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FILM AND LAMINATE FILM FOR METAL DEPOSITION

The present invention relates to a film and a laminate film for metal deposition, which films provide excellent deposition properties, excellent adhesive strength between a deposited metal layer and the film for metal deposition, and good appearance both before and after metal deposition.

Metal-deposited films obtained by depositing metal on plastics film are widely used as packaging materials because of their excellent gas barrier and light-shielding properties. Such films are commonly formed of polyethylene terephthalate or polypropylene: polyolefin film has poor adhesive strength to a deposited metal layer. Many proposals have been made to improve the adhesion of a polyolefin film; for example, JP-B-57-14377 (the term "JP-B" as used herein means an examined Japanese patent publication) and JP-A-56-72037 (the term "JP-A" as used herein means an unexamined published Japanese patent application) disclose modifying polypropylene with unsaturated carboxylic acids and blending the modified polypropylene with polypropylene or a mixture of polypropylene and a large amount of an inorganic filler; and JP-B-60-51553 discloses improving the adhesion of polypropylene by gradually cooling it when forming a film to yield a roughened surface.

However, the above expedients are still inadequate. The polypropylene modified by graft polymerization and



then blended exhibits insufficient improvement in adhesive strength to a deposited metal layer; and in the cases of mixing a large amount of an inorganic filler and making a surface-roughened film by gradually cooling, a metal-deposited layer having a good appearance is not obtained.

Accordingly, an object of the invention is to provide a polyolefin film having greatly improved adhesive strength to a deposited metal layer without damaging the characteristics such as good appearance and heat resistance that the polyolefin inherently possesses.

It has been found that a film for metal deposition, which has excellent adhesive strength to a deposited metal layer, good deposition properties, and good appearance after deposition can be obtained by using a resin composition obtained by blending a relatively small amount of a specific ethylene copolymer with a specific crystalline ethylene polymer to prepare a film or a laminate film.

The film for metal deposition according to the present invention is formed from a resin composition comprising:

(I) from 90.5 to 99.9% by weight of a crystalline ethylene polymer having a melting point of from 120 to 130° and a density of from 0.910 to 0.940 g/cm³, and

(II) from 0.1 to 9.5% by weight of at least one ethylene copolymer having an ethylene content of from 50 to 90 or 95% by weight selected from an ethylene-(meth)acrylate copolymer, and ethylene-(meth)acrylic acid copolymer, an ethylene-unsaturated glycidyl monomer-vinyl acetate



terpolymer, and an ethylene-unsaturated dicarboxylic anhyde-(meth)acrylate terpolymer.

The laminate film for metal deposition according to the present invention comprises a substrate layer having on at least one surface thereof a layer for metal deposition formed from the above resin composition.

The crystalline ethylene polymer used in the present invention is an ethylene- α -olefin copolymer obtained by copolymerizing ethylene with α -olefin having 3 to 20 carbon atoms using a transition metal catalyst such as a Ziegler catalyst. Copolymerization reaction is usually conducted at a polymerization temperature of from 30 to 300°C and a polymerization pressure of from atmospheric pressure to 3,000 kg/cm² in the presence or absence of a solvent. Propylene, butene-1, 4-methylpentene-1, hexene-1, and octene-1 are preferred as the α -olefin.

It is important that the crystalline ethylene polymer (I) has a melting point of from 120 to 130°C and a density of from 0.910 to 0.940 g/cm³. If either one or both of the melting point and the density are outside the above range(s), the adhesive strength of a deposited metal layer to the film for metal deposition are poor or the gloss or heat resistance of a metal-deposited film or the non-deposited film are poor, resulting in poor appearance; and such a film cannot be used in the present invention.

From the standpoint of the adhesive strength to a deposited metal layer, gloss and heat resistance, it is

preferred that the crystalline ethylene polymer has a melting point of from 122 to 128°C and a density of from 0.915 to 0.935 g/cm³.

The ethylene copolymers (II) are obtained by copolymerizing a monomer capable of radically copolymerizing (hereinafter referred to as a "comonomer"), with ethylene using a free radical-generator such as an organic peroxide or oxygen. The copolymerization reaction is usually conducted at a polymerization temperature of from 130 to 300°C and a polymerization pressure of from 500 to 3,000 kg/cm².

Examples of the ethylene-(meth)acrylate copolymer are copolymers of ethylene with methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, or 2-ethylhexyl acrylate. Of these, the copolymer of ethylene and methyl methacrylate is preferred.

Examples of the ethylene-(meth)acrylic acid copolymer are copolymers of ethylene with methacrylic acid or acrylic acid.

Examples of the ethylene-unsaturated glycidyl monomer-vinyl acetate terpolymer are terpolymers of ethylene, an unsaturated glycidyl monomer such as glycidyl acrylate, glycidyl methacrylate or monoglycidyl itaconate, and vinyl acetate. Of these, a terpolymer of ethylene, glycidyl methacrylate and vinyl acetate is preferred.

