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(54) Title: METALLIZED FILMS AND METHODS OF MAKING METALLIZED FILMS

(57) Abstract: Disclosed is a metal oxide coated film and the process for producing the metallized film comprising providing a film having two surfaces, at least one of which comprises a high surface energy polymer, wherein the high surface energy polymer has a surface energy (ASTM D2578) of at least 30 dynes/cm, a Young's Modulus (ASTM D790) of at least 1500 MPa, and a melting point (ASTM D3418) of at least 130°C; imparting a first oxidizing plasma to the high surface energy polymer surface of the film; depositing a layer of metal oxide on the oxidized high surface energy polymer surface to produce a metal oxide surface; optionally, imparting a second oxidizing plasma to the metal oxide layer; and isolating the metallized film.



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METALLIZED FILMS AND METHODS OF MAKING METALLIZED FILMS**CROSS-REFERENCE TO RELATED APPLICATION**

[0001] This application claims the benefit of and priority to USSN 61/613,595, filed
5 March 21, 2012 which is incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to biaxially oriented metallized films, and in particular, methods to coat a film with a metal oxide coating.

BACKGROUND

10 [0003] Polymeric film structures are used in many commercial applications. One particularly important application is the food packaging industry. Film structures employed in the food packaging industry are chosen and/or designed to provide characteristics necessary for proper food containment. Such characteristics include water vapor barrier properties, oxygen and gas barrier properties, and flavor and aroma barrier properties. One
15 commonly employed structure includes a flexible and durable multilayer polymeric film substrate that provides the film structure with structural integrity and water vapor barrier properties, and at least one coating adhered thereto that provides the film structure with oxygen, gas barrier, and flavor aroma barrier properties.

[0004] One or both of the outer exposed surfaces of the film may be surface-treated to
20 increase the surface energy of the film to render the film receptive to metallization, coatings, printing inks, and/or lamination, for example, as in US 4,345,005. The surface treatment can be carried out according to one of the methods known in the art, including, but not limited to, corona discharge, flame treatment, plasma treatment, chemical treatment, or treatment by means of a high power flame. Such treatments are described in, for example, US
25 2011/0318589 with regard to treating a metallizable film layer, namely, a high surface energy polymer such as ethylene vinyl alcohol copolymer (EvOH).

[0005] While it is known to metallize films to improve their oxygen and water impermeability, it would be desirable to have the option to impart such a barrier and also have a transparent film. This can be done by applying metal oxide layers, such as in US
30 5,688,556; US 5,792,550; and US 5,981,079. Such metal oxide barriers allow for transparency, if desired, while maintaining lower oxygen and water transmission. However, given the thin, brittle nature of such metal oxide film coating, there are still problems with maintaining the oxygen and water barriers when the films are flexed and stretched. What is

needed are stronger, more durable films with metal oxide barrier coatings. The inventor has provided such here. Other publications of interest include a pamphlet from Bobst Group, "Vacuum deposited AlOx clear barrier coatings for flexible packaging" (October 11, 2011). Also, US 8,043,674; US 7,473,439; US 6,399,159; US 6,472,081; US 6,623,866; US 5 6,723,431; US 6,773,818; US 2008/0318036, and US 2011/0318589.

SUMMARY

[0006] Disclosed herein is a transparent metallized film having a M/A/B/C/D structure comprising a core layer (C) comprising (or consisting essentially of or consisting of) polypropylene, the layer having a first and second side; an adhesive layer (B) on the first side 10 of the core layer; a high surface energy polymer layer (A) adhered to the adhesive layer, wherein the high surface energy polymer has a surface energy (ASTM D2578) of at least 30 dynes/cm or 32 dynes/cm, and a Modulus (ASTM D790) of at least 1500 MPa or 1600 MPa or 2000 MPa and a melting point (ASTM D3418) of at least 130°C or 135°C or 140°C; a metal oxide layer (M) on the high surface energy polymer layer; a skin layer (D) on the 15 second side of the core layer; wherein the metallized film has a total thickness within the range of from 10 µm or 12 µm to 20 µm or 26 µm or 30 µm; and an optical density of less than 0.5 or 0.2 or 0.1 or 0.05 or 0.04 or 0.03 O.D.

[0007] Also disclosed is a process for producing a transparent metallized film comprising providing a film having two surfaces, at least one of which comprises a high surface energy 20 polymer, wherein the high surface energy polymer has a surface energy (ASTM D2578) of at least 30 dynes/cm or 32 dynes/cm, and a Young's Modulus (ASTM D790) of at least 1500 MPa or 1600 MPa or 2000 MPa and a melting point (ASTM D3418) of at least 130°C or 135°C or 140°C; imparting a first oxidizing plasma to the high surface energy polymer surface of the film; depositing a layer of metal oxide on the oxidized high surface energy 25 polymer surface to produce a metal oxide surface; optionally, imparting a second oxidizing plasma to the metal oxide layer; and isolating the metallized film.

[0008] The various descriptive elements and numerical ranges disclosed herein for the metallized film or method of making the metallized film can be combined with other descriptive elements and numerical ranges to describe the invention(s); further, for a given 30 element, any upper numerical limit can be combined with any lower numerical limit described herein.

DETAILED DESCRIPTION

[0009] The present invention is directed to a metal oxide coated film (or “metallized film”), and process of making that metal oxide coated film, that is useful in label and/or packaging applications where low oxygen and water permeability is desirable. The film may be transparent or colored, preferably white. Most desirably, the metallized film is transparent. The invention is achieved at least in part by a pre-metallization and optional post-metallization treatment of a polymer film having a high surface energy polymer surface. Preferably, the high surface energy polymer is both pre- and post-metallization treated. One desirable method of treating the surface of the high energy polymer is plasma treatment, and thus the method is often referred to as “pre-plasma” treatment and “post-plasma” treatment. Any equipment suitable for isolating the film to be metallized, holding an adequate vacuum, vaporizing a desirable metal, and imparting the oxidizing treatments may be used. Most preferable metallizing conditions are described further herein.

[0010] Low energy plastics, such as polypropylene (PP), polyethylene (PE) and Teflon™ (PTFE) are essentially “non-stick” plastics. Their molecular structure inhibits the adhesion and printing processes - this molecular structure is basically inert or inactive - these polymers are said to have a low surface energy. The surface energy or the wettability of a particular substrate is measured in dynes/cm (or ergs/cm²) and, when tested, untreated PP and PE will have a low surface energy (usually 30 to 32 dynes/cm). The most common method of determining the surface energy is to measure the contact angle of a water droplet on the substrate surface. The contact angle between the solid and the fluid is the angle measured within the fluid, between the solid surface and the tangent plane to the liquid surface at the point of intersection. A contact angle of greater than 90° indicates that the fluid (which is ink or adhesive in this case) has not wet the surface. Conversely, an angle of less than 90° means that the fluid has wet the surface - if the angle approaches zero then the surface is completely wetted by the fluid.

