

METALLIZED FILM STRUCTURE

This invention relates to the field of metallized polymer films. It more particularly relates to a sealable biaxially oriented composite metallized film structure in which the sealable skin layer contains a particulate cross
5 linked hydrocarbyl substituted polysiloxane.

In the packaging of certain types of foods, such as snack foods including candies, potato chips, cookies and the like, it is common practice to employ a multi-layer
10 film. Polypropylene films are widely used in the packaging industry due to their superior physical properties, such as, transparency, stiffness, moisture barrier characteristics and others. Despite these highly desirable properties, unmodified polypropylene film has the
15 disadvantageous property of having a high inherent coefficient of friction and film-to-film destructive blocking on storage. This high film-to-film coefficient of friction makes polypropylene films difficult to be successfully employed in automatic packaging equipment in their
20 unmodified form.

Coefficient of friction characteristics of polypropylene and other thermoplastic films are beneficially modified by the inclusion in the polymer of slip agents. Most of these slip agents are migratory, such as poly-
25 dialkyl siloxane or fatty amides, such as, erucamide and oleamide. Although they do reduce the coefficient of friction, their effectiveness depends upon the ability to migrate to the surface of the film. The development of the desired low coefficient of friction value is strongly
30 dependent upon the type and amounts of amides, and time and temperature aging effects. Even the heat history of the film while in storage and shipping and during subsequent converter processes, significantly affects the coefficient of friction. In addition, the presence of these types of
35 fatty acid amides on the film surface results in visible adverse appearance effects, manifested by an increase in

haze, a decrease in gloss and the presence of streaks. These materials also adversely effect the wetability and adhesion of solvent and water-based inks, coatings and adhesives.

5 To overcome the problems associated with migratory slip agents, non-migratory systems were developed. A material described to be a non-migratory slip agent is a particulate cross linked hydrocarbyl-substituted polysiloxane which is available worldwide from Toshiba Silicone Co., Ltd. and in
10 the United States from General Electric Co. and marketed under the name TOSPEARL

Additional descriptions of olefinic polymer films in which particulate siloxane resins are employed to provide improved films will be found in U.S. Patent Nos. 4,966,933;
15 4,769,418; 4,652,618; and 4,594,134.

U.S. Patent No. 4,966,933 describes a propylene polymer film containing 100 parts by weight of a propylene polymer, 0.01 to 0.5 parts by weight of a fine powder of a cross
20 linked silicone resin and 0.3 to 3.0 parts by weight of a hydroxy-fatty acid glyceride.

This invention provides a metallized film which has low coefficient of friction, for good machinability, good heat sealability, low haze, good gloss (of unmetallized film), nonblocking properties and good to excellent barrier
25 properties.

More specifically, the invention provides a metallized film structure which includes an olefinic polymer core layer having at least one skin layer comprising an olefin polymer having an external surface which is sealable and
30 machinable, the layer containing a non-migratory particulate cross linked hydrocarbyl-substituted polysiloxane. Particularly preferred particulate cross linked hydrocarbyl-substituted polysiloxanes include the polymonoalkylsiloxanes. On the other side of the olefin
35 polymer core layer there is an olefinic polymer layer having a metallizable external surface which is free of the

non-migratory particulate cross linked hydrocarbyl-substituted polysiloxane. The non-migratory slip agent does not, to any meaningful degree, effect metallized film barrier properties or lamination bond strengths to other oriented polypropylene based films or polyester based films.

Even more specifically, the invention relates to a metallized film structure comprising a first outer skin layer (a) of an olefin co- or ter-polymer having an external surface which is sealable and machinable on one side of a core olefinic polymer layer (b), the first skin layer containing a non-migratory particulate cross linked hydrocarbyl-substituted polysiloxane, on an opposite side of the core layer there is a second outer skin layer (c) which includes an ethylene homopolymer which is free of the particulate cross linked hydrocarbyl substituted polysiloxane of the first skin layer, the second skin layer having a metal deposited thereon.