Examples of the ethylene-unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer are terpolymers of

ethylene, an unsaturated dicarboxylic anhydride such as maleic anhydride, citraconic anhydride or tetrahydrophthalic anhydride, and (meth)acrylate such as ethyl acrylate or methyl methacrylate. Of these, a terpolymer of ethylene, maleic anhydride and ethyl acrylate is preferred.

From the standpoint of cost and ease of handling, the copolymer of ethylene and methyl methacrylate is particularly preferred as the ethylene copolymer (II).

The ethylene copolymer used in the present invention preferably has the melting point of 50°C or higher from the standpoint of heat resistance.

The resin composition comprising the specific crystalline ethylene polymer and the specific ethylene copolymer each described above is used as the film for metal deposition of the present invention. The amounts of both components used are such that the amount of the crystalline ethylene polymer is from 90.5 to 99.9% by weight and the amount of the ethylene copolymer is from 0.1 to 9.5% by weight. If the amount of the ethylene copolymer is less than 0.1% by weight, an improved effect in adhesive strength of the deposited metal layer is insufficient, and if it exceeds 9.5% by weight, the appearance of non-deposited film is poor or the metal gloss of a deposited film is insufficient.

In the resin composition, the amount of the ethylene copolymer is preferably from 0.2 to 9.0% by weight, and more preferably from 0.4 to 8.0% by weight.

It is preferred in the resin composition to add an

anti-oxidizing agent having a melting point of 75°C or higher in an amount of from 0.01 to 0.2 part by weight and an anti-blocking agent in an amount up to 3 parts by weight, per 100 parts by weight of the resin compositions, from the standpoints of a processing stability in forming a film and ease of handling the film. If an anti-oxidizing agent having a melting point of less than 75°C is used or an anti-oxidizing agent is used in an amount exceeding 0.2 part by weight, the adhesive strength of a deposited metal layer is undesirably decreased. If the amount of the anti-oxidizing agent added is less than 0.01 part by weight, the processing stability in forming the film is insufficient. Examples of the anti-oxidizing agent are tetra[methylene-3-(3,5-di-tertiarybutyl-4-hydroxyphenyl)-propionate]methane (tradename: "Irganox 1010", manufactured by Nippon Ciba Geigy Co., Ltd.), 1,3,5,-trimethyl-2,4,6-tris-(3,5-di-tertiarybutyl-4-hydroxybenzyl)benzene (tradename: "Irganox 1330"), and tris(3,5-di-tertiarybutyl-4-hydroxybenzyl)isocyanurate (tradename: "Irganox 3114"). Of these, tetra[methylene-3-(3,5-di-tertiarybutyl-4-hydroxyphenyl)-propionate]methane is preferred.

An inorganic material fine powder or a polymeric material such as a crosslinked type polymeric bead or nylon can be used as the anti-blocking agent, and the amount thereof added is 0 to 3 parts by weight per 100 parts by weight of the resin composition and the substrate layer. Where the addition amount exceeds 3 parts by weight, the appearance of the laminate film obtained is damaged. Silicon oxide, aluminum

silicate, hydrotalcite, and crosslinked PMMA-bead, each having an average particle diameter of from 0.3 to 10 μm , are useful as the anti-blocking agent.

The resin composition for forming the film for metal deposition of the present invention can be obtained by mixing the crystalline ethylene polymer, the ethylene copolymer, and if necessary, the anti-oxidizing agent and/or the anti-blocking agent. The mixing methods which can be employed are various conventional methods for mixing the respective components in the ranges described above, for example, a method in which the components are dry blended using a mixer such as a Henschel mixer or a tumbler blender, and a method in which after mixing, the mixture is further melt-kneaded and pelletized using a single screw extruder or a multi-screw extruder. Mixing of the respective components can be conducted by a method in which all the components are mixed at once or by a method in which a part thereof is mixed in advance and the remainder is then mixed.

Where the film for metal deposition of the present invention is formed into a laminate film, the substrate layer therefor can be selected from polymers which can be formed into a film, cellophane, paper, paper board, fabric, aluminum, and the like.

Examples of the polymer which can be used include a crystalline polyolefin, a polyamide resin, a polyester resin, polyvinyl alcohol, and polyvinyl chloride. Of these, crystalline polyolefin is preferred from the standpoint of

rigidity of the laminate film, the appearance thereof after deposition and ease in forming the film; and a crystalline ethylene polymer or a crystalline propylene polymer, each having a melting point of 120°C or higher, is more preferred.

The film for metal deposition of the present invention can be prepared by a conventional film-forming process such as a T-die process by melt-kneading and extruding the resin composition using an extruder, or a tubular process. In particular, the film is suitably prepared by a process for preparing an unstretched film by the T-die process.

The thickness of the film of the present invention is not particularly limited, but is preferably from 10 to 500 μm , and more preferably from 10 to 100 μm .

