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(54) LAMINATED FILM

(71) We, TORAY INDUSTRIES, INC., a body corporate organised according to the laws of Japan, of 2, Nihonbashi-Muromachi 2-Chome, Chuo-ku, Tokyo 103, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a composite film having a high degree of resistance to gas permeation, and good water resistance and mechanical properties, a process for the manufacture of the film and packages comprising it.

Saponified ethylene-vinyl acetate copolymers (hereinafter referred to as "polymer A") have previously been proposed for providing films with a high resistance to gas permeation (hereinafter "gas-barrier" films), in an unstretched or slightly uniaxially stretched state (less than 1.8 times the original length). Since these films have poor resistance against water permeation, they are usually laminated with a polyolefin and/or a polyester film using an appropriate adhesive. These proposed laminated films, however, have several drawbacks:

(1) When the laminated film is used for packaging water-containing materials or kept in conditions of high temperature and high humidity, small wrinkles or ripples soon appear on the surface of laminated film because of water absorption by layer of polymer A and eventually delamination will occur.

(2) Since the minimum thickness of polymer A layer to assure low gas permeability is greater than 15 μm in most cases, the total thickness of the laminated film is such as to impede processing.

(3) Glue-lamination processes are sometimes troublesome, because it is not easy to prevent wrinkles, air bubbles, residual solvents, etc. nor to keep stable adhesion strength. Besides, the production cost of the laminated films becomes high, as a result of lower yield.

A laminated corona-treated biaxially oriented polypropylene film extrusion-laminated with saponified ethylene/vinyl acetate copolymer and then with polyethylene, has some similarity to the composite film of the invention, but has insufficient gas barrier properties, water resistance and bonding strengths between layers. Therefore, its flatness deteriorates greatly when it is stored in an environment of high temperature and high humidity, or when it contains water-containing materials.

The present invention provides a laminated film comprising at least three layers, of materials A, B and C, in that order.

Layer A is an essentially uniaxially oriented layer comprising a saponified ethylene/vinyl acetate copolymer containing from 20 to 50 mole % ethylene units and being at least 90% saponified (polymer A);

Layer B is an essentially uniaxially oriented layer comprising a modified polyolefin (polymer B); this is an olefin polymer containing a polar functional group; examples are given below;

Layer C is a biaxially oriented layer of a propylene homopolymer or a copolymer of propylene and at least one other α -olefin.

Preferably, the ratio of thicknesses of the layers A: B: C is 1:0.05 to 10:5 to 40. The laminated composite film of the invention has the following advantages in addition to excellent gas barrier property:

(1) The composite film, though having a polymer A layer on one surface, has good gas barrier properties and water resistance, and remains relatively flat even when

subjected to high temperature and high humidity;

2) its mechanical strengths, for example, impact strength and tear strength, are good;

5 3) the laminate may be highly oriented because the stretchability of a composite web comprising extrusion laminated A and B layers and longitudinally stretched C layer in a stenter is improved compared with that of a film consisting of only A component;

10 4) when the free surface of the A layer is extrusion-or glue-laminated with a heat-sealing layer, for example, polyethylene or ethylene-propylene copolymer, the resulting laminated composite film has higher water resistance in addition to heat-sealing strength, and therefore retains more flatness under the influence of water and shows less delamination in an atmosphere of high temperature and high humidity.

15 Polymer A has from 20 to 50 mole %, preferably from 25 to 40 mole %, of ethylene units and more than 90%, preferably more than 95%, of degree of saponification, and, with this formulation, is melt-extrusible, with a resulting high gas barrier property. Intrinsic viscosity of the polymer A, measured in a solvent consisting of 85 weight% of phenol and 15 weight % of water, is advantageously in the range from 0.07 to 0.17 l/g, preferably from 0.09 to 0.15 l/g. When an intrinsic viscosity of the saponified polymer is lower than 0.07 l/g, it forms a layer in a laminated film that may be brittle and difficult to be stretched without cracks, which lower its gas barrier property and water resistance. When its intrinsic viscosity is higher than 0.17 l/g, its extrusion temperature becomes closer to its decomposition temperature. Therefore, gas bubbles in its layer or at the boundary between layers are often present, which increases film cleavages or breakages during stretching process.