The invention further relates to a method of making a metallized film comprising the steps of coextruding a film structure, the film structure comprising a heat sealable outer layer (a) comprising an olefinic co- or terpolymer containing a particulate cross linked hydrocarbyl-substituted polysiloxane; a core layer (b) comprising an olefinic polymer and a metallizable outer layer (c) comprising an ethylene homopolymer which is free of the particulate cross linked hydrocarbyl-substituted polysiloxane of layer (a); and metallizing the surface of the outer layer (c) by depositing a metal thereon.

By improved machinability it is meant that the film exhibits a low coefficient of friction and has improved anti-slip and non-blocking characteristics.

The film structure comprises an upper heat sealable layer comprising an olefinic copolymer or terpolymer having an external surface which is sealable and machinable, the layer containing, as slip agent, a particulate cross linked

hydrocarbyl-substituted polysiloxane, a core layer comprising an olefinic polymer, and a lower metallizable layer comprising an olefinic homopolymer.

A particularly preferred polymer employed as the core layer of the film herein is polypropylene, particularly highly isotactic polypropylene. The preferred polypropylenes are well known in the art. Typically, they are formed by polymerizing propylene in the presence a stereospecific catalyst system. They can have a melt index at 230°C ranging from 0.1 to 25. The crystalline melting point is usually 160°C. The number average molecular weight typically ranges from 25,000 to 100,000. The density typically ranges from 0.90 to 0.91.

For descriptive purpose only, the film structures of the present invention will be described as having an upper skin layer (a), a core layer (b) and a lower skin layer (c). As may be appreciated by those skilled in the art, the use of the terms upper and lower to refer to particular skin layers is merely relative. Moreover, although referred to as skin layers, the upper and lower layers may have additional structures bonded thereto, based on the functional requirements of the overall structure.

The polymer materials which are contemplated for use in forming skin layer (a) are suitably exemplified by heat sealable polyolefinic copolymers and terpolymers and blends thereof. The copolymers are exemplified by and include block copolymers, for example of ethylene and propylene, random copolymers, for example of ethylene and propylene. The terpolymers are exemplified by ethylene-propylene-butene-1 terpolymers. Also, heat sealable blends can be utilized in providing layer (a). Thus, along with the copolymer or terpolymer there can be polypropylene homopolymer, e.g. one which is the same as, or different from, the polypropylene homopolymer constituting core layer (b) or other material which does not impair the heat sealability of this layer.

Suitable ethylene-propylene-butene-1 (EPB) terpolymers are those obtained from the random inter-polymerization of from 1 to 8 wt.% ethylene, preferably from 3 to 7 wt.% ethylene with from 1 to 10 wt.% butene-1, preferably from 2 to 8 wt.% butene-1 with propylene representing the balance. The foregoing EPB terpolymers are for the most part characterized by a melt index at 230°C of from 2 to 16 and advantageously from 3 to 7, a crystalline melting point of from 100°C to 140°C, an average molecular weight of from 25,000 to 100,000 and a density within the range of from 0.89 to 0.92 gm/cm³.

The ethylene-propylene (EP) random copolymers generally contain from 2 to 8 wt.% ethylene, specifically 3 to 7 wt.% ethylene, the balance being made up of propylene. The copolymers can have a melt index at 230°C generally ranging from 2 to 15 and preferably from 3 to 8. The crystalline melting point is usually from 125°C to 150°C and the number average molecular weight range is from 25,000 to 100,000. The density will usually range from 0.89 to 0.92 gm/cm³.

In general, where blends of EPB terpolymer and EP random copolymer are used, such blends will contain from 10 to 90 wt.% EPB terpolymer and preferably from 40 to 60 wt.% EPB terpolymer, the balance being made up of EP random copolymer.

Prior to extrusion, in accordance with the present invention, the heat seal layer (a) is compounded with an effective amount of a non-migratory slip agent. Preferred non-migratory slip agents are selected from the group of particulate cross linked hydrocarbyl-substituted polysiloxanes. Particularly preferred are the particulate cross linked polymonoalkylsiloxanes. Most particularly preferred are non-meltable polymonoalkylsiloxanes characterized as having a mean particle diameter of 0.5 to 20.0 μ , typically determined by known scanning electron micrograph measurement techniques, and a three dimensional structure of siloxane linkages. Such materials are

commercially available from Shin Etsu under various product designations and from Toshiba Silicone Co., Ltd., worldwide, and in the United States from General Electric Co., and are marketed under the trade name Tospearl.