The laminate film for metal deposition can be prepared by melt-kneading and extruding a layer for metal deposition and a substrate layer using two extruders and laminating the two layers in the molten state by a conventional process such as a feed block process or a co-extruding multilayer die process, and then cooling with a cooling roll. Further, the laminate film can be prepared in the form of a layer for metal deposition/substrate layer/polypropylene copolymer using three extruders, and a method for laminating a layer for metal deposition on the substrate layer with a dry laminating process or an extrusion laminating process. A co-extrusion laminating

process is preferred and an unstretched co-extrusion laminating process is more preferred.

The thickness ratio in the laminate film is not particularly limited, but it is preferred that the thickness of the deposited layer is 1/2 to 1/100 of the total thickness of the laminate film from the standpoints of rigidity and cost.

The film for metal deposition of the present invention is preferably subjected to a surface treatment on the surface thereof on which metal is deposited by a conventional method such as a corona treatment, a flame treatment or a plasma treatment so that the wetting index becomes 37 dunes/cm or more.

The film for metal deposition of the present invention can suitably be used as a film for depositing thereon a metal such as aluminum, gold, silver, copper, nickel, chromium, titanium, tin, or zinc by a method such as an electric heating method, an ion beam method, a sputtering method, or an ion plating method, under vacuum. It is particularly suitable where aluminum is used.

The thickness of a deposited metal layer is usually from 50 to 1,000 Å.

The present invention will be explained in more detail by reference to the following Examples, but the present invention is not construed as being limited thereto.

The measurement values of the respective items in the description and the following Examples were measured by the following methods:

(1) Melt Flow Rate:

According to JIS K7210, a crystalline ethylene polymer and an ethylene copolymer were measured by the method of Condition-4 and a crystalline propylene polymer was measured by the method of Condition-14.

(2) Melting Point:

Using a differential scanning calorimeter ("DSC" manufactured by Perkin-Elmer Co., Ltd.), 10 mg of a test piece was melted at 220°C for 5 minutes under a nitrogen atmosphere and the temperature was lowered to 40°C at a temperature-lowering rate of 5°C/minute. The temperature was raised at a rate of 5°C/minute to determine a peak temperature in the maximum peak of the melt endothermic curve as a melting point.

The melting point of indium (In) which was measured with the above measurement instrument at the temperature-raising rate of 5°C/minute was 156.6°C.

(3) Density:

Measured according to JIS K6760.

(4) Wetting Index:

Measured according to JIS K6768.

(5) Haze:

Measured according to JIS K7105.

(6) Gloss:

A 45° specular gloss was measured according to JIS K7105.

(7) Deposition Property:

An electric heating type deposition apparatus was used to deposit aluminum on a film under vacuum of 2×10^{-5} Torr and the appearance of a deposited surface was visually observed.

(8) Metallic Luster:

A 60° specular gloss was measured according to JIS Z8741.

(9) Adhesive Strength:

A deposited surface of a metal-deposited film and a polypropylene-biaxially stretched film having a thickness of $25 \mu\text{m}$ (OPP) were bonded by a dry laminate method applying a polyurethane adhesive in an amount of 3 g/m^2 in terms of a solid content. The bonded film was heat treated at 40°C for 24 hours and then allowed to stand at 23°C for 2 hours. The adhesive strength between the deposited film layer and the OPP layer was measured with a tensile tester.

EXAMPLE 1

97.5% by weight of an ethylene-hexene-1 copolymer having a melt flow rate of 2.0 g/10 minutes , a melting point of 123°C and a density of 0.919 g/cm^3 as a crystalline ethylene polymer (I) and 2.5% by weight of an ethylene-methyl methacrylate copolymer having a melt flow rate of 6.9 g/10 minutes , an ethylene content of 85% by weight and a melting point of 95°C as an ethylene copolymer (II) were mixed with a Henschel mixer, and the mixture was then melt-extruded at 220°C to pelletize it. The crystalline ethylene polymer (I) used contained 0.1% by weight of Irganox 1010 as an anti-oxidizing

agent and 0.1% by weight of hydrotalcite DHT-4A (manufactured by Kyowa Chemical Co., Ltd.) as an anti-blocking agent, and the ethylene copolymer (II) used did not contain additives such as an anti-oxidizing agent and an anti-blocking agent. The pellets obtained above were melt-extruded with a monolayer T-die extruding machine at a die temperature of 220°C and cooled with a cooling roll at 30°C. One surface of the resulting film was subjected to a corona discharge treatment to obtain film having a thickness of 30 μm and a wetting index of 47 dynes/cm.

This film was measured for haze and gloss. Further, aluminum was deposited on a corona-treated surface of this film to evaluate deposition property, metallic luster and adhesive strength.

The results obtained are shown in Table 1 below.

