

FILM COMPOSITION

The invention relates to a film composition which is capable of being metallized. More specifically, the invention relates to a polymeric film substrate having a polyvinyl alcohol (PVOH) skin layer which is capable of being metallized. The invention also relates to metallized films.

Oriented plastic film, specifically biaxially oriented polypropylene film is widely used for packaging products, particularly foods. No single unmodified polymeric film, however, has the gas and moisture barrier characteristics needed for packaging.

The present invention is directed to a film composition capable of being metallized comprising a polymeric substrate having a surface which is modified by a maleic anhydride modified propylene homopolymer or copolymer, the modified surface of the polymer substrate having a skin layer of polyvinyl alcohol.

The film composite of this invention offers excellent metal adhesion. It is resistant to flavor scalping and protects ink decals. Without primer, the film adheres well to ink and is ink printable. The film also provides excellent flavor/aroma barrier properties, lamination bond strength and optical clarity.

The multilayer film structure of this invention comprises a substrate of polyolefin, typically polypropylene. The preferred polypropylene matrix material has the following characteristics: density of 0.91 g.cc; melting point of 160°C or higher; melt flow rate of 2 to 4.

The polyolefin substrate is modified by a maleic anhydride modified polypropylene. The maleic anhydride modified polypropylene skin layer can be prepared by any process, for example, the process disclosed in U.S. Patent Nos. 3,433,777 and 4,198,327. A simple process for its preparation is described in U.S. 5,153,074. The maleic anhydride modified polypropylene can also be interblended into the substrate, by melt blending it with the substrate polyolefin or it can be coextruded with

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the substrate polymer. A commercially available maleic anhydride modified polypropylene or propylene copolymer has the following physical characteristics: density of 0.90 (ASTM D1505), Vicat softening point of 143°C (ASTM D1525); Shore 5 hardness of 67°C (ASTM 2240); melting point of 160°C (ASTM D2117). The maleic anhydride modified polypropylene acts as a tie layer which adheres the substrate to the PVOH. It is important to use the maleic anhydride modified polypropylene since without it the substrate is incompatible with the PVOH. 10 Maleic anhydride modified polypropylene is sold commercially by a variety of sources, e.g. it is sold under the tradename "ADMER" by Mitsui, "BYNEL" by DuPont, and "PLEXAR" by Quantum. Usually, if extrusion coated, the modified substrate is stretched in the machine direction 4 to 7 times and then flame 15 treated.

A layer of polyvinyl alcohol (PVOH) is applied to the surface of the modified substrate. In instances where the substrate is coextruded with the maleic anhydride modified polypropylene, it is important to apply the PVOH to the modified 20 surface, otherwise, the PVOH will have difficulty adhering to the substrate. The PVOH can be applied in a thin layer by any effective process. The layer can range in thickness from 0.01 mil to 0.20 mil. Three processes of note are 1) coextrusion of a PVOH skin and the modified substrate with the use of a 25 selector plug or multicavity die; 2) extrusion coating the PVOH layer onto the surface of the modified substrate between the machine direction orientation and the transverse direction orientation; 3) co-lamination of a thin film of PVOH onto the surface of the modified polypropylene sheet between the machine 30 direction orientation step and the transverse direction orientation step. Usually, when the PVOH layer is extrusion coated onto the substrate, the film is stretched 5 to 12 times in the transverse direction and flame treated.

For extrusion coating and co-lamination, it is preferable 35 to corona or flame treat the bonding surface of the substrate prior to application of the PVOH.

A heat sealable film can be applied to the substrate on the

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side opposite to the PVOH. This can be accomplished by coextruding a heat sealable polymer, copolymer or trimer, such as ethylene-propylene-butene, onto the substrate.