25 Depending on application of the composite film of this invention, additives, for example, stabilizers, antioxidants, plasticizers, fillers, crystallizing agents, lubricating agents and antistatic agents, may be present in polymer A. Layer A may contain polymer A blended with other polymers as long as the properties of polymer A and hence layer A are not greatly changed.

Examples of polymer B are as follows:

35 (1) An olefin polymer graft polymerized with at least one ethylenically unsaturated dicarboxylic acid or acid derivative, preferably a polyolefin, for example, polypropylene or polyethylene, graft-copolymerized with at least one monomer selected from the α , β -ethylenically unsaturated dicarboxylic acids, for example, maleic acid, fumaric acid, itaconic acid, and their acid anhydrides, acid esters, acid amides, and acid imides.

40 (2) Copolymer of ethylene with an α , β -unsaturated monocarboxylic acid or acid derivative, especially acrylic or methacrylic acid and/or their metallic salts.

(3) Polyolefin that is graft-polymerized with α , β -ethylenically unsaturated monocarboxylic acids and/or their alkyl esters, or acid metallic salts.

45 (4) Saponified copolymer that is graft-polymerized with a monomer selected from the above-mentioned unsaturated acids.

50 Polymers selected from (1) and (2) are especially preferred in this invention. Specific examples of the polymer B are polyolefins, for example, polypropylene, a copolymer of ethylene and propylene or polyethylene, graft-polymerized with α , β -ethylenically unsaturated dicarboxylic acids or anhydrides (preferably maleic acid anhydride) in an amount of less than 1.0% by weight. Layer B may contain polymer B blended with other polymers and additives that do not deleteriously affect its properties.

55 Polymer C is polypropylene, i.e., the homopolymer, or a copolymer of propylene with at least one other α -olefin, for example, ethylene, butene or hexene. Intrinsic viscosity of polymer C, measured in tetralin at 135°C, is advantageously in the range from 1.6 to 2.7 dl/g (preferably from 1.8 to 2.3), and its isotactic index (I.I.) is advantageously in the range from 85 to 99% (preferably from 90 to 98%).

60 Layer C may contain polymer C blended with other polymers, for example, polyethylene, poly-4-methyl-pentene-1, polyterpene, hydrogenated petroleum resin derived from naphtha, copolymer of ethylene/vinyl acetate, or polymer B, provided that properties of polymer C are not greatly changed. Further, depending on its application, additives, for example, antioxidants, antistatic agents, inorganic fine particles, pigments, plasticizers or organic lubricating agents, may be present.

The thickness of layer A depends on the required gas barrier property of the

composite film, and in most cases it is less than 15 μm thick, preferably in the range from 1 to 10 μm , because the composite film of the present invention has good gas barrier property compared with conventional films.

5 When the thickness of layer C is less than five times as thick as that of layer A, mechanical properties and dimensional stability at high temperature may be adversely affected. When the thickness of layer C exceeds forty times as thick as that of layer A, the heat-sealing strength of a packaging material having a heat-sealable layer attached to layer A may be reduced, hence reducing bag or package
10 producing speeds and thus lowering the productivity. When the thickness of layer B is lower than 5% of that of layer A, the bonding strength of each layer may not be sufficient, and delamination may tend to occur when the composite film is kept under conditions of high temperature and high humidity. When the thickness of layer B exceeds that of layer A, the bonding strength is sufficient, but the transparency of the composite film may be reduced when waste film or trimmed
15 edges are recycled as is usually the case in film manufacture.

The composite film of the invention may preferably be prepared as follows: Polymers A and B are fed to separate extruders, and coextruded through an adapter in the pipe prior to a single manifold die, or through a double manifold die, onto a uniaxially oriented polymer C film with a thickness ratio of polymer A to B
20 in the range of A:B = 1:1 to 0.05. Meanwhile polymer C is fed to another extruder, and extruded on to a casting drum to form an unstretched film which is then stretched from 3 to 10 times, preferably 4 to 7 times, in the longitudinal direction at a temperature between 90 to 150°C, preferably between 110° to 140°C. Polymers A and B layers are extrusion-laminated on to this uniaxially oriented polymer C film
25 in the order: A/B/C. The width of the polymer A/B layers laminated onto the polymer C layer is preferably narrower than the separation between opposite stenter clips and is narrower than the width of the polymer C layer in order to reduce amounts of polymer A and B in the trimmed edges which are to be recycled. To get good stretchability, the polymer A may contain water, preferably from 1 to
30 10% by weight, at extrusion, or the laminated film may be passed through a hot water or steam bath.