COMPARATIVE EXAMPLE 1

A film was formed in the same manner as in Example 1, except that the ethylene copolymer (II) was not used. The film had a wetting index of 45 dynes/cm. This film was measured and evaluated in the same manners as in Example 1.

The results obtained are shown in Table 1 below.

EXAMPLES 2 TO 5 AND COMPARATIVE EXAMPLES 2 TO 7

Films were formed, measured and evaluated in the same manners as in Example 1, except that the kind of the crystalline ethylene polymer (I) or the amounts of the

crystalline ethylene polymer (I) used and the ethylene copolymer (II) used were changed.

The results obtained are shown in Table 1 below.

EXAMPLES 6 TO 9

Films were formed, measured and evaluated in the same manners as in Example 1, except that the kind of the ethylene copolymer (II) was changed.

The results obtained are shown in Table 2 below.

EXAMPLE 10

A blend of 95.0% by weight of the crystalline ethylene polymer (I) and 5.0% by weight of the ethylene copolymer (II) each used in Example 1 was used as the resin composition for a layer for deposition, and a crystalline propylene-ethylene-butene-1 copolymer having a melt flow rate of 6.2 g/10 minutes, a propylene content of 92% by weight, an ethylene content of 2% by weight, a butene content of 6% by weight and a melting point of 139°C was used as the substrate layer. Melt laminating extrusion was conducted at a die temperature of 220°C using two extruders and a double layer T-die connected thereto, followed by cooling with a cooling roll at 30°C, and further subjecting the layer for deposition to a corona discharge treatment. A laminate film having a wetting index of 46 dynes/cm and composed of a layer for deposition having a thickness of 10 μ m and a substrate layer having a thickness of 25 μ m was obtained.

This laminate film was measured and evaluated in the same manner as in Example 1.

The results obtained are shown in Table 3 below.

COMPARATIVE EXAMPLE 8

A film was formed in the same manner as in Example 10, except that the crystalline ethylene polymer (I) used in Example 2 was used as the resin composition for a layer for deposition. This film had a wetting index of 45 dynes/cm. This film was measured and evaluated in the same manners as in Example 1.

The results obtained are shown in Table 3 below.

TABLE 1

Resin Composition														
Crystalline ethylene polymer					Ethylene copolymer					Film Properties and Deposition Property				
Type	Melting point (°C)	Density (g/cm ³)	Amount (wt%)	Type	content (wt%)	Melting point (°C)	Amount (wt%)	Haze (Z)	Gloss (Z)	Deposition property	Metallic luster (Z)	Adhesive strength (g/15 mm)		
Example 1	(a)	123	0.919	97.5	(A)	85	95	2.5	1.1	144	Good	900	430	
Example 2	(b)	125	0.932	97.5	(A)	85	95	2.5	4.3	137	Good	850	400	
Example 3	(c)	127	0.929	97.5	(A)	85	95	2.5	2.4	141	Good	860	450	
Example 4	(a)	123	0.919	99.5	(A)	85	95	0.5	1.1	145	Good	910	370	
Example 5	(a)	123	0.919	93.0	(A)	85	95	7.0	2.0	136	Good	860	460	
Comparative Example 1	(a)	123	0.919	100	-	-	-	-	1.2	153	Good	910	110	
Comparative Example 2	(a)	123	0.919	99.95	(A)	85	95	0.05	1.2	152	Good	900	170	
Comparative Example 3	(c)	127	0.929	90.0	(A)	85	95	10.0	4.1	114	Good	790	470	
Comparative Example 4	(d)	115	0.899	97.5	(A)	85	95	2.5	0.9	140	Poor (Broken)	measurement impossible	measurement impossible	
Comparative Example 5	(e)	132	0.956	97.5	(A)	85	95	2.5	14.6	95	Good	720	95	
Comparative Example 6	(f)	112	0.925	95.0	(A)	85	95	5.0	6.0	93	Good	770	200	
Comparative Example 7	(g)	142	0.896	95.0	(A)	85	95	5.0	11.4	63	Good	570	70	

TABLE 2

		Resin Composition				Film Properties and Deposition Property				
		Crystalline ethylene polymer		Ethylene copolymer		Deposition property		Metallic luster		Adhesive strength (g/15 mm)
Type	Melting point (°C)	Density (g/cm ³)	Amount (wtZ)	Type	Ethylene content (wtZ)	Melting point (°C)	Amount (wtZ)	Haze (Z)	Gloss (Z)	
Example 6	(a) 123	0.919	97.5	(B)	91	101	2.5	0.9	153	Good 360
Example 7	(a) 123	0.919	97.5	(C)	63	54	2.5	1.3	149	Good 500
Example 8	(a) 123	0.919	97.5	(D)	91	105	2.5	1.0	153	Good 410
Example 9	(a) 123	0.919	97.5	(E)	83	94	2.5	2.5	134	Good 450

