, wherein the $CaCO_3$ has a top cut d98 of 8 μm.

137. The method of any of Claims 117-136, wherein the $CaCO_3$ has a surface area of 3.3-10.0 m^2/g.

138. The method of Claim 137, wherein the $CaCO_3$ has a surface area of 3.3-5.5 m^2/g.

139. The method of Claim 137, wherein the $CaCO_3$ has a surface area of 5.5 m^2/g.

140. The method of any of Claims 117-139, wherein the $CaCO_3$ has been treated with a surface treatment agent at a treatment level of 0.3-2.3% by weight.

141. The method of Claim 140, wherein the treatment level is 0.8-1.1% by weight.

142. The method of Claim 140, wherein the treatment level is 1.1% by weight.

143. The method of any of Claims 140-142, wherein the surface treatment agent is one or more fatty acids have 8 to 24 carbon atoms.

144. The method of Claim 143, wherein the surface treatment agent is one or more of arachidic acid, behenic acid, capric acid, cerotic acid, isostearic acid, lauric acid, myristic acid, montanic acid, palmitic acid and stearic acid.

145. The method of Claim 144, wherein the surface treatment agent comprises stearic acid.

146. The method of any of Claims 117-145 which further comprises forming the masterbatch composition in a pellet.

147. A masterbatch composition prepared by the method of any of Claims 117-146.

148. A calcium carbonate masterbatch composition comprising 50% by weight calcium carbonate of 1.4 μm median diameter particle size, a top cut particle size d98 of 8.0 μm, with a 1.1% by weight stearic acid surface treatment, in a 50% by weight high density polyethylene (HDPE) carrier resin of $0.962 g/cm^3$ density and 6.5 dg/min melt index.

149. A method of making a film comprising polyolefin and calcium carbonate ($CaCO_3$), wherein the method comprises blending (a) the masterbatch composition of Claim 147 or 148 and (b) a polyolefin base resin.

150. The method of Claim 149, wherein the polyolefin base resin is a high density polyethylene (HDPE).

151. The method of Claim 149 or 150, wherein the base resin has a melt index of 0.05 - 2.0 dg/min.

152. The method of Claim 151, wherein the base resin has a melt index of 1 dg/min.

153. The method of Claim 150, wherein the HDPE is a medium molecular weight high density polyethylene (MMW-HDPE).

154. The method of Claim 153, wherein the MMW-HDPE has a melt index of 0.85 to 1.5 dg/min.

155. The method of any of Claims 149-154, wherein the base resin has a density of 0.958-0.963 g/cm^3.

156. The method of Claim 155, wherein the base resin has a density of 0.962 g/cm^3.

157. The method of any of Claims 149-156, which further comprises coextruding a film layer comprising polyolefin and calcium carbonate with a film layer comprising one or more of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), and ethylene acrylic acid (EAA).

158. The method of Claim 157, which comprises coextruding an inner film layer comprising one or more of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA), and ethylene acrylic acid (EAA), a core film layer comprising polyolefin and calcium carbonate ($CaCO_3$), and an outer film layer comprising polyolefin and calcium carbonate ($CaCO_3$).

159. The method of Claim 157 or 158, wherein the concentration of ethylene vinyl acetate (EVA), ethylene ethyl acetate (EEA) or ethylene acrylic acid (EAA) in the film layer comprising EVA, EEA or EAA is 15-20% by weight.

160. The method of any of Claims 157-159, wherein the ethylene vinyl acetate (EVA) has a density of 0.95 g/cm^3.

161. The method of any of Claims 157-160, wherein the ethylene vinyl acetate (EVA) has a melt index of 1.5 dg/min.

162. The method of any of Claims 158-161, wherein the film has a weight distribution by layer of 25-35% outer layer, 50-60% core layer, and 10-20% inner layer.

163. The method of Claim 162, wherein the film has a weight distribution by layer of 30% outer layer, 55% core layer, and 15% inner layer.

164. The method of any of Claims 157-163, wherein $CaCO_3$ is present in the film in a total concentration of 5%-35% by weight.

165. The method of Claim 164, wherein $CaCO_3$ is present in the film in a total concentration of 20%-30% by weight.

166. The method of Claim 164, wherein the concentration of $CaCO_3$ in the film is 25% by weight.

167. A film made by the method of any of Claims 149-166.

168. The film of any of Claims 1-116 and 167, wherein the moisture vapor transmission rate (MVTR) is reduced in comparison to the film in the absence of $CaCO_3$.

169. The film of Claim 168, wherein the moisture vapor transmission rate (MVTR) is reduced by 10-30% compared to the MVTR of the film in the absence of $CaCO_3$.

170. The film of Claim 169, wherein the moisture vapor transmission rate (MVTR) is reduced by 20-30% compared to the MVTR of the film in the absence of $CaCO_3$.

171. The film of Claim 170, wherein the moisture vapor transmission rate (MVTR) is reduced by 25-30% compared to the MVTR of the film in the absence of $CaCO_3$.

172. The film of any of Claims 1-116 and 167-171, wherein the moisture vapor transmission rate (MVTR) is 0.213-0.230 g water vapor-mil/100 in^2 of film/day at 37.5 °C and 100% relative humidity.

173. The film of Claim 172, wherein the moisture vapor transmission rate (MVTR) is 0.213 g water vapor-mil/100 in^2 of film/day at 37.5 °C and 100% relative humidity.

174. A packaging film comprising the film of any of Claims 1-116 and 167-173.

175. The packaging film of Claim 174, wherein the film is a packaging film for moisture-sensitive materials.

176. The packaging film of Claim 174 or 175, wherein the film is a food packaging film, an animal feed packaging film or a pharmaceutical packaging film.

177. The film of Claim 176, wherein the food products are dry food products.

178. The film of Claim 177, wherein the dry food is cereal or crackers.