The laminated film is then heated to 120 to 180°C, preferably in the range of 140 to 165°C, stretched from 5 to 15 times, preferably 7 to 12 times, in the transverse direction, and heat-set at a temperature between 130°C, preferably
35 140°C, and a temperature which is at least 5 degrees C lower than the melting point of polymer A. The gas barrier properties, water resistance and other properties of the composite film are much improved by stretching and heat-setting, and much more improved if polymer A layer is hydrous.

When the heat-setting temperature is above 5 degrees C below the melting point of polymer A, not only are the properties of the composite film, for example, mechanical properties, gas barrier properties and water resistance, lowered, but also the composite film tends to break during heat-setting process. When the heat-setting temperature is lower than 130°C the advantages deriving from heat-setting
40 may not be obtained.

Layers A and B may also be extrusion-laminated onto the transversely stretched polymer C film and then the laminated film is stretched in longitudinal direction.

The phrase "essentially uniaxially stretched" when used to refer to layers A and B, may be explained as follows:

50 Layers A and B are usually molecular-oriented during a stretching process. But when the stretching temperature of the laminated film is higher than the melting point of layer B, layer B melts and flows, reducing or losing molecular orientation. When the heat-setting temperature is higher than the relaxation temperature of the layers A and B, the molecular orientation of polymer A and B
55 layers tends to disappear.

Properties of the composite film are determined according to the following methods.

1. Oxygen permeability (cc/m².24 hr/sheet)
60 Oxy-Tran 100 oxygen permeation tester manufactured by Modern Controls, Inc., U.S.A., is used. Measurement is carried out at 20°C and 100% relative humidity using a film specimen stored in an atmosphere of 20°C and 100% relative humidity for a day in advance.

2. Water resistance

A film specimen is boiled at 90°C and kept for 30 minutes. Appearance of the

- composite film is observed after boiling and classified according to the following grades:
- O: Good. Surface flatness of the composite film does not change before and after boiling test.
- 5 Δ: Poor. Surface flatness of the composite film changes slightly. 5
- X: Bad. Surface flatness of the composite film changes appreciably.
3. Heat shrinkage
- After a composite film is kept in an oven controlled at 120°C for 15 minutes, its dimensional change is measured.
- 10 4. Heat-sealing strength 10
- Polymer A layer of composite film is anchor-coated with polyurethane adhesive to give a final coat weight of 0.5 g/m². Then, the anchor-coated film is glue-laminated with low-density polyethylene film (40 μm). The heat-sealing strength is evaluated by heat-sealing the glue-laminated film employing a heat-sealing pressing, for 0.5 second, at 140°C and at 1 kg/cm² (gauge) pressure.
- 15 15
- Example 1.
- Polymer A: Saponified ethylene/vinyl acetate copolymer having 33 mole % ethylene units, degree of saponification of at least 99 mole %, an intrinsic viscosity of 0.12 l/g, and melting point of 178°C
- 20 Polymer B: Polypropylene having intrinsic viscosity of 2.2 dl/g and I.I. of 97%, graft-polymerized with 0.4% by weight maleic anhydride 20
- Polymer C: Polypropylene having intrinsic viscosity of 2.2 dl/g, and I.I. of 97%.
- 25 Polymer C was extruded at 285°C to form cast film of thickness 800 μm and 1,200 μm (used for Film No. 2). The cast film was stretched 5 times its original length in the longitudinal direction at 120°C using stretching rolls. Polymer A and B were fed to separate extruders, coextruded at 240°C through an adapter in the pipe prior to a single manifold die, and laminated onto the uniaxially stretched polypropylene (polymer C) base film, in the order A/B/C. Thickness ratio of A/B was changed by varying the screw rotation rate. Steam at 105°C was sprayed onto the surface of polymer A layer of the laminated film and the water content of polymer A layer was adjusted to 8 weight %. The laminated film was then stretched 8 times the original width in the transverse direction, and heat-set at 160°C with relaxation of 5% in the transverse direction by a stenter. Gas barrier and physical properties of the composite film are shown in Table 1. The composite films (No. 1 to No. 4) of this invention has good gas barrier property. These films were relatively free from defects in surface flatness after the boiling test, and had good water resistance and dimensional stability at an elevated temperature. The heat-sealing strength of the composite films was between 1.0 to 1.2 kg/cm.
- 30 30
- 35 35