Resin Composition

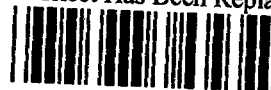
Resin Composition																			
Crystalline ethylene polymer				Ethylene copolymer				Film Properties and Deposition Property											
Melting point		Density		Amount		Ethylene		Melting point		Substrate Layer		Haze Gloss		Deposition Property		Metallic luster		Adhesive strength	
Type	(°C)	(g/cm ³)	(wt%)	Type	(wt%)	content	(wt%)	point	(°C)	Amount	(wt%)	(Z)	(Z)	property	(Z)	luster	(g/15 mm)		
Example 10 (a)	123	0.919	95.0	(A)	85	95	5.0	(h)	3.0	138	Good	860	250						
Comparative Example 8 (a)	123	0.919	100	-	-	-	-	(h)	2.5	139	Good	870	120						

The types of the crystalline ethylene polymer, the ethylene copolymer and the substrate layer used in the Examples and the Comparative Examples are as follows.

	<u>Melt flow rate</u> (g/10 minutes)
(a) Ethylene/hexene-1 copolymer	2.0
(b) Ethylene/hexene-1 copolymer	2.1
(c) Ethylene/hexene-1 copolymer (75 parts) + high density polyethylene (25 parts)	2.7
(d) Ethylene/butene-1 copolymer	3.9
(e) High density polyethylene	15
(f) Low density polyethylene	4.0
(g) Ethylene (4 wt%)/propylene copolymer	7.2
(h) Propylene (92 wt%)/ethylene (2 wt%)/ butene-1 (6 wt%) copolymer (melting point: 139°C)	6.2
(A) Ethylene/methyl methacrylate (15 wt%) copolymer	6.9
(B) Ethylene/methyl methacrylate (9 wt%) copolymer	3.6
(C) Ethylene/methyl methacrylate (37 wt%) copolymer	45
(D) Ethylene/ethyl acrylate (6 wt%)/maleic anhydride (3 wt%) copolymer	5.3
(E) Ethylene/glycidyl methacrylate (12 wt%)/ vinyl acetate (5 wt%) copolymer	6.8

As can be seen from the results shown in the Tables above, by using a single layer film or a laminate film, which is prepared using a resin composition comprising a specific crystalline ethylene polymer (I) and a specific ethylene

copolymer (II) in specific amounts, a film for metal deposition having greatly improved deposition property and adhesive strength to a deposited metal layer can be obtained without damaging the characteristics such as appearance, heat resistance and the like a polyolefin film inherently possesses.



CLAIMS:

1. A film for metal deposition formed of a resin composition comprising:

(I) from 90.5 to 99.9% by weight of a crystalline ethylene polymer having a melting point of from 120 to 130°C and a density of from 0.910 to 0.940 g/cm³, and

(II) from 0.1 to 9.5% by weight of at least one ethylene copolymer having an ethylene content of from 50 to 95% by weight selected from an ethylene-(meth)acrylate copolymer, an ethylene-(meth)acrylic acid copolymer, an ethylene-unsaturated glycidyl monomer-vinyl acetate terpolymer, and an ethylene-unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer.

2. A film as claimed in claim 1, wherein said crystalline ethylene polymer (I) is an ethylene- α -olefin copolymer.

3. A film as claimed in claim 2, wherein said α -olefin is propylene, butene-1, 4-methylpentene-1, hexene-1, or octene-1.

4. A film as claimed in claim 1, 2 or 3, wherein said crystalline ethylene polymer (I) has a melting point of from 122 to 128°C and a density of from 0.915 to 0.935 g/cm³.

5. A film as claimed in any preceding claim, wherein said ethylene-(meth)acrylate copolymer is a copolymer of ethylene and methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate or 2-ethylhexyl acrylate;





said ethylene-(meth)acrylic acid copolymer is a copolymer of ethylene and methacrylic acid or acrylic acid; said ethylene-unsaturated glycidyl monomer-vinyl acetate terpolymer is an ethylene-glycidyl methacrylate-vinyl acetate terpolymer; and said ethylene-unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer is an ethylene-maleic anhydride-ethyl acrylate terpolymer.

6. A film as claimed in any preceding claim, wherein said ethylene copolymer (II) is present in an amount of from 0.2 to 9.0% by weight.

7. A film as claimed in claim 6, wherein said ethylene copolymer (II) is present in an amount of from 0.4 to 8.0% by weight.

8. A film as claimed in any preceding claim, wherein said ethylene copolymer (II) has a melting point of 50°C or more.

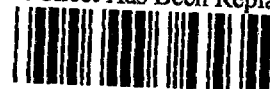
9. A laminate film for metal deposition comprising a substrate layer having formed on at least one surface thereof a layer for metal deposition comprising a film as claimed in any preceding claim.