[0011] Use of a corona, plasma, flame, or other surface treatment will raise the surface energy level to values in excess of 42 dynes/cm. The inventor has found that starting with a high surface energy polymer will further enhance this effect. Ideally, the surface energy of the plastic should be 7 to 10 dynes/cm higher than the surface tension of the substance (solid or liquid) that will bind to the surface. For example, a printing ink having a surface tension of 30 dynes/cm would not adequately wet or bond to a material having a surface energy less than 37 to 40 dynes/cm.

[0012] A “plasma” is a mixture of free electrons, ions, radicals, and molecular fragments created when energy, such as electricity or microwaves, is applied to a gas. The inventor has found that treating polymer surfaces with plasma improves bondability in several ways. It removes grease and other organic contaminants that inhibit adhesion. It etches the surface of the plastic at a microscopic level, which improves the bond’s mechanical strength. And, most importantly, plasma chemically activates the surface of the plastic, making it more wettable and more likely to react with an adhesive. The inventor has found that a desirable sequence of such treatments on particular high surface energy polymer layers on a film will enhance the overall performance of the film.

[0013] The invention described herein includes a process for producing a colored or transparent, preferably transparent, metallized film. The process includes first providing a film having two surfaces, at least one of which comprises a high surface energy polymer, wherein the high surface energy polymer has a surface energy (ASTM D2578) of at least 30 dynes/cm or 32 dynes/cm, a Young’s Modulus (ASTM D790) of at least 1500 MPa or 1600 MPa or 2000 MPa, and a melting point (ASTM D3418) of at least 130°C or 135°C or 140°C. The film may have any number of layers, but preferably is a 4-layer film wherein the high surface energy polymer layer is exposed on one face and adhered to a core film layer on its other face, with or without an intervening film layer. The pre-plasma step includes imparting a first oxidizing plasma to the high surface energy polymer surface of the film; followed by depositing a layer of metal oxide on the oxidized high surface energy polymer surface to produce a metal oxide surface adhered to the exposed surface of the high surface energy polymer. Optionally, but preferably, a post-plasma step involves imparting a second oxidizing plasma to the metal oxide layer. A metallized film is isolating that can be used alone or adhered to some substrate, such as by lamination or overcoating, for further use.

[0014] Desirably, the film useful in the invention is an oriented polypropylene film having at least a core layer comprising polypropylene and a layer comprising (or consisting essentially of, or consisting of) the high surface energy polymer. The metallized film of the invention, which is made from the polypropylene film, is colored or transparent, preferably transparent, and having a M/A/B/C/D structure comprising a core layer (C) comprising (or consisting essentially of or consisting of) polypropylene, the layer having a first and second side; an adhesive layer (B) on the first side of the core layer; the high surface energy polymer layer (A) adhered to the adhesive layer, wherein the high surface energy polymer is as described herein; a metal oxide layer (M) on the high surface energy polymer layer; and a

skin layer (D) on the second side of the core layer. The inventive metallized film has a total thickness within the range of from 10 μm or 12 μm to 20 μm or 26 μm or 30 μm ; and an optical density of less than 0.5 or 0.2 or 0.1 or 0.05 or 0.04 or 0.03 O.D. If colored, the pigment or coloring agent may be an “additive” as described further below in any one or
5 more of the film layers. Preferably, additives that impart color (e.g., titanium dioxide) and/or cause cavitation (e.g., calcium carbonate) are absent from all layers of the metallized film.

[0015] When stating that the film or film layer “consists essentially of” the named components or layers, what is meant is that no other major components or layers are present that influence the claimed properties; preferably, “consisting essentially of” means that one or
10 more additives, if present, are present to no more than 5 wt% or 3 wt% or 1 wt% of the film or film layer.

Description of the polypropylene film.

[0016] The “polypropylene” of the core (C) layer of the film to be metallized is a homopolymer or copolymer comprising from 60 wt% or 70 wt% or 80 wt% or 85 wt% or 90
15 wt% or 95 wt% or 98 wt% or 99 wt% to 100 wt% propylene-derived units (and comprising within the range of from 0 wt% or 1 wt% or 5 wt% to 10 wt% or 15 wt% or 20 wt% or 30 wt% or 40 wt% C2 and/or C4 to C10 α -olefin derived units) and can be made by any desirable process using any desirable catalyst as is known in the art, such as a Ziegler-Natta catalyst, a metallocene catalyst, or other single-site catalyst, using solution, slurry, high
20 pressure, or gas phase processes. Polypropylene copolymers are useful polymers in certain embodiments, especially copolymers of propylene with ethylene and/or butene, and comprise propylene-derived units within the range of from 70 wt% or 80 wt% to 95 wt% or 98 wt% by weight of the polypropylene. In any case, useful polypropylenes have a melting point (ASTM D3418) of at least 125°C or 130°C or 140°C or 150°C or 160°C, or within a range of
25 from 125°C or 130°C to 140°C or 150°C or 160°C. A “highly crystalline” polypropylene is useful in certain embodiments, and is typically isotactic, and comprises 100 wt% propylene-derived units (propylene homopolymer), and has a relatively high melting point of from greater than (greater than or equal to) 140°C or 145°C or 150°C or 155°C or 160°C or 165°C.

[0017] The term “crystalline,” as used herein, characterizes those polymers which possess
30 high degrees of inter- and intra-molecular order. Preferably, the polypropylene has a heat of fusion (Hf) greater than 60 J/g or 70 J/g or 80 J/g, as determined by DSC analysis. The heat of fusion is dependent on the composition of the polypropylene; the thermal energy for the highest order of polypropylene is estimated at 189 J/g, that is, 100% crystallinity is equal to a

heat of fusion of 189 J/g. A polypropylene homopolymer will have a higher heat of fusion than a copolymer or blend of homopolymer and copolymer. Also, the polypropylenes useful herein may have a glass transition temperature (ISO 11357-1, T_g) preferably between -20°C or -10°C or 0°C to 10°C or 20°C or 40°C or 50°C. Preferably, the polypropylenes have a
5 Vicat softening temperature (ISO 306, or ASTM D 1525) of greater than 120°C or 110°C or 105°C or 100°C, or within a range of from 100°C or 105°C to 110°C or 120°C or 140°C or 150°C, or a particular range of from 110°C or 120°C to 150°C.

[0018] Preferably, the polypropylene has a melt flow rate (“MFR”, 230°C, 2.16 kg, ASTM D1238) within the range of from 0.1 g/10 min or 0.5 g/10 min or 1 g/10 min to 4 g/10
10 min or 6 g/10 min or 8 g/10 min or 10 g/10 min or 12 g/10 min or 16 g/10 min or 20 g/10 min. Also, the polypropylene may have a molecular weight distribution (determined by GPC) of from 1.5 or 2.0 or 2.5 to 3.0 or 3.5 or 4.0 or 5.0 or 6.0 or 8.0, in certain embodiments. Examples of commercially available propylene polymers include, but are not limited to, Total 3371 (Total Petrochemicals Company), or PP4712 (ExxonMobil Chemical
15 Company). An example of a suitable commercially available high crystallinity polypropylene (HCPP) is Total Polypropylene 3270, available from Total Petrochemicals.