TABLE 1

Sample No.	Thickness of the composite film					Oxygen permeability (cc/m ² 24 hr.)	Water resistance	Heat shrinkage (%)	
	Thickness of layer (μm)			Thickness ratio				MD	TD
	A	B	C	A : B : C					
1	2	2	20	1 : 1 : 10	6.6	0	3.3	0.4	
2	2	2	30	1 : 1 : 15	6.5	0	3.4	0.3	
3	4	1	20	1 : 0.25 : 5	3.2	0	3.0	0.7	
4	4	0.3	20	1 : 0.075 : 5	3.3	0	3.0	0.8	

Example 2.

Polymer A: Saponified ethylene/vinyl acetate copolymer having 28 mole % ethylene units, degree of saponification of 99 mole %, an intrinsic viscosity of 0.15 l/g, and melting point of 179°C.

5

Polymer B: Polyethylene having melt index of 0.8 g/10 min and density of 0.93 g/cm³, graft-polymerized with maleic anhydride (0.5% by weight).

5

Polymer C: Polypropylene copolymer having 0.7% by weight ethylene units, intrinsic viscosity of 2.0 dl/g and I.I. of 96%.

10 Polymer C was extruded at 280°C and cast onto a casting drum cooled at 30°C to form a cast film having a thickness of 800 μm.

The cast film was stretched 5 times the original length in the longitudinal direction at 120°C. Polymer A containing 3 weight % of water and polymer B were coextruded at 200°C and laminated onto the uniaxially stretched polymer C film in the order A/B/C. The laminated film was then stretched 5 times the original width in the transverse direction, and heat-set at various temperature with relaxation of 1% in the transverse direction, using a stenter. Properties of the composite film are shown in Table 2.

15

TABLE 2

Sample No.	Thickness of the composite film				Heat-set temperature (°C)	Oxygen permeability (cc/m ² 24 hr.)	Water resistance
	Thickness of layer (μm)			Thickness ratio			
	A	B	C				
7	1	1	20	1 : 1 : 20	160	13.0	0
8	1	1	20	1 : 1 : 20	140	13.3	0
9	1	1	20	1 : 1 : 20	130	13.7	0
Comparative Example 1	4	1	20	1 : 0.25 : 5	no fixation	105.0	X

Composite films (Films No. 7 to No. 9) of this invention which had been heat-set at a temperature higher than 130°C, had good gas barrier and water resistance properties. In a recycling test, transparency of Film No. 7, which had been mixed with 50 weight % of waste films of Film No. 7 into polymer C layer, was good and its haziness was 3.0%.

Comparative Example 1

Biaxially oriented film of polymer C of Example 1 having a thickness of 20 μm was subjected to corona discharge. Then polymer A and B were extrusion-laminated onto this treated side of polymer C film to get A/B/C film (4/1/20 μm) similar to Film No. 3. It was very difficult to extrusion laminate A/B layers uniformly on C layer. Oxygen permeability of this laminated films was 105 cc/m² 24 hr/sheet. Delamination of the film was observed between C and B layer in the boiling test.

WHAT WE CLAIM IS:—

1. A laminated film having at least three layers A, B, C, in the order stated layer A being an essentially uniaxially stretched layer comprising polymer A, which is an at least 90% saponified ethylene/vinyl acetate copolymer containing from 20 to 50 mole% ethylene units;
2. layer B being an essentially uniaxially stretched layer comprising polymer B, which is a modified olefin polymer (as hereinbefore defined); and
3. layer C being a biaxially stretched layer comprising polymer C, which is a