10. A resin composition for forming a film for metal deposition and comprising

(I) from 90.5 to 99.9% by weight of a crystalline ethylene polymer having a melting point of from 120 to 130°C and a density of from 0.910 to 0.940 g/cm³, and

(II) from 0.1 to 9.5% by weight of at least one ethylene copolymer having an ethylene content of from 50





to 95% by weight selected from an ethylene-(meth)acrylate copolymer, an ethylene-(meth)acrylate acid copolymer, an ethylene-unsaturated glycidyl monomer-vinyl acetate terpolymer, and an ethylene-unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer.



ABSTRACT

FILM AND LAMINATE FILM FOR METAL DEPOSITION

A film for receiving a deposited metal layer is formed of a resin composition comprising (I) 90.5 - 99.9wt% crystalline ethylene polymer having a melting point of 120 - 130°C and a density of 0.910 - 0.940 g/cm³, and (II) 0.1 - 9.5wt% of at least one ethylene copolymer having a 50 - 95wt% ethylene content and selected from ethylene-(meth)acrylate copolymer, ethylene-(meth)acrylic acid copolymer, ethylene-unsaturated glycidyl monomer-vinyl acetate terpolymer, and ethylene-unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer.

The film, which may be laminated, provides excellent adhesive strength to the deposited layer and has a good appearance.

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then blended exhibits insufficient improvement in adhesive strength to a deposited metal layer; and in the cases of mixing a large amount of an inorganic filler and making a surface-roughened film by gradually cooling, a metal-deposited layer having a good appearance is not obtained.

Accordingly, an object of the invention is to provide a polyolefin film having greatly improved adhesive strength to a deposited metal layer without damaging the characteristics such as good appearance and heat resistance that the polyolefin inherently possesses.

It has been found that a film for metal deposition which has excellent adhesive strength to a deposited metal layer, good deposition properties, and good appearance after deposition can be obtained by using a resin composition obtained by blending a relatively small amount of a specific ethylene copolymer with a specific crystalline ethylene polymer to prepare a film or a laminate film.

The film for metal deposition according to the present invention is formed from a resin composition comprising:

(I) from 90.5 to 99.9% by weight of a crystalline ethylene polymer having a melting point of from 120 to 130° and a density of from 0.910 to 0.940 g/cm³, and

(II) from 0.1 to 9.5% by weight of at least one ethylene copolymer having an ethylene content of from 50 to 90 or 95% by weight selected from an ethylene-(meth)acrylate copolymer, and ethylene-(meth)acrylic acid copolymer, and ethylene-ethylenically unsaturated glycidyl monomer-vinyl acetate

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terpolymer, and an ethylene-ethylenically unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer.

The laminate film for metal deposition according to the present invention comprises a substrate layer having on at least one surface thereof a layer for metal deposition formed from the above resin composition.

The crystalline ethylene polymer used in the present invention is an ethylene- α -olefin copolymer obtained by copolymerizing ethylene with α -olefin having 3 to 20 carbon atoms using a transition metal catalyst such as a Zieg catalyst. Copolymerization reaction is usually conducted at a polymerization temperature of from 30 to 300°C and a polymerization pressure of from atmospheric pressure to 3,000 kg/cm² in the presence or absence of a solvent. Propylene, butene-1, 4-methylpentene-1, hexene-1, and octene-1 are preferred as the α -olefin.

It is important that the crystalline ethylene polymer (I) has a melting point of from 120 to 130°C and a density of from 0.910 to 0.940 g/cm³. If either one or both of the melting point and the density are outside the above range(s), the adhesive strength of a deposited metal layer to the film for metal deposition are poor or the gloss or heat resistance of a metal-deposited film or the non-deposited film are poor, resulting in poor appearance; and such a film cannot be used in the present invention.

From the standpoint of the adhesive strength to a deposited metal layer, gloss and heat resistance, it is

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CLAIMS:

1. A film for metal deposition formed of a resin composition comprising:

(I) from 90.5 to 99.9% by weight of a crystalline ethylene polymer having a melting point of from 1130°C and a density of from 0.910 to 0.940 g/cm³, and

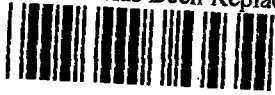
(II) from 0.1 to 9.5% by weight of at least one ethylene copolymer having an ethylene content of from 50 to 95% by weight selected from an ethylene-(meth)acrylate copolymer, an ethylene-(meth)acrylic acid copolymer, an ethylene-ethylenically unsaturated glycidyl monomer-vinyl acetate terpolymer, and an ethylene-unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer.

2. A film as claimed in claim 1, wherein said α -olefin is propylene, butene-1, 4-methylpentene-1, hexene-1, or octene-1.

3. A film as claimed in claim 1 or 2, wherein said crystalline ethylene polymer (I) has a melting point of from 122 to 128°C and a density of from 0.915 to 0.935 g/cm³.