5 Particulate, spherical materials comprising acryl resins such as EPOSTAR manufactured by Nippon Shokubai Co., Ltd., are also contemplated. Other commercial sources of similar suitable materials are also known to exist. Especially preferred are the spherical particulates ranging in size
10 from 2 to 3 μ . By non-migratory, it is meant that these particulates do not change location throughout the layers of the film in the manner of the migratory slip agents, e.g., polydialkylsiloxane or fatty amides. The amount employed typically ranges from 0.1% to 0.4% by weight, more
15 specifically 0.15% to 0.3% by weight, based upon the entire weight of the skin layer resin.

Preferred for use in forming lower skin layer (c) are metallizable polymeric materials. Typical examples of such materials are those selected from the group consisting of
20 ethylene homopolymers such as linear low density polyethylene (LLDPE), low density polyethylene (LDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE) or blends thereof. Other contemplated metallizable resins which might not require the non-migratory slip agent
25 for metal adhesion include ethylene-vinyl alcohol copolymer (EVOH), ethylene-vinyl acetate copolymer (EVA) and polypropylene homopolymer. High density polyethylene is a particularly preferred polymeric material for forming this skin layer. In general, the density ranges from between 0.94 to
30 0.96 g/cm³ and over. This skin layer is formed without adding the non-migratory particulate which is included in the formulation of skin layer (a). Thus, skin layer (c) is considered to be free of the non-migratory particulate used in skin layer (a). This does not however, exclude the
35 incidental presence of the non-migratory particulate which might occur upon subsequent handling of the finished film,

for example upon winding the film onto a roll, whereby non-migratory particulates from skin layer (a) might be sloughed onto the external surface of or imbedded into skin layer (c). In one embodiment of the invention the skin layer (c) consists essentially of high density polyethylene.

Either or both layers (a) and (c) can also contain pigments, fillers, stabilizers, light protective agents or other suitable modifying ingredients if desired. Further, skin layers (a) and/or (c) can optionally contain a minor amount of an additional antiblock material, such as silica, clays, talc, glass, and the like. These antiblock materials can be used alone, or different sizes and shapes can be blended to optimize machinability. The major proportion of these particles, for example, anywhere from more than half to as high as 90 wt.% or more, will be of such a size that a significant portion of their surface area, will extend beyond the exposed surface of such skin layer.

Core layer (b) can contain anti-static agents, e.g., cocoamine or N,N bis(2-hydroxyethyl) sterylamine. Suitable amines include mono-, di, or tertiary amines.

Core layer (b) will usually represent from 70 to 95% of the thickness of the overall film laminate or an even higher percentage thereof. Typically, upper skin layer (a) and lower skin layer (c) are coextensively applied to each major surface of core layer (b), usually by being coextruded directly thereon.

In any event, in forming the three layer structure layers (a), (b) and (c) can be coextruded from a conventional extruder through a flat sheet die, the melt streams being combined in an adapter prior to being extruded from the die. Each of the skin layers (a) and (c) can comprise, for example, approximately 6.0% of the total thickness of the laminate. After leaving the die orifice, the laminate structure is chilled and the quenched sheet is then heated and stretched, e.g., five to eight times in the

machine direction (MD) and then subsequently, for example, eight to twelve times in the transverse direction (TD). The edges of the film can be trimmed. The film laminate is then, usually, wound on a reel.

5 As a result of the biaxial orientation of the film structure herein, several physical properties of the composite layers, such as flex-crack resistance, Elmendorff tear strength, elongation, tensile strength, impact strength and cold strength properties are improved.

10 The overall thickness of the laminate is not critical and advantageously can range from 5 microns to 60 microns.

When an opaque label or film structure is desired, the core layer of the film structure of the present invention may be formed in accordance with U.S. Patent No. 4,377,616.