The PVOH skin is then metallized by deposition of a metal thereon. Any typical process for metallization known in the art can be employed. Typical metals contemplated are aluminum, copper, chromium, magnesium, nickel, zinc, tin, silver, gold, titanium, silicon, bismuth, or any compound containing the foregoing metals or combination thereof. An aluminum coating, which is most typically employed, can be of a thickness which yields an optical density of 1.5 to 3.5. The thickness of the aluminum coating needed to meet this optical density is, typically, from 50 to 1000 angstroms. The PVOH surface adequately adheres to metal. Although we have found that it is advantageous to surface treat, by flame or corona treatment, the PVOH prior to metallization, this is not necessary.

We discovered that extrudable grades of PVOH which can be melt processed avoid the blocking problems which are experienced when PVOH is applied through a solution coating process, as described in EPA 461,772. Since PVOH is melt processed there are no blocking problems and the film can be easily wound into a roll. Also because of the extrusion process, a layer ranging from 0.01 mil to 0.20 mil can be applied, this cannot be accomplished from the solution coating processes disclosed in EPA 461,772 or U.S. 5,192,620 which usually achieve a layer ranging from 0.02 to 0.06 mil. A commercial source of extrudable PVOH is Vinex resin manufactured by Air Products and Chemicals, Inc.

The advantages of using 100% PVOH in multilayer films, as disclosed herein are extensive. Since 100% PVOH is employed, the film is a better oxygen barrier than previous films made with PVOH copolymers or blends. We have also found that the surface properties provided by the PVOH are responsible for superior metal adhesion, ink printing and lamination. The surface tension of PVOH is high. Without flame or corona treatment, the surface tension is about 37 dyne/cm, as compared to the surface tension of polypropylene of 29 dyne/cm. After

surface treatment, the surface tension of PVOH can be greater than 55 dyne/cm. Additionally, since PVOH possesses an extremely high melting and softening point, ranging from higher than 170 °C, the film exhibits no metal fracture during
 5 extrusion lamination using 10 lbs/rm LDPE at 620°F. The following Table 1 presents a comparison between the melting point and metal fracture of multi-layered polypropylene films having skin layers of EVOH, PVOH/EAA and 100% PVOH:

TABLE 1

10 POLYMER	MELTING POINT, °C	METAL FRACTURE
EVOH	158	little-none
PVOH/EAA*	-100	some
PVOH	>170	None
* ethylene acrylic acid		

15 Any grade of PVOH can be employed for the skin layer. In general partially hydrolyzed grades (of about 88% hydrolysis) can be used and even PVOH with 70% or higher hydroxyl content can be used.

20 The heat sealable layer employed herein and applied during coextrusion can be an ethylene propylene (EP) copolymer or an ethylene propylene butene-1 (EPB) terpolymer which, as noted above is, typically, located opposite the PVOH skin layer. The ratio of ethylene to propylene to
 25 butene-1 can be from 0 to 15% ethylene, 70 to 100% propylene and 0 to 15% butene-1; that is, 2% ethylene, 94% propylene and 4% butene-1.

A printable surface which is adhered to the metallized film by an adhesive such as low density polyethylene can be
 30 any polymer such as polyolefin homopolymer, copolymer or terpolymer, polycarbonate or polyester. The characteristic of the printable surface is one with a surface free energy of 34 dynes/cm or higher.

As demonstrated in the following Examples the PVOH in
 35 combination with the metallization and coating with an appropriate lamination film will improve oxygen barrier, moisture barrier and aroma barrier properties over other structures. While, in these examples, metallization is accomplished by conventional vacuum deposition, it can also

be accomplished by conventional vapor deposition. Additionally, although polypropylene is shown as the substrate, other polyolefin films may be used such as polyethylene, polyesters, polybutene, olefin copolymers, 5 polyamides, polycarbonate and polyacrylonitrile.

The following Examples illustrate the invention.

Example 1

This example is for comparative purposes.