[0019] The film used to make the metallized film can be made by any suitable method known, and is preferably made by co-extruding the three or four layers together in the desired compositions and thicknesses. In certain embodiments, the films (or labels) herein may also
20 be characterized in certain embodiments as being biaxially oriented. Examples of methods of making the films useful for metallizing include a tenterd or blown process, LISIM™, and others. Further, the working conditions, temperature settings, lines speeds, etc. will vary depending on the type and the size of the equipment used. Nonetheless, described generally herein is one method of making the films useful for metallizing described throughout this
25 specification. In a particular embodiment, the films are formed and biaxially oriented using the “tenterd” method. In the tenterd process, line speeds of greater than 100 m/min to 400 m/min or more, and outputs of greater than 2000 kg/hr to 4000 kg/hr or more are achievable. In the tenter process, the various materials that make up the film layers are melt blended and coextruded, such as through a 3 or 4-layer die head, into the desired film structure.
30 Preferably, the A/B/C/D layers are all coextruded polymer compositions to form the “film”. The formed, oriented “film” can then be metallized to form the “metallized” or metal oxide coated film.

[0020] The so called “adhesive” (B) layer can be made by any desirable polymer composition known to promote the adhesion of a relatively polar polymer (such as the high surface energy polymer) to the polypropylene core. Suitable polymers include polyolefins such as polyethylene, polypropylene, polybutylene, and copolymers of ethylene-propylene and ethylene-propylene-butylene. Also suitable as adhesive layers are acid-modified versions of these polymers such as maleic anhydride modified polymers. The Admer™ series of polymers (Mitsui) are suitable for adhesive layers of the film.

[0021] The so called “skin” layer (D) is preferably a polyolefin such as polyethylene, polypropylene, polybutylene, polystyrene, and copolymers of ethylene-propylene and ethylene-propylene-butylene. Particularly, the skin layer may be linear low density polyethylene, low density polyethylene, medium density polyethylene, and high density polyethylene. Propylene-based elastomers may also be used such as copolymers of polypropylene having from 5 wt% to 20 wt% C2 to C8 α -olefin derived units (for example, Vistamaxx™ elastomers available from ExxonMobil Chemical Company, Baytown, Texas), or ethylene-based elastomers having from 10 wt% to 40 wt% C3 to C8 α -olefin derived units may also be useful alone or in combination with polyethylene or polypropylene (for example, Exact™ elastomers available from ExxonMobil Chemical Company, Baytown, Texas).

[0022] The so called “high surface energy polymer” layer (A) is any suitable polymer that can be formed as by lamination or coating into a thin film, characterized as having a surface energy (ASTM D2578) of at least 30 dynes/cm or 32 dynes/cm; or preferably a surface energy within the range of from 30 or 32 to 40 or 45 or 50 or 60 dynes/cm. The high surface energy polymer has a Young’s Modulus (ASTM D790) of at least 1500 MPa or 1600 MPa or 2000 MPa; or preferably a Young’s Modulus within the range of from 1500 MPa to 5000 MPa or 10,000 MPa or 20,000 MPa. The high surface energy polymer also has a melting point (ASTM D3418) of at least 130°C or 135°C or 140°C, or preferably within the range of from 130°C or 140°C to 170°C or 180°C or 190°C. Preferably, the high surface energy polymer is selected from nylon, polyester, ethylene vinyl alcohol copolymer (EvOH), polyethylene terephthalate, polyvinylchloride, acrylate-based polymers, methacrylate-based polymers, polyurethane, polyalkylimine, acid-modified polyolefins (e.g., maleic anhydride grafted), silane-grafted polyolefins, polyetherester-amide block copolymer, and blends of any of these.

[0023] Most preferably, the high surface energy polymer is EvOH having an ethylene content within the range of from 35 mol% or 38 mol% or 42 mol% to 54 mol% or 58 mol%

or 62 mol% or 65 mol%. The EvOH preferably has a melting point (DSC) of less than 170°C or 165°C; or within the range of from 130°C or 140°C to 170°C or 180°C. Also, the EvOH preferably has a crystallization temperature (DSC) of greater than 150°C or 155°C; or within the range of from 120°C or 130°C or 135°C to 145°C or 150°C or 160°C. Also, the EvOH
5 preferably has a melt index (2.16 kg, 210°C) of greater than 12 g/10 min or 13 g/10 min or 13.5 g/10 min; or within a range of from 8 g/10 min or 10 g/10 min or 12 g/10 min to 16 g/10 min or 18 g/10 min or 20 g/10 min or 24 g/10 min.

Details of Metallizing and Oxidation Treatments.

[0024] The polypropylene film having the high surface energy polymer layer adhered
10 thereto can be metallized by any suitable means that results in the inventive metallized films. The metallizing equipment typically comprises at least one large chamber that can be evacuated with little or no vapor from pump oils and is capable of batch metallizing the film. Desirably, the film is placed in the equipment in the form of a roll and is unrolled while it is pre-plasma treated, metallized, then, if desired, post-plasma treated.

[0025] The pre-plasma treatment is preferably carried out using a first oxidizing plasma
15 comprising within the range from 5 wt% or 10 wt% to 30 wt% or 50 wt% oxygen, based on the total weight of gas, the remainder an inert gas (e.g., nitrogen or argon). Preferably, when used, the second oxidizing plasma comprises within the range from 60 wt% or 70 wt% to 85 wt% or 95 wt% or 100 wt% oxygen, based on the total weight of gas, the remainder an inert
20 gas.

[0026] Preferably, the pressure within the metallizing chamber is less than 4 or 2 or 0.5 x
10⁻⁴ mbar with no flow of gas, and maintained to less than 4 or 2 or 0.5 x 10⁻³ mbar with gas
flow during any step (pre-plasma, metallize, post-plasma) of the process. Preferably, the
surface of the high surface energy polymer is oxidized with a gas pressure of less than 4 x 10⁻³
25 mbar; or within the range of from 0.1 x 10⁻³ mbar or 0.5 x 10⁻³ mbar or 1.2 x 10⁻³ mbar to 3
x 10⁻³ or 4 x 10⁻³ mbar of pressure. Preferably, the metal oxide layer is oxidized with a gas
pressure of less than 4 x 10⁻² mbar; or within the range of from 1.0 x 10⁻² mbar or 1.5 x 10⁻²
mbar to 3 x 10⁻² or 4 x 10⁻² mbar of pressure. The pressures will of course vary depending on
the amount of oxygen and/or inert gas placed in the chamber during each step.

[0027] For both pre- and post-oxidation processes, it is desirable to use the highest energy
30 practical that the equipment will allow. Preferably, the oxidizing plasma is generated with a
power within the range of from 4 kW or 5 kW to 8 kW or 10 kW or 14 kW or 20 kW. The
film is preferably unwound from a roll within the vacuum chamber of the metallizer, treated,

and metallized, and then rewound in the metallizer. Preferably, the film is unwound with a tension of from 20 N/m or 30 N/m to 80 N/m or 90 N/m or 100 N/m. Also, preferably, the metallized film is wound with a tension of from 20 N/m or 30 N/m or 40 N/m to 80 N/m or 90 N/m or 100 N/m.