15 Where opacifying agents are desired, they may be incorporated in the core composition of this invention, in a proportion of up to 10%, preferably at least 1%, by weight. Suitable conventional opacifying agents can be added to the melt mixture of the core polymer before
20 extrusion thereof into a film. Opacifying compounds are generally well known in this area. They may be exemplified by iron oxides, carbon black, aluminum, aluminum oxide, titanium dioxide, and talc.

25 The processability and machinability of the film may be further enhanced by the inclusion in the polymeric material used to form one or both skin layers of a small percentage of finely subdivided inorganic material. Such inorganic material not only can impart antiblock characteristics to the multi-layer film structure of the present invention,
30 but also can further reduce the coefficient of friction of the resultant film.

35 Contemplated finely divided inorganic materials, referred to above may be exemplified by syloid, a synthetic amorphous silica gel, having a composition of 99.7% SiO_2 ; diatomaceous earth having a composition of, for example, 92% SiO_2 , 3.3% Al_2O_3 , and 1.2% Fe_2O_3 which has an average

particle size of 5.5 microns, which particles are porous and irregularly shaped; dehydrated kaolinite (Kaopolite SF) having a composition of 55% SiO_2 , 44% Al_2O_3 and 0.14% Fe_2O_3 , which has an average particle size of 0.7 microns, and which particles are thin flat platelets; and synthetic, precipitated silicates, for example Sipernat 44, a material having a composition of 42% SiO_2 , 36% Al_2O_3 , and 22% Na_2O .

The polyolefin blends used to coextrude the multi-layer high opacity film structures contemplated herein are suitably formed by employing commercially available intensive mixers, such as those of the Bolling or Banbury type.

The exposed surface of skin layer (c) is metallized. This occurs by application of a thin layer of metal. Metal deposition techniques are well known in the art. Typically, the metal layer is applied to an optical density of 1.5 to 5.0, specifically 2.1 to 5.0. Usually vacuum deposition is the method of choice. While aluminum is a contemplated metal, other metals, e.g. zinc, gold, silver, etc. which are capable of being vacuum deposited to the surface of the film can also be employed.

Typically, prior to metallization, the surface of skin layer (c) is treated to improve metal adhesion by corona or flame treatment.

The resulting metallized film has low water vapor transmission rate characteristics and low oxygen transmission rate characteristics. These improved physical properties make the film ideally suited for packaging food products, even those comprising liquids.

In one aspect of the invention, an important feature is the ratio of the size of the particulate cross linked hydrocarbyl-substituted polysiloxane and the thickness of the skin layer. The typical ratio, in terms of particulate to skin thickness is from 1.25 to 2.5, specifically from 1.5 to 2.00. When the ratio of particulate to skin thickness is above 2.5, the barrier properties of the film deteriorate. When the ratio is lower than 1.5 machin-

ability deteriorates.

EXAMPLES

The following specific examples demonstrate particular aspects of the present invention. Unless indicated to be
5 on some other basis, all parts and percentages are by weight. Particulate sizes are reported by the manufacturers as being determined by measuring the diameter of the particles by scanning electron micrograph.

Coefficient of friction values referred to herein are
10 determined according to the procedure of ASTM D-1894-78, using TMI equipment (without delay). Haze and gloss values referred to herein are determined according to the procedures of ASTM D-1003-61 and D-2457-70, respectively.

Minimum seal temperature is determined using a Wrap-
15 Aide Crimp Sealer Model J or K. The crimp sealer is set to a dial pressure of 20, dwell time of 0.75 seconds and starting temperature of 93°C. A film specimen is prepared so that when two surfaces are placed together the resulting film is approximately 6.35 cm in the transverse direction
20 by 7.62 cm in the machine direction. The specimen is then inserted squarely, smoothly and flatly into the crimp sealer jaws so that a small amount protrudes beyond the back end of the jaws. The transverse direction of the film is parallel to the sealer jaws.