- propylene homopolymer or a copolymer of propylene and at least one other α -olefin.
2. A film as claimed in claim 1, wherein the ratio of thickness of the layers A, B and C is 1:0.05 to 10:5 to 40.
- 5 3. A film as claimed in claim 1 or claim 2, wherein polymer A comprises from 25 to 40 mole per cent ethylene units. 5
4. A film as claimed in any one of claims 1 to 3, wherein polymer A is at least 95% saponified.
- 10 5. A film as claimed in any one of claims 1 to 4, wherein the intrinsic viscosity of polymer A is between 0.07 to 0.17 l/g. 10
6. A film as claimed in claim 5, wherein the intrinsic viscosity of polymer A is between 0.09 to 0.15 l/g.
7. A film as claimed in any one of claims 1 to 6, wherein polymer A contains additives.
- 15 8. A film as claimed in any one of claims 1 to 7, wherein layer A comprises a blend of polymer A with other polymers. 15
9. A film as claimed in any one of claims 1 to 8, wherein polymer B is an olefin polymer graft polymerized with at least one ethylenically unsaturated dicarboxylic acid or acid derivative.
- 20 10. A film as claimed in any one of claims 1 to 8, wherein polymer B is an ethylene/ α,β -unsaturated monocarboxylic acid or acid derivative copolymer. 20
11. A film as claimed in claim 10, wherein the derivative is a metal salt.
12. A film as claimed in claim 13, wherein polymer C is a copolymer of propylene and ethylene, butene or hexene.
- 25 13. A film as claimed in any one of claims 1 to 12, wherein the intrinsic viscosity of polymer C is between 1.8 and 2.3 dl/g. 25
14. A film as claimed in any one of claims 1 to 13, wherein layer C also comprises additives.
15. A film as claimed in any one of claims 1 to 14, wherein layer C comprises a blend of polymer C with other polymers.
- 30 16. A film as claimed in claim 1, which comprises a layer A of an ethylene/vinyl acetate copolymer, comprising 33 mole % ethylene units, saponified to at least 99 mole %, a layer B of a polypropylene graft-copolymerized with 0.4% by weight maleic anhydride and a layer C of polypropylene. 30
- 35 17. A film as claimed in claim 1, wherein layer A comprises a 99 mole % saponified ethylene/vinyl acetate copolymer containing 28 mole % ethylene units, layer B comprises polyethylene graft-copolymerized with 0.5 weight % maleic anhydride, and layer C comprises a propylene/0.7% by weight ethylene copolymer. 35
- 40 18. A film as claimed in any one of claims 1 to 17, having a heat-sealable layer bonded to a free surface of a layer A. 40
19. A film as claimed in claim 1, substantially as described in any one of the Examples herein.
- 45 20. A process for the manufacture of a film as claimed in any one of claims 1 to 19, wherein layers A and B are melt-extruded onto a uniaxially oriented layer C and the laminate is stretched in a direction transverse to the orientation of layer C. 45
21. A process for the manufacture of a film as claimed in claim 1, which comprises coextruding layers A and B onto a uniaxially oriented layer C and stretching the laminate in a direction transverse to the orientation of layer C.
- 50 22. A process as claimed in claim 20 or claim 21, wherein stretching is carried out at right angles to the orientation of layer C. 50
23. A process as claimed in any one of claims 20 to 22, wherein the orientation of layer C is longitudinal.
24. A process as claimed in any one of claims 20 to 23, wherein the degree of stretching of layer C is from 3 to 10 times.
- 55 25. A process as claimed in any one of claims 20 to 24, wherein the degree of transverse orientation is from 5 to 15 times. 55
26. A process as claimed in any one of claims 20—26, wherein after transverse orientation the film is heat-set.
27. A process as claimed in claim 26, wherein heat-setting is carried out at a temperature of at least 130°C.
- 60 28. A process as claimed in claim 27, wherein heat-setting is carried out at a temperature of from 130°C to 140°C. 60
29. A process as claimed in any one of claims 26 to 28, wherein heat-setting is carried out at a temperature which is at least 5 degrees C lower than the melting point of polymer A.
- 65 65

30. A process as claimed in any one of claims 20 to 29, wherein polymer A is hydrous.

31. A process as claimed in claim 20 or claim 21, carried out substantially as hereinbefore described.

5 32. A process as claimed in claim 20 or claim 21, carried out substantially as described in any one of the Examples herein. 5

33. A film, whenever prepared by a process as claimed in any one of claims 20 to 32.

10 34. A package comprising a film as claimed in any one of claims 1 to 19 or claim 33. 10

35. A method of packaging a material comprising surrounding it by a film as claimed in any one of claims 1 to 19 or claim 33.

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