5 **[0028]** The film, once pre-plasma treated, is metallized as is known in the art by vaporizing the desired metal. Desirable metals include aluminum, gold, silver, nickel, silicon, and others known in the art. Preferably, either aluminum, silicon or a mixture thereof is heated to the desired vaporizing temperature and the vapors directed to the face of the film having been pre-oxidized. Oxygen, or oxygen mixed with an inert gas, may be added to the
10 metal vapor during the metallizing process. The resultant metal oxide layer has a thickness within the range of from 1 Å or 5 Å or 10 Å to 40 Å or 50 Å or 70 Å or 100 Å.

[0029] The resultant metallized film preferably has an optical density of less than 0.5 or 0.2 or 0.1 or 0.05 or 0.04 or 0.03 O.D. Further, the metallized film has an oxygen transmission rate, at 0% relative humidity and 23°C of less than 4 or 3 or 2 g/m²·day.
15 Finally, the metallized film has a total thickness within the range of from 10 μm or 12 μm to 20 μm or 26 μm or 30 μm.

[0030] The resultant metallized film can be further processed by any desirable means. Preferably, the inventive metallized film is laminated or coated on the metal oxide face of the film with some substrate. Desirable substrates can include polypropylene, polyethylene,
20 polyethylene terephthalate, polyurethane, nylons, cellulosic materials, and other plastics or thermoplastics or elastomers. The final product is particularly useful for use as labels, especially pressure sensitive labels when an adhesive is present, and also packaging for articles, especially food products. When used as a label, it is desirable to have a skin “D” layer that will accept an adhesive, or another film layer that will accept an adhesive.

25 **Additives.**

[0031] Additives may be present in one or more layers of the metallized films of the invention. Typically, the additives are present, if at all, at a level of from 0.1 wt% or 0.5 wt% to 1 wt% or 2 wt% or 3 wt% or 5 wt%, by weight of the materials in the given layer. In some cases, such as for cavitating or opacifying agents, the amounts can be within the range of
30 from 5 wt% to 10 wt% or 15 wt% or 20 wt% or 30 wt%, by weight of the given layer. Examples of additives include, but are not limited to, opacifying agents, colorants (e.g., dyes, pigments), cavitating agents, slip agents, antioxidants, anti-fog agents, anti-static agents, anti-block agents, fillers, moisture barrier additives, gas barrier additives, and combinations

thereof. Such additives may be used in effective amounts, which vary depending upon the application and the property desired.

[0032] Examples of suitable opacifying agents, or colorants include iron oxide, carbon black, aluminum, titanium dioxide (TiO₂), calcium carbonate (CaCO₃), polybutylene terephthalate (PBT), talc, beta nucleating agents, common dyes or pigments, and combinations thereof.

[0033] Cavitating or void-initiating additives may include any suitable organic or inorganic material that is incompatible with the polymer material(s) of the layer(s) to which it is added, at the temperature of biaxial orientation, in order to create an opaque film. Examples of suitable void-initiating particles are PBT, nylon, solid or hollow pre-formed glass spheres, metal beads or spheres, ceramic spheres, calcium carbonate, talc, chalk, or combinations thereof. The average diameter of the void-initiating particles typically may be within the range of from 0.1 μm to 2 μm or 3 μm or 5 μm or 8 μm or 10 μm. Cavitation may also be introduced by beta-cavitation, which includes creating beta-form crystals of polypropylene and converting at least some of the beta-crystals to alpha-form polypropylene crystals and creating a small void remaining after the conversion. Preferred beta-cavitated embodiments of the core layer may also comprise a beta-crystalline nucleating agent. Substantially any beta-crystalline nucleating agent ("beta nucleating agent" or "beta nucleator") may be used.

[0034] Slip agents may include higher aliphatic acid amides, higher aliphatic acid esters, waxes, silicone oils, and metal soaps. Such slip agents may be used in amounts ranging from about 0.1 wt% to about 2 wt%, based on the total weight of the layer to which it is added. An example of a slip additive that may be useful is erucamide.

[0035] Non-migratory slip agents, used in one or more skin layers of the multi-layer films, may include polymethyl methacrylate (PMMA). The non-migratory slip agent may have a mean particle size in the range of from about 0.5 μm to about 8 μm, or about 1 μm to about 5 μm, or about 2 μm to about 4 μm, depending upon layer thickness and desired slip properties. Alternatively, the size of the particles in the non-migratory slip agent, such as PMMA, may be greater than about 20% of the thickness of the skin layer containing the slip agent, or greater than about 40% of the thickness of the skin layer, or greater than about 50% of the thickness of the skin layer. The size of the particles of such non-migratory slip agents may also be at least about 10% greater than the thickness of the skin layer, or at least about 20% greater than the thickness of the skin layer, or at least about 40% greater than the

thickness of the skin layer. Generally, spherical, particulate non-migratory slip agents are contemplated, including PMMA resins, such as Epostar™ (commercially available from Nippon Shokubai Co., Ltd.). Other commercial sources of suitable materials are also known to exist. “Non-migratory” means that these particulates generally do not change location throughout the layers of the film in the manner of migratory slip agents. A conventional polydialkyl siloxane, such as silicone oil or gum additive having a viscosity within the range of from 10,000 or 20,000 or 50,000 to 500,000 or 800,000 or 1,000,000 or 2,000,000 centistokes (25°C), is also contemplated.

[0036] Suitable anti-oxidants may include phenolic anti-oxidants, such as Irganox™ 1010 (Ciba Specialty Chemicals). Such an anti-oxidant is generally used in amounts ranging from about 0.1 wt% to about 2 wt%, based on the total weight of the layer(s) to which it is added.

[0037] Anti-static agents may include alkali metal sulfonates, polyether-modified polydiorganosiloxanes, polyalkylphenylsiloxanes, and tertiary amines. Such anti-static agents may be used in amounts ranging from about 0.05 wt% to about 3 wt%, based upon the total weight of the layer(s).

[0038] Examples of suitable anti-blocking agents may include silica-based products such as Sylobloc™ 44 (Grace Davison Products), PMMA particles such as Epostar (Nippon Shokubai Co., Ltd.), or polysiloxanes such as Tospearl™ (GE Bayer Silicones). Such an anti-blocking agent comprises an effective amount up to about 3000 ppm of the weight of the layer(s) to which it is added.

[0039] Fillers may include finely divided inorganic solid materials, such as silica, fumed silica, diatomaceous earth, calcium carbonate, calcium silicate, aluminum silicate, kaolin, talc, bentonite, clay, wollastonite, and pulp.

[0040] Suitable moisture and gas barrier additives may include effective amounts of low-molecular weight resins, hydrocarbon resins, particularly petroleum resins, styrene resins, cyclopentadiene resins, and terpene resins.