25 The jaws are closed and immediately after the sealing bar rises the specimen is removed from the jaws of the sealer. A JDC-type cutter is used to cut the film into a one inch strip. The amount of force needed to separate the seal is determined on an Alfred-Suter crimp seal strength
30 testing unit. The amount of force need to pull the seal apart is recorded in N/m. In order to determine the minimum temperature required to form a seal requiring 77.03 N/m peel force, the crimp seals are formed at temperatures raised by 2.8 degree increments until one temperature
35 yields a seal value of less then 77.03 N/m and the next

temperature yields a seal value of greater than or equal to 77.03 N/m.

A chart method (using an established chart) for a 77.03 N/m minimum seal temperature (MST) is used or a calculation is used. However, in the examples, the chart method was used. In the calculation method the following equation is employed:

$$[(77.03 \text{ N/m} - V_1) + (V_2 - V_1)] \times (2.8) + T_1 = \text{MST in } ^\circ\text{C};$$

where

- 10 V_1 = seal value obtained prior to achieving 77.03 N/m
- V_2 = seal value obtained subsequent to achieving 77.03 N/m
- 2.8 = 2.8 degree C increment in seal temperature
- T_1 = temperature prior to achieving 77.03 N/m.

In Examples 1 and 2, a coextruded biaxially oriented film structure is produced in which the first skin layer contains two different loadings of non-migratory slip agent in a ratio of particulate size in terms of mean particle diameter to skin thickness of 1.6.

Example 1

- 20 A core layer of polypropylene (sold by Himont under the product designation PH-384) is coextruded with an ethylene-propylene copolymer sealant layer (sold by Fina under the product designation EOD-94-21) containing 1500 ppm of (0.15% by weight) non-migratory particulate cross linked
- 25 hydrocarbyl-substituted polysiloxane slip agent (sold by Shin Etsu under the product designation KMP-590). The average diameter of the particulates is 2.5 μ . On the other side of the core, a high density polyethylene metallizable skin layer (sold by Exxon under the product
- 30 designation HX0353.67) is coextruded. The film is oriented 5 times in the machine direction and 8 times in the transverse direction. The final film has a thickness of about 17.78 microns. The seal skin layer thickness is 1.5 μ while the high density polyethylene skin thickness is
- 35 0.5 μ .

Example 2

A film identical to the film of Example 1 is produced except that the amount of non-migratory particulate cross linked hydrocarbyl substituted polysiloxane is 3000 ppm (0.3% by weight). The performance of the films of Examples 1 and 2 is reported in Table 1.

Table 1				
Additive Loading (ppm)	Minimum Seal Temperature (°C)	Coefficient of Friction (constant velocity)	% Haze	% Gloss
Example 1 1500	96.7	0.52	1.85	94.4
Example 2 3000	98.3	0.46	2.55	90.5

Examples 3-4

In these examples two film samples are made as described in Example 1 except that the particulate is 4-5 μ average diameter (sold by Shin Etsu under the product designation X-52-1186). The ratio of particle size to skin thickness is from 2.63 to 3.29.

In Example 3 the particulate loading is 1500 (0.15 wt.%).

In Example 4 the particulate loading is 3000 (0.30 wt.%).

The performance of these films is reported in Table 2.

Table 2				
Additive Loading (ppm)	Minimum Seal Temperature (°C)	Coefficient of Friction (constant velocity)	% Haze	% Gloss
Example 3 1500	98.9	0.43	1.85	91.3
Example 4 3000	100.6	0.36	2.55	89.8

Examples 5-6

In these examples two films are prepared as described in Example 1 except that the seal layer is an ethylene-propylene-butene-1 terpolymer. In Example 5, the seal layer contains 3000 ppm (0.3 wt.%) of the non-migratory particulate cross linked hydrocarbyl-substituted polysiloxane having an average diameter of 2.5 μ (sold by Shin Etsu under product designation KMP-590). As in Examples 1 to 2, the ratio of particle size to skin thickness is 1.6. In Example 6, the seal layer contains 3000 ppm of similar non-migratory particulates having an average diameter of 4-5 μ (sold by Shin Etsu under the product designation X-52-1186). As in Examples 3 to 4, the ratio of particle size to skin thickness is 2.63 to 3.29. The performance of the films is reported in Table 3.