A polypropylene homopolymer film was coextruded to make 10 a 0.90 mil film, using maleic anhydride grafted polypropylene as a tie layer and an ethylene-propylene-butene terpolymer as a heat seal layer on the other side. The film was metallized on the maleic anhydride grafted polypropylene side with aluminum in a vacuum to an optical density of 2.5. The film 15 was then extrusion laminated with 75 gauge polypropylene film using 10 lbs/ream LDPE hot melt. The properties of the multilayer film are set forth in Table 1.

Example 2

This example demonstrates a process for making a film in 20 accordance with the present invention which has superior air and moisture barrier properties.

A polypropylene film was made by coextruding a polypropylene substrate with an ethylene-propylene-butene terpolymer sealant on one side and a tie skin of maleic 25 anhydride grafted polypropylene skin on the opposite side. The film was stretched in the machine direction five times. The film was flame treated on the tie skin side. PVOH was extrusion coated on the treated tie skin side and the film was stretched in the transverse direction eight times before 30 it was again flame treated on the PVOH side and wound up in a mill roll. The film was vacuum metallized on the PVOH side with aluminum to an optical density of 2.5. The aluminum coating thickness was 300 to 500 angstroms. The film was extrusion laminated with 75 gauge polypropylene film using 10 35 lbs/ream LDPE hot melt. The properties of the film are set forth in the following Table 1.

Each film was made to a thickness of 0.90 mil. The tie

layer (maleic anhydride grafted polypropylene) was about 0.05 mil in both examples.

Barrier properties were measured on the metallized films produced. Water vapor transmission rate ($\text{g}/100 \text{ in}^2/24 \text{ hr}$) was measured at 100°F , 90% RH. Oxygen transmission rate ($\text{cc}/100 \text{ in}^2/24 \text{ hr}$) was measured at 73°F , 0% RH. The level of aluminum adhesion to the substrate was measured by reporting the % metal pickoff after 3 pulls on the aluminum surface with Scotch Brand 610 tape. The lamination bond (g/in) was measured by laminating the metallized surface to a layer of polypropylene film of about 0.75 mil in thickness using 10 lb/ream of molten low density polyethylene at a melt temperature of 325°C in a laminating machine. The film obtained was then pulled apart to measure the lamination bond strength in a conventional pulling machine. Typical lamination bond strength testing machines are the Alfred Suter Tester and the Sintech Tensile Tester. Properties obtained are as follows:

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Table 2

Ex.	Metallizable Skin	Treatment Level, dyne/cm	Table 2		Metal Pickoff, %	Lamination Bond, g/in
			OTR ¹	WVTR ¹		
5						
1	PP (Control)	40	10.0	0.15	80	80
2	PVOH (6 ga)	> 56	0.024	0.06	5	171
10	1----					
	2	oxygen transmission rate				
		water vapor transmission rate				

As shown in Table 1 the oxygen barrier and moisture barrier properties of the film are excellent and the metal-to-film adhesion is appropriate for most purposes.

CLAIMS

1. A film composition which comprises a polymeric substrate having at least one surface which is modified by a maleic anhydride modified propylene homopolymer or copolymer, the modified surface of the polymer substrate having a skin layer, capable of being metallized, consisting essentially of polyvinyl alcohol.
2. A film composition according to claim 1 in which the maleic anhydride modified propylene homopolymer or copolymer is a discrete layer.
3. A film composition according to claim 1 or 2 in which the substrate comprises an oriented homopolymer or copolymer of propylene.
4. A film composition according to any preceding claim in which one side of the film has a heat seal layer thereon.
5. A film composition according to any preceding claim in which the polyvinyl alcohol skin layer is essentially free from crosslinking agent.
6. A film composition according to any preceding claim in which the polyvinyl alcohol skin layer comprises extrudable polyvinyl alcohol.



7. A film composition of claim 11 in which the polyvinyl alcohol skin layer is a partially hydrolyzed grade.

8. A metallized film composition according to any 5 preceding claim in which the skin layer consisting of essentially polyvinyl alcohol has a metal layer directly thereon.

9. A metallized film composition according to claim 8 10 in which there is a heat sealable layer on the substrate opposite the skin layer.