[0041] Optionally, one or more skin layers may be compounded with a wax or coated with a wax-containing coating, for lubricity, in amounts ranging from about 2 wt% to about 15 wt% based on the total weight of the skin layer. Any conventional wax, such as, but not limited to, Carnauba™ wax (commercially available from Michelman Corporation) and Be Square™ wax (commercially available from Baker Hughes Corporation), that is useful in thermoplastic films is contemplated.

[0042] The following are non-limiting examples of the inventive metallized films and the inventive process for making them.

EXAMPLES

[0043] In the tests described herein, an oriented polypropylene film was coated with the aluminum oxide coating as described. The film being tested was a 4-layer film having an A/B/C/D structure, wherein the core "C" layer was a polypropylene homopolymer, the "D" layer a polyethylene skin layer, and an adhesive layer "B" is Admer™ (Mitsui Chemical), which is a maleic anhydride modified polyolefin on the opposing face, and an EvOH layer "A" on the Admer layer. The EvOH is Eval™ G156B or G176B (Kuraray), both with 48 mol% ethylene content and melting point (ISO 11357, DSC) of 157°C and 160°C, respectively, and both have a melt index (2.16 kg, 210°C) of about 15 g/10 min, and both have a Young's Modulus of from 2300 and 1900 MPa, respectively; a fluoropolymer is present with the EvOH used in layer "A" via a masterbatch made by Ampacet and containing 99% Eval G176B + 1% Kynar™ flex 2821. This base film had an optical density of 0.02 O.D. and a total thickness of about 18 µm.

[0044] In comparative films, films with an EvOH layer "A" using Soarnol™ grades from Nippon Gohsei were tested but failed. These Soarnal grades have ethylene contents of from 25 mol% to 40 mol%, melt indices (2.16 kg, 210°C) of from 3-12 g/10 min, and melting point in the range from 170°C to 195°C.

[0045] The metallizer was made by General Vacuum Equipment Ltd (Bobst Group) and performed the metallizing of the film in one step as a batch under vacuum, where the film was unwound, plasma treated, metallized, then plasma treated a second time before the coated film was wound in a metallizing chamber under vacuum, while the optical density of the film could be measured before and after metallizing. The optical density (O.D.) target was 0.5, which in the system, was equivalent to an aluminum wire feed speed of 26 cm/min and 1.6 mm wire diameter with no oxygen flow during metallizing, thus producing only an aluminum coating. However, during the tests aluminum oxide was generated by injecting oxygen into the chamber where the aluminum was heated to about 1400°C to 1500°C to evaporate the metal (evaporation zone) creating reactive aluminum oxide deposition.

[0046] The control loop of the metallizer was based on reading the optical density by optical sensor and controlling the oxygen flow. The set point was 0.13 O.D. Pre-plasma (plasma before coating) was set at 6 kW power and using 500 sccm flow rate of 80% N2 + 20% O2 gas mixture. The process drum temperature was -15°C. The evaporation zone

pressure was at 1.3×10^{-3} mbar when O₂ flow was on. Before starting the evaporation process with O₂ flow off the pressure value was 5.1×10^{-4} mbar. The winding zone pressure was at $2.0 - 2.9 \times 10^{-2}$ mbar and did not change when O₂ flow was on. The line speed of the moving film being unwound then wound was 420 m/min. A gas wedge 2 liter/min was used
5 (a gas wedge is an air flow between the film and the process drum helping in improving heat exchange and in preventing wrinkles and creases over the process drum). The film was unwound with a tension 60 N/m to 80 N/m, and rewound with a tension 50 N/m. The post-plasma treatment was set at 6 kW power. The film was run such that the "A" layer was coated or "metallized", thus forming an M/A/B/C/D structured film, wherein "M" is a metal
10 or metal oxide layer. The aluminum oxide coated film had an optical density of 0.03 O.D. and a total thickness of about 18 μm .

[0047] The resulting oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) measurements (ASTM F1249) of coating the film with aluminum oxide, with various combinations of pre- and post-plasma treatment are presented in Tables 1 and 2. The
15 metal oxide side of the film was facing the water in the WVTR measurements. In Tables 1 and 2, different rolls of films were tested, that being indicated in parenthesis in the far left column. In the Tables, "slit" means that the rolls have been slit (cut) as is known in the art, then tested for OTR and WVTR. Also in the Tables, the terms "West" and "East" refer to the two sides of the film relative to the "Center", as different parts of the film are measured
20 across its surface from one side to another.

[0048] The strength of the aluminum oxide coatings of the invention and their ability to maintain impermeability was tested by adhering or laminating to a substrate and performing flexure tests. The OTR conditions were 73/0 and the WVTR conditions were 100/90. 18 μ EvOH skin of aluminum oxide coated films with pre- and post-plasma were extrusion
25 laminated with BiorTM18LPX-2 (a biaxially oriented polypropylene film) using LDPE ("Extr"); and an 18 μ EvOH skin of aluminum oxide coated with pre- and post-plasma were adhesive laminated with 18LPX-2 using polyurethane ("Adh"). The films are tested by extending 2% and 8%, then measuring OTR and WVTR. The Gelbo flex test is a special test where the sample (the laminated film) is held by the two edges and twisted several times.
30 The Gelbo test is performed using a GFT 392 instrument for 10 or 20 cycles, as indicated. The oxygen and water permeability is then tested, the results of which are in the Tables 3 and 4, below. Three measurements (in different locations on the film) were performed and recorded.

[0049] The Gelbo Flex (ASTM F392 D) tests were performed at 2, 10, and 20 cycles. The instrument was a Gelbo Flex Tester, B&B Motor & Control Corp. No. 92142. Hayssen tests were performed using a Hayssen Ultima II - VFF and S Model 95-16-HR. Flexed WVTR and OTR property comparisons against Hayssen formed packages indicate the Hayssen data is comparable to the Gelbo Flex condition, certainly for WVTR and to some degree for the OTR values. The Hayssen test is where the film goes through a forming collar used to create the tube for vertical packaging. The Hayssen test is aimed to demonstrate the barrier degradation after the film moved through the forming collar by pulling it in the Vertical Form Fin (or Lap) Seal (VFFS) packaging machine.