Table 3				
Particulate Average Diameter (microns)	Minimum Seal Temperature (°C)	Coefficient of Friction (constant velocity)	% Haze	% Gloss
Example 5 2.5	98.3	0.48	2.00	90.3
Example 6 4-5	99.4	0.36	2.10	90.8

Examples 7-10

In these Examples a film similar to that described in Example 1 is produced except that a 4 micron average diameter non-migratory particulate cross linked

- 5 hydrocarbyl-substituted polysiloxane antiblock is added (sold by GE under the product designation Tospearl 145). The ratio of particle size to skin thickness is 2.63.

In Example 7, 1500 ppm (0.15 wt.%) of Tospearl 145 is added to the copolymer sealant layer.

- 10 In Example 8, 3000 ppm (0.3 wt.%) of the Tospearl 145 is added to the copolymer sealant layer.

- In Examples 9 and 10 the sealant layer is an ethylene-propylene-butene-1 terpolymer (sold by Montell under the product designation KT-225P). The Tospearl 145 is added to
15 a loading of 1500 ppm (0.15 wt.%) in Example 9 and 3000 ppm (0.3 wt.%) in Example 10.

The performance of the films of these examples is reported in Table 4.

Table 4				
20 Example	Minimum Seal Temperature (°C)	Coefficient of Friction (constant velocity)	% Haze	% Gloss
7	102.2	0.44	1.40	92.1
8	102.2	0.37	1.70	91.2
9	99.4	0.40	1.45	92.3
10	99.4	0.32	1.75	91.8

- 25 It can be seen from the results reported in the foregoing examples that the film products of this invention demonstrate acceptable seal temperatures, excellent machinability, low haze and high gloss.

Examples 11-12

In these examples the high density polyethylene skin layer of the films of Examples 1 and 3 is metallized by flame treating the surface and vacuum deposition of aluminum to an optical density of 2.3. Samples of the finished film of each example are unwound from the collection roll and subjected to barrier tests. The water vapor transmission rate (WVTR) of the film of example 1 is 0.155 grams/m²/24 hours at 100°F. The oxygen transmission rate of this film is 26.3 cc/m²/24 hours at 21°C and 0% relative humidity.

The oxygen barrier property of the metallized film of Example 3 is found to be 80.44 cc/m²/24 hours at 21°C and 0% relative humidity. Because of the poor oxygen barrier property, the WVTR is not tested.

WHAT IS CLAIMED IS:

1. A metallized film structure comprising a first outer skin layer (a), having an external surface which is sealable, comprising a propylene co- or terpolymer and a non-migratory particulate cross linked hydrocarbyl substituted polysiloxane, on one side of a core olefinic polymer layer (b), and on an opposite side of the core layer (b), a second outer skin layer (c) which is an ethylene homopolymer which is free of the particulate cross linked hydrocarbyl substituted polysiloxane of the first skin layer, the external surface of the second skin layer having a metal deposited thereon.
2. The metallized film structure of claim 1 in which the particulate cross linked hydrocarbyl-substituted polysiloxane of layer (a) is a cross linked polymonosiloxane.
3. The metallized film structure of claim 2 in which the particulate cross linked non-meltable polymonoalkyl-siloxane is characterized as having an average particle diameter of 0.5 to 20 microns.
4. The metallized film structure of claim 1 in which the propylene co- or terpolymer of skin layer (a) is selected from the group consisting of ethylene-propylene copolymers and ethylene-propylene-butene-1 terpolymers.
5. The metallized film structure of claim 4 in which the second outer skin layer (c) is medium or high density polyethylene.
6. The metallized film structure of claim 5 in which the olefinic polymer of the core layer is polypropylene.



7. The metallized film structure of claim 5 in which at least one outer surface thereof is treated by flame or corona treatment.

5 8. The metallized film structure as described in claim 1 in which the ratio of particle size to thickness of the (a) skin layer ranges from 1.25 to 2.5.

10 9. The metallized film structure as described in claim 1 in which either the outer skin layer (a) or the outer skin layer (b) or both contain a finely divided inorganic particle which imparts antiblock characteristics.

10. The metallized film structure as defined in claim 9 in which the inorganic material is silica.