4. A film as claimed in any preceding claim, wherein said ethylene-(meth)acrylate copolymer is a copolymer of ethylene and methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate or 2-ethylhexyl acrylate;





said ethylene-(meth)acrylic acid copolymer is a copolymer of ethylene and methacrylic acid or acrylic acid; said ethylene-unsaturated glycidyl monomer-vinyl acetate terpolymer is an ethylene-glycidyl methacrylate-vinyl acetate terpolymer; and said ethylene-unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer is an ethylene-maleic anhydride-ethyl acrylate terpolymer.

5. A film as claimed in any preceding claim, wherein said ethylene copolymer (II) is present in an amount of from 0.2 to 9.0% by weight.

6. A film as claimed in claim 5, wherein said ethylene copolymer (II) is present in an amount of from 0.4 to 8.0% by weight.

7. A film as claimed in any preceding claim, wherein said ethylene copolymer (II) has a melting point of 50°C or more.

8. A laminate film for metal deposition comprising a substrate layer having formed on at least one surface thereof a layer for metal deposition comprising a film as claimed in any preceding claim.

9. A resin composition for forming a film for metal deposition and comprising

(I) from 90.5 to 99.9% by weight of a crystalline ethylene polymer having a melting point of from 120 to 130°C and a density of from 0.910 to 0.940 g/cm³, and

(II) from 0.1 to 9.5% by weight of at least one ethylene copolymer having an ethylene content of from 50



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to 95% by weight selected from an ethylene-(meth)acrylate copolymer, an ethylene-(meth)acrylate acid copolymer, an ethylene-unsaturated glycidyl monomer-vinyl acetate terpolymer, and an ethylene-ethylenically unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer.



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ABSTRACT

FILM AND LAMINATE FILM FOR METAL DEPOSITION

A film for receiving a deposited metal layer is formed of a resin composition comprising (I) 90.5 - 99.9wt% crystalline ethylene polymer having a melting point of 120 - 130°C and a density of 0.910 - 0.940 g/cm³, and (II) 0.1 - 9.5wt% of at least one ethylene copolymer having a 50 - 95wt% ethylene content and selected from ethylene-(meth)acrylate copolymer, ethylene-(meth)acrylic acid copolymer, ethylene-ethylenically unsaturated glycidyl monomer-vinyl acetate terpolymer, and ethylene-unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer.

The film, which may be laminated, provides excellent adhesive strength to the deposited layer and has a good appearance.

✓ Claim(s) : page 1. to page 3.
✓ Drawing(s) : page 2. to page 2.
✓ Abstract : page 3. to page 3.

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DATE OF RECEIPT: 30/12/98

Film And Laminate Film For Metal Deposition And A Resin Composition
For Forming A Film

The present invention relates to a film and a laminate film for metal deposition, which films provide excellent deposition properties, excellent adhesive strength between a deposited metal layer and the film for metal deposition, and good appearance both before and after metal deposition.

Metal-deposited films obtained by depositing metal on plastics film are widely used as packaging materials because of their excellent gas barrier and light-shielding properties. Such films are commonly formed of polyethylene terephthalate or polypropylene: polyolefin film has poor adhesive strength to a deposited metal layer. Many proposals have been made to improve the adhesion of a polyolefin film; for example, JP-B-57-14377 (the term "JP-B" as used herein means an examined Japanese patent publication) and JP-A-56-72037 (the term "JP-A" as used herein means an unexamined published Japanese patent application) disclose modifying polypropylene with unsaturated carboxylic acids and blending the modified polypropylene with polypropylene or a mixture of polypropylene and a large amount of an inorganic filler; and JP-B-60-51553 discloses improving the adhesion of polypropylene by gradually cooling it when forming a film to yield a roughened surface.

However, the above expedients are still inadequate. The polypropylene modified by graft polymerization and

then blended exhibits insufficient improvement in adhesive strength to a deposited metal layer; and in the cases of mixing a large amount of an inorganic filler and making a surface-roughened film by gradually cooling, a metal-deposited layer having a good appearance is not obtained.

Accordingly, an object of the invention is to provide a polyolefin film having greatly improved adhesive strength to a deposited metal layer without damaging the characteristics such as good appearance and heat resistance that the polyolefin inherently possesses.

It has been found that a film for metal deposition, which has excellent adhesive strength to a deposited metal layer, good deposition properties, and good appearance after deposition can be obtained by using a resin composition obtained by blending a relatively small amount of a specific ethylene copolymer with a specific crystalline ethylene polymer to prepare a film or a laminate film.

The film for metal deposition according to the present invention is formed from a resin composition comprising:

(I) from 90.5 to 99.9% by weight of a crystalline ethylene polymer having a melting point of from 120 to 130° and a density of from 0.910 to 0.940 g/cm³, and

(II) from 0.1 to 9.5% by weight of at least one ethylene copolymer having an ethylene content of from 50 to 90 or 95% by weight selected from an ethylene-(meth)-acrylate copolymer, and ethylene-(meth)acrylic acid copolymer, and ethylene-ethylenically unsaturated glycidyl monomer-vinyl acetate

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terpolymer, and an ethylene-ethylenically unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer.