10

Table 1. Oxygen Transmission Rates for films

Sample	Unslit					Slit				
	1	2	3	4	5	6	7	8	9	10
Treatment:	pre Ar 80% O ₂					pre Ar 80% O ₂				
Measurement (roll number)	20%/post	None	pre-only	post only	pre/post	20%/post	None	pre-only	post only	pre/post
OTR 0% RH (West) (1)	3.253	2.023	1.190	5.258	1.715	1.249	2.647	1.039	2.262	1.423
OTR 0% RH (West) (2)	1.542	2.203	0.889	2.065	1.938	0.897	3.088	1.809	2.696	1.112
OTR 0% RH (Center) (1)	1.387	2.541	2.618	4.523	1.713	1.713	2.280	1.694	3.212	1.708
OTR 0% RH (Center) (2)	1.421	2.400	2.684	3.275	1.592	1.592	2.258	1.138	2.966	1.877
OTR 0% RH (East) (1)	1.587	1.619	1.565	2.088	2.150	2.638	1.892	1.224	2.272	1.421
OTR 0% RH (East) (2)	1.515	1.377	1.498	2.062	1.939	1.485	1.726	0.989	2.102	1.232
OTR 70% RH (West) (1)	-	-	-	-	-	-	-	0.458	1.226	-
OTR 70% RH (West) (2)	-	-	-	-	-	-	-	0.520	0.908	-
OTR 70% RH (Center) (1)	3.110	1.873	0.989	1.035	0.841	1.407	1.506	1.559	1.743	0.809
OTR 70% RH (Center) (2)	2.010	2.489	1.005	1.157	0.865	1.364	1.329	1.507	1.770	0.536
OTR 70% RH (East) (1)	-	1.715	-	-	-	0.835	-	-	-	1.067
OTR 70% RH (East) (2)	-	2.145	-	-	-	0.752	-	-	-	1.232
OTR 50% RH (Center) (1)	-	-	0.871	1.207	0.971	0.437	1.175	0.558	1.566	0.952
OTR 50% RH (Center) (2)	-	-	0.848	1.119	0.985	0.789	1.010	0.624	1.976	0.982

Table 2. Water Vapor Transmission Rates for films and Averages

Sample	Unslit					Slit				
	1	2	3	4	5	6	7	8	9	10
Treatment:	pre Ar 80% O ₂	None	pre- only	post only	pre/post	pre Ar 80% O ₂ 20%/post	None	pre-only	post only	pre/post
Measurement (roll number)										
WVTR 100% RH (West) (3)	-	-	-	-	-	-	-	-	5.77	-
WVTR 100% RH (West) (4)	-	-	-	-	-	-	-	-	5.365	-
WVTR 100% RH (Center) (1)	0.909	1.696	2.303	2.193	1.059	1.345	1.139	1.080	2.396	1.572
WVTR 100% RH (Center) (2)	0.930	1.673	2.845	1.815	1.111	1.401	1.264	1.029	2.377	1.627
WVTR 100% RH (East) (1)	0.965	2.039	2.177	1.338	1.819	0.865	0.851	1.044	1.525	0.984
WVTR 100% RH (East) (2)	1.378	1.901	2.214	1.624	1.434	0.835	0.817	0.734	2.003	1.110
WVTR 90% RH (West) (1)	-	-	-	-	-	-	1.274	-	-	-
WVTR 90% RH (West) (2)	-	-	-	-	-	-	1.288	-	-	-
WVTR 90% RH (Center) (1)	-	-	-	-	-	-	1.520	-	-	-
WVTR 90% RH (Center) (2)	-	-	-	-	-	-	1.402	-	-	-
WVTR 90% RH (East) (1)	-	1.465	-	-	-	-	1.179	-	-	-
WVTR 90% RH (East) (2)	-	2.017	-	-	-	-	1.229	-	-	-
OTR 0% RH average	1.78	2.03	1.74	3.21	1.84	1.60	2.32	1.32	2.59	1.15
1σ	0.72	0.45	0.75	1.40	0.20	0.59	0.50	0.35	0.44	0.31
OTR 70% RH average	2.56	2.06	1.00	1.10	0.85	1.09	1.42	1.01	1.41	0.91
1σ	0.78	0.34	0.01	0.09	0.02	0.34	0.13	0.60	0.42	0.30
WVTR 100% RH average	1.09	1.58	1.93	1.48	1.23	1.13	1.15	0.92	3.67	1.22
1σ	0.19	0.41	0.74	0.49	0.35	0.24	0.27	0.15	1.76	0.30
WVTR 90% RH average	-	1.74	-	-	-	-	1.32	-	-	-
1σ	-	0.39	-	-	-	-	0.12	-	-	-

Table 3. Extension Durability Tests

Area of film	Adh		Extr		Adh, 2% Extr		Extr, 2% Extr		Adh, 8% Extr		Extr, 8% Extr	
	OTR, cc/m ²	WVTR, g/m ²	OTR, cc/m ²	WVTR, g/m ²	OTR, cc/m ²	WVTR, g/m ²	OTR, cc/m ²	WVTR, g/m ²	OTR, cc/m ²	WVTR, g/m ²	OTR, cc/m ²	WVTR, g/m ²
west	2.933	1.079	4.019	1.037	14.274	2.069	6.443	1.037	66.44	2.782	84.213	-
center	2.872	1.009	4.052	1.131	17.762	1.835	5.244	1.049	65.596	2.726	90.555	-
east	2.994	1.148	3.985	0.942	10.785	2.302	7.642	1.025	67.284	2.837	77.871	-

Table 4. Hayssen and Gelbo Durability Tests

Area of film	Adh, Post Hayssen		Extr, Post Hayssen		Adh, Gelbo, 10 Flex		Extr, Gelbo, 10 Flex		Adh, Gelbo, 20 Flex	
	OTR, cc/m ²	WVTR, g/m ²	OTR, cc/m ²	WVTR, g/m ²	OTR, cc/m ²	WVTR, g/m ²	OTR, cc/m ²	WVTR, g/m ²	OTR, cc/m ²	WVTR, g/m ²
west	2.615	0.947	5.494	1.126	10.503	1.161	24.021	1.326	12.434	1.403
center	2.709	0.949	5.797	1.132	10.853	1.147	19.644	1.4	15.198	1.405
east	2.521	0.945	5.192	1.12	10.152	1.175	28.398	1.251	9.669	1.4

[0050] Having described the various aspects of the inventive metallized films and method of making the films, described here in numbered embodiments is:

1. A process for producing a metallized film comprising:
providing a film having two surfaces, at least one of which comprises a high surface
5 energy polymer, wherein the high surface energy polymer has a surface energy (ASTM D2578) of at least 30 dynes/cm or 32 dynes/cm, a Young's Modulus (ASTM D790) of at least 1500 MPa or 1600 MPa or 2000 MPa, and a melting point (ASTM D3418) of at least 130°C or 135°C or 140°C;
imparting a first oxidizing plasma to the high surface energy polymer surface of the
10 film;
depositing a layer of metal oxide on the oxidized high surface energy polymer surface to produce a metal oxide surface;
optionally, imparting a second oxidizing plasma to the metal oxide layer; and
isolating the metallized film.
- 15 2. The process of numbered embodiment 1, wherein the film is an oriented polypropylene film having a core layer comprising polypropylene and a layer comprising (or consisting essentially of, or consisting of) the high surface energy polymer.
3. The process of any one of embodiments 1 or 2, wherein the first oxidizing plasma comprises within the range from 5 wt% or 10 wt% to 30 wt% or 50 wt% oxygen, based on
20 the total weight of gas, the remainder an inert gas.
4. The process of any one of the previous numbered embodiments, wherein the second oxidizing plasma comprises within the range from 60 wt% or 70 wt% to 85 wt% or 95 wt% or 100 wt% oxygen, based on the total weight of gas, the remainder an inert gas.
5. The process of any one of the previous numbered embodiments, wherein the
25 oxidizing plasma is generated with a power within the range of from 4 kW or 5 kW to 8 kW or 10 kW or 14 kW or 20 kW.
6. The process of any one of the previous numbered embodiments, wherein the metallized film has an optical density of less than 0.5 or 0.2 or 0.1 or 0.05 or 0.04 or 0.03 O.D.
- 30 7. The process of any one of the previous numbered embodiments, wherein the film is unwound from a roll within the vacuum chamber with a tension of from 20 N/m or 30 N/m to 80 N/m or 90 N/m or 100 N/m.
8. The process of any one of the previous numbered embodiments, wherein the

metallized film is wound onto a roll within the vacuum chamber with a tension of from 20 N/m or 30 N/m or 40 N/m to 80 N/m or 90 N/m or 100 N/m.