The laminate film for metal deposition according to the present invention comprises a substrate layer having on at least one surface thereof a layer for metal deposition formed from the above resin composition.

The crystalline ethylene polymer used in the present invention is an ethylene- α -olefin copolymer preferably obtained by copolymerizing ethylene with α -olefin having 3 to 20 carbon atoms using a transition metal catalyst such as a Ziegler catalyst. Copolymerization reaction is usually conducted at a polymerization temperature of from 30 to 300°C and a polymerization pressure of from atmospheric pressure to 3,000 kg/cm² in the presence or absence of a solvent. Propylene, butene-1, 4-methylpentene-1, hexene-1, and octene-1 are preferred as the α -olefin.

It is important that the crystalline ethylene polymer (I) has a melting point of from 120 to 130°C and a density of from 0.910 to 0.940 g/cm³. If either one or both of the melting point and the density are outside the above range(s), the adhesive strength of a deposited metal layer to the film for metal deposition are poor or the gloss or heat resistance of a metal-deposited film or the non-deposited film are poor, resulting in poor appearance; and such a film cannot be used in the present invention.

From the standpoint of the adhesive strength to a deposited metal layer, gloss and heat resistance, it is

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CLAIMS :

1. A film for metal deposition formed of a resin composition comprising :

(I) from 90.5 to 99.9% by weight of a crystalline copolymer of ethylene and an α -olefin having 3 to 20 carbon atoms having a melting point of from 120 to 130°C and a density of from 0.910 to 0.940 g/cm³, and

(II) from 0.1 to 9.5% by weight of at least one ethylene copolymer having an ethylene content of from 50 to 95% by weight selected from an ethylene-(meth)acrylate copolymer, an ethylene-(meth)acrylic acid copolymer, an ethylene-ethylenically unsaturated glycidyl monomer-vinyl acetate terpolymer, and an ethylene-ethylenically unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer.

2. A film as claimed in claim 1, wherein said α -olefin is propylene, butene-1, 4-methylpentene-1, hexene-1, or octene-1.

3. A film as claimed in claim 1 or 2, wherein said crystalline ethylene polymer (I) has a melting point of from 122 to 128°C and a density of from 0.915 to 0.935 g/cm³.

4. A film as claimed in any preceding claim, wherein said ethylene-(meth)acrylate copolymer is a copolymer of ethylene and methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate or 2-ethylhexyl acrylate;



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said ethylene-(meth)acrylic acid copolymer is a copolymer of ethylene and methacrylic acid or acrylic acid; said ethylene-unsaturated glycidyl monomer-vinyl acetate terpolymer is an ethylene-glycidyl methacrylate-vinyl acetate terpolymer; and said ethylene-unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer is an ethylene-maleic anhydride-ethyl acrylate terpolymer.

5. A film as claimed in any preceding claim, wherein said ethylene copolymer (II) is present in an amount of from 0.2 to 9.0% by weight.

6. A film as claimed in claim 5, wherein said ethylene copolymer (II) is present in an amount of from 0.4 to 8.0% by weight.

7. A film as claimed in any preceding claim, wherein said ethylene copolymer (II) has a melting point of 50°C or more.

8. A laminate film for metal deposition comprising a substrate layer having formed on at least one surface thereof a layer for metal deposition comprising a film as claimed in any preceding claim.

9. A resin composition for forming a film for metal deposition and comprising

(I) from 90.5 to 99.9% by weight of a crystalline copolymer of ethylene and an α -olefin having 3 to 20 carbon atoms having a melting point of from 120 to 130°C and a density of from 0.910 to 0.940 g/cm³, and

(II) from 0.1 to 9.5% by weight of at least one ethylene copolymer having an ethylene content of from 50



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to 95% by weight selected from an ethylene-(meth)acrylate copolymer, an ethylene-(meth)acrylate acid copolymer, an ethylene-ethylenically unsaturated glycidyl monomer-vinyl acetate terpolymer, and an ethylene-ethylenically unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer.



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ABSTRACT

Film And Laminate Film For Metal Deposition And A Resin Composition
For Forming A Film

A film for receiving a deposited metal layer is formed of a resin composition comprising (I) 90.5 - 99.9wt% crystalline ethylene polymer having a melting point of 120 - 130°C and a density of 0.910 - 0.940 g/cm³, and (II) 0.1 - 9.5wt% of at least one ethylene copolymer having a 50 - 95wt% ethylene content and selected from ethylene-(meth)acrylate copolymer, ethylene-(meth)acrylic acid copolymer, ethylene-ethylenically unsaturated glycidyl monomer-vinyl acetate terpolymer, and ethylene-ethylenically unsaturated dicarboxylic anhydride-(meth)acrylate terpolymer.

The film, which may be laminated, provides excellent adhesive strength to the deposited layer and has a good appearance.