9. The process of any one of the previous numbered embodiments, wherein the metal oxide layer is further oxidized with a gas pressure of less than 4×10^{-2} mbar; or within the range of from 1.0×10^{-2} mbar or 1.5×10^{-2} mbar to 3×10^{-2} or 4×10^{-2} mbar of pressure.

10. The process of any one of the previous numbered embodiments, wherein the surface of the high surface energy polymer is oxidized with a gas pressure of less than 4×10^{-3} mbar; or within the range of from 0.1×10^{-3} mbar or 0.5×10^{-3} mbar or 1.2×10^{-3} mbar to 3×10^{-3} or 4×10^{-3} mbar of pressure.

11. The process of any one of the previous numbered embodiments, wherein the high surface energy polymer is selected from nylon, polyester, ethylene vinyl alcohol copolymer (EvOH), polyethylene terephthalate, polyvinylchloride, acrylate-based polymers, methacrylate-based polymers, polyurethane, polyalkylimine, acid-modified polyolefins, polyetherester-amide block copolymer, and blends of any of these.

12. The process of any one of the previous numbered embodiments, wherein the high surface energy polymer is EvOH having an ethylene content within the range of from 35 mol% or 38 mol% or 42 mol% to 54 mol% or 58 mol% or 62 mol% or 65 mol%.

13. The process of any one of the previous numbered embodiments, wherein the high surface energy polymer is EvOH having a melting point (DSC) of less than 170°C or 165°C; or within the range of from 130°C or 140°C to 170°C or 180°C.

14. The process of any one of the previous numbered embodiments, wherein the high surface energy polymer is EvOH having a crystallization temperature (DSC) of greater than 150°C or 155°C; or within the range of from 120°C or 130°C or 135°C to 145°C or 150°C or 160°C.

15. The process of any one of the previous numbered embodiments, wherein the high surface energy polymer is EvOH having a melt index (2.16 kg, 210°C) of greater than 12 g/10 min or 13 g/10 min or 13.5 g/10 min; or within a range of from 8 g/10 min or 10 g/10 min or 12 g/10 min to 16 g/10 min or 18 g/10 min or 20 g/10 min or 24 g/10 min.

16. The process of any one of the previous numbered embodiments, wherein the metal oxide layer has a thickness within the range of from 1 Å or 5 Å or 10 Å to 40 Å or 50 Å or 70 Å or 100 Å.

17. The process of any one of the previous numbered embodiments, wherein the metal oxide is selected from aluminum oxide, silicon oxide, or a combination thereof.

18. The process of any one of the previous numbered embodiments, wherein the metallized film has an oxygen transmission rate (0% relative humidity and 23°C) of less than 4 or 3 or 2 g/m²·day.
19. The process of any one of the previous numbered embodiments, wherein the metallized film has a total thickness within the range of from 10 μm or 12 μm to 20 μm or 26 μm or 30 μm.
20. The process of any one of the previous numbered embodiments, further comprising adhering (laminating or overcoat) a substrate to the metal oxide surface.
21. The process of any one of the previous numbered embodiments, wherein the metallized film is cut into a label.
22. The process of any one of the previous numbered embodiments, wherein the metallized film is cut into packaging for articles.
23. A metallized film having a M/A/B/C/D structure comprising:
a core layer (C) comprising (or consisting essentially of or consisting of) polypropylene, the layer having a first and second side;
an adhesive layer (B) on the first side of the core layer;
a high surface energy polymer layer (A) adhered to the adhesive layer, wherein the high surface energy polymer has a surface energy (ASTM D2578) of at least 30 dynes/cm or 32 dynes/cm, and a Modulus (ASTM D790) of at least 1500 MPa or 1600 MPa or 2000 MPa and a melting point (ASTM D3418) of at least 130°C or 135°C or 140°C;
a metal oxide layer (M) on the high surface energy polymer layer; and
a skin layer (D) on the second side of the core layer;
wherein the metallized film has a total thickness within the range of from 10 μm or 12 μm to 20 μm or 26 μm or 30 μm; and an optical density of less than 0.5 or 0.2 or 0.1 or 0.05 or 0.04 or 0.03 O.D. when no colorants are present.
24. The film of numbered embodiment 23, wherein the metal oxide layer has a thickness within the range of from 1 Å or 5 Å or 10 Å to 40 Å or 50 Å or 70 Å or 100 Å.
25. The film of any one of numbered embodiments 23 or 24, wherein the metal oxide is selected from aluminum oxide, silicon oxide, or a combination thereof.
26. The film of any one of the previous numbered embodiments 23-25, wherein the high surface energy polymer is selected from nylon, polyester, ethylene vinyl alcohol copolymer (EvOH), polyethylene terephthalate, polyvinylchloride, acrylate-based polymers,

methacrylate-based polymers, polyurethane, polyalkylimine, acid-modified polyolefins, polyetherester-amide block copolymer, and blends of any of these.

27. The film of any one of the previous numbered embodiments 23-26, wherein the high surface energy polymer is EvOH having an ethylene content within the range of from 35
5 mol% or 38 mol% or 42 mol% to 54 mol% or 58 mol% or 62 mol% or 65 mol%.

28. The film of any one of the previous numbered embodiments 23-27, wherein the high surface energy polymer is EvOH having a melting point (DSC) of less than 170°C or 165°C; or within the range of from 130°C or 140°C to 170°C or 180°C.

29. The film of any one of the previous numbered embodiments 23-28, wherein the high
10 surface energy polymer is EvOH having a crystallization temperature (DSC) of greater than 150°C or 155°C; or within the range of from 120°C or 130°C or 135°C to 145°C or 150°C or 160°C.

30. The film of any one of the previous numbered embodiments 23-29, wherein the high surface energy polymer is EvOH having a melt index (2.16 kg, 210°C) of greater than 12
15 g/10 min or 13 g/10 min or 13.5 g/10 min; or within a range of from 8 g/10 min or 10 g/10 min or 12 g/10 min to 16 g/10 min or 18 g/10 min or 20 g/10 min or 24 g/10 min.

31. The film of any one of the previous numbered embodiments 23-30, wherein the metal oxide surface has a thickness within the range of from 1 Å or 5 Å or 10 Å to 40 Å or 50 Å or 70 Å or 100 Å.

20 32. The film of any one of the previous numbered embodiments 23-31, further comprising a substrate bound to the metal oxide layer.

33. A label or packaging formed from the film of any one of the previous numbered embodiments 23-32.

[0051] Also disclosed is the use of the metallized film of any one of the previous
25 numbered embodiments 23-31 for producing a label or packaging. A particular use of the metallized film is as a component of a label, preferably a pressure sensitive label.

CLAIMS

1. A process for producing a metallized film comprising:
providing a film having two surfaces, at least one of which comprises a high surface
energy polymer, wherein the high surface energy polymer has a surface energy
5 (ASTM D2578) of at least 30 dynes/cm, a Young's Modulus (ASTM D790) of
at least 1500 MPa, and a melting point (ASTM D3418) of at least 130°C;
imparting a first oxidizing plasma to the high surface energy polymer surface of the
film;
depositing a layer of metal oxide on the oxidized high surface energy polymer surface
10 to produce a metal oxide surface;
optionally, imparting a second oxidizing plasma to the metal oxide layer; and
isolating the metallized film.
2. The process of claim 1, wherein the film is an oriented polypropylene film having a
15 core layer comprising polypropylene and a layer comprising (or consisting essentially
of, or consisting of) the high surface energy polymer.
3. The process of claim 1, wherein the first oxidizing plasma comprises within the range
from 5 wt% to wt% oxygen, based on the total weight of gas, the remainder an inert
20 gas.
4. The process of claim 1, wherein the second oxidizing plasma comprises within the
range from 60 wt% to 100 wt% oxygen, based on the total weight of gas, the
remainder an inert gas.
25
5. The process of claim 1, wherein the oxidizing plasma is generated with a power
within the range of from 4 kW to 20 kW.
6. The process of claim 1, wherein the metallized film has an optical density of less than
30 0.5 O.D.
7. The process of claim 1, wherein the film is unwound from a roll within the vacuum
chamber with a tension of from 20 N/m to 100 N/m.

8. The process of claim 1, wherein the metallized film is wound onto a roll within the vacuum chamber with a tension of from 20 N/m to 100 N/m.
- 5 9. The process of claim 1, wherein the metal oxide layer is further oxidized with a pressure of less than 4×10^{-2} mbar.
10. The process of claim 1, wherein the surface of the high surface energy polymer is oxidized with a gas pressure of less than 4×10^{-3} mbar.
- 10 11. The process of claim 1, wherein the high surface energy polymer is selected from nylon, polyester, ethylene vinyl alcohol copolymer (EvOH), polyethylene terephthalate, polyvinylchloride, acrylate-based polymers, methacrylate-based polymers, polyurethane, polyalkylimine, acid-modified polyolefins, polyetherester-amide block copolymer, and blends of any of these.
- 15 12. The process of claim 1, wherein the high surface energy polymer is EvOH having an ethylene content within the range of from 35 mol% to 65 mol%.
- 20 13. The process of claim 1, wherein the high surface energy polymer is EvOH having a melting point (DSC) of less than 170°C.
14. The process of claim 1, wherein the high surface energy polymer is EvOH having a crystallization temperature (DSC) of greater than 150°C.
- 25 15. The process of claim 1, wherein the high surface energy polymer is EvOH having a melt index (2.16 kg, 210°C) of greater than 12 g/10 min.
16. The process of claim 1, wherein the metal oxide layer has a thickness within the range of from 1 Å to 100 Å.
- 30 17. The process of claim 1, wherein the metal oxide is selected from aluminum oxide, silicon oxide, or a combination thereof.

18. The process of claim 1, wherein the metallized film has an oxygen transmission rate (0% relative humidity and 23°C) of less than 4 g/m²•day.
- 5 19. The process of claim 1, wherein the metallized film has a total thickness within the range of from 10 μm to 30 μm.
20. The process of claim 1, further comprising adhering (laminating or overcoat) a substrate to the metal oxide surface.
- 10 21. The process of claim 1, wherein the metallized film is cut into a label.
22. The process of claim 1, wherein the metallized film is cut into packaging for articles.
- 15 23. A metallized film having a M/A/B/C/D structure comprising:
a core layer (C) comprising (or consisting essentially of or consisting of)
polypropylene, the layer having a first and second side;
an adhesive layer (B) on the first side of the core layer;
a high surface energy polymer layer (A) adhered to the adhesive layer, wherein the
20 high surface energy polymer has a surface energy (ASTM D2578) of at least
30 dynes/cm, and a Modulus (ASTM D790) of at least 1500 MPa and a
melting point (ASTM D3418) of at least 130°C;
a metal oxide layer (M) on the high surface energy polymer layer; and
a skin layer (D) on the second side of the core layer;
25 wherein the metallized film has a total thickness within the range of from 10 μm to 30
μm; and an optical density of less than 0.5 O.D. when no colorants are present.
24. The film of claim 23, wherein the metal oxide layer has a thickness within the range
of from 1 Å to 100 Å.
- 30 25. The film of claim 23, wherein the metal oxide is selected from aluminum oxide,
silicon oxide, or a combination thereof.

26. The film of claim 23, wherein the high surface energy polymer is selected from nylon, polyester, ethylene vinyl alcohol copolymer (EvOH), polyethylene terephthalate, polyvinylchloride, acrylate-based polymers, methacrylate-based polymers, polyurethane, polyalkylimine, acid-modified polyolefins, polyetherester-amide block copolymer, and blends of any of these.
27. The film of claim 23, wherein the high surface energy polymer is EvOH having an ethylene content within the range of from 35 mol% to 65 mol%.
28. The film of claim 23, wherein the high surface energy polymer is EvOH having a melting point (DSC) of less than 170°C.
29. The film of claim 23, wherein the high surface energy polymer is EvOH having a crystallization temperature (DSC) of greater than 150°C.
30. The film of claim 23, wherein the high surface energy polymer is EvOH having a melt index (2.16 kg, 210°C) of greater than 12 g/10 min.
31. The film of claim 23, wherein the metal oxide surface has a thickness within the range of from 1 Å to 100 Å.
32. The film of claim 23, further comprising a substrate bound to the metal oxide layer.
33. A label or packaging formed from the film of claim 23.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. B32B27/08 C23C14/00 C23C14/08 C23C16/40
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B32B C23C

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 728 622 A1 (MITSUBISHI PLASTICS INC [JP]) 6 December 2006 (2006-12-06) claims 1,14,15 paragraphs [0016], [0019], [0021] -----	1-33
X	EP 1 787 796 A1 (DAINIPPON PRINTING CO LTD [JP]) 23 May 2007 (2007-05-23) claims 1,2,5,6,8 paragraphs [0021], [0028] -----	1-33



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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