



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 080 762 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
07.03.2001 Bulletin 2001/10

(51) Int. Cl.⁷: **A63H 27/10**

(21) Application number: **99918296.7**

(86) International application number:
PCT/JP99/02333

(22) Date of filing: **27.04.1999**

(87) International publication number:
WO 99/58216 (18.11.1999 Gazette 1999/46)

(84) Designated Contracting States:
BE DE FR GB

(30) Priority: **12.05.1998 JP 12834898**

(71) Applicant: **GUNZE LIMITED**
Ayabe-shi, Kyoto, 623-0011 (JP)

(72) Inventors:
• **NIWA, Osamu**
Fukushima Plastics Co., Ltd.
Fukushima 969-1104 (JP)

- **BIWAKI, Hidekazu**
Moriyama Plant
Moriyama-shi Shiga 524-8501 (JP)
- **OKA, Takahiro**
Gunze Limited
Chuo-ku Tokyo 103-0027 (JP)

(74) Representative:
Perrey, Ralf, Dr. Dipl.-Chem.
Müller-Boré & Partner,
Grafinger Strasse 2
81671 München (DE)

(54) **FILM FOR VAPOR DEPOSITION BALLOON**

(57) The present invention provides a film for forming a vapor deposited balloon, which comprises a five-layer structure composed of a polyamide resin layer, a polyolefin layer, a polyamide resin layer, an adhesive resin layer and a seal layer.

EP 1 080 762 A1

Description**TECHNICAL FIELD**

5 [0001] The present invention relates to a film for forming a vapor deposited balloon and a method for manufacturing the same.

BACKGROUND ART

10 [0002] Conventionally used as a film for forming a vapor deposited balloon is a laminate film having a three-layer structure consisting of a layer of nylon 6, an adhesive resin layer and a layer of LLDPE.

[0003] Further, Japanese Unexamined Patent Publication No. 290650/1995 proposes a laminate film having a five-layer structure consisting of a polyamide resin layer, a saponified copolymer layer of ethylene and vinyl acetate, a polyamide resin layer, an adhesive resin layer and a polyolefin resin layer.

15 [0004] These films, however, have the defect of curling.

[0005] An object of the present invention is to provide a film for forming a vapor deposited balloon, which is free of curling.

DISCLOSURE OF INVENTION

20 [0006] The present invention provides a film for forming a vapor deposited balloon, the film having a five-layer structure consisting of a polyamide resin layer, a polyolefin layer, a polyamide resin layer, an adhesive resin layer and an LLDPE layer.

[0007] In the film for forming a vapor deposited balloon according to the invention, the polyamide resin layer comprises crystalline or amorphous nylon such as nylon 6 (poly- ϵ -caprolactam), nylon 66 (polyhexamethylene adipamide), nylon 12 (a polymer of lactam of 12-aminododecanoic acid), nylon 6-66 copolymer, nylon 6-12 copolymer or the like. The polyamide resin layer preferably comprises about 70-95 wt.% of crystalline nylon and about 30-5 wt.% of amorphous nylon, more preferably about 80-90 wt.% of crystalline nylon and about 20-10 wt.% of amorphous nylon. Nylon 6-66 copolymer is a copolymer of nylon 6 (poly- ϵ -caprolactam) and nylon 66 (polyhexamethylene adipamide), and preferably contains nylon 6 in a proportion of about 30 mole % or more, more preferably about 50 mole % or more, further more preferably about 70 mole % or more. The nylon copolymer preferably has a molecular weight of about 13,000 to about 33,000. The two polyamide resin layers of the film may be the same or different as long as they contain the above components. Each polyamide resin layer has a thickness of about 1-15 μm , preferably about 3-10 μm . Examples of amorphous nylons include copolymers or terpolymers of dicarboxylic acid (e.g., terephthalic acid and isophthalic acid) and diamine (e.g., hexamethylenediamine).

[0008] Any polyolefin layer that is capable of bonding the two polyamide resin layers together can be used without limitation. The polyolefin layer preferably comprises polyolefin such as polyethylene or polypropylene, more preferably linear low density polyethylene (LLDPE) and/or low density polyethylene (LDPE), especially LLDPE. The polyolefin layer has a thickness of about 1-6 μm , preferably about 1.5-4 μm . The polyolefin layer may contain, in addition to or in place of polyolefin such as LLDPE, a polyolefin-based adhesive resin such as grafted LLDPE. The polyolefin layer preferably comprises a polyolefin-based adhesive resin.

[0009] Any adhesive resin layer that is capable of bonding the polyamide resin layer and the seal layer together may be used without limitation. A preferred adhesive resin is LLDPE treated by graft reaction. The adhesive resin layer has a thickness of about 1-6 μm , preferably about 1.5-3 μm .

45 [0010] The seal layer comprises LLDPE or LDPE, especially LLDPE. The seal layer has a thickness of about 2-20 μm , preferably about 5-10 μm .

[0011] The total thickness of the layers of the film for forming a balloon according to the invention is about 10-70 μm , preferably about 15-35 μm .

[0012] Preferably, the polyamide shrinkable multilayer film of the invention is a flat film. The layers of the film are co-extruded from a T-die into a flat film and the film is subjected to simultaneous or sequential biaxial stretching. The laminate film may be formed by any method without limitation, but generally formed by extrusion casting on a chilled roll. The film thus obtained is simultaneously or sequentially stretched in biaxial directions, thereby giving a film of the invention. The stretching may be carried out in the machine direction using a roll stretching machine and in the transverse direction using a tenter stretching machine.

55 [0013] The stretch ratio in machine direction is about 1.2-5 and the stretch ratio in transverse direction is about 2.5-5. Stretching in machine direction is carried out at about 60-120°C, preferably about 70-100°C. Stretching in transverse direction is carried out at about 70-180°C, preferably about 100-160°C.

[0014] After stretching, heat treatment may optionally be carried out. There is no limitation on the heat treatment

method, but the heat treatment is generally carried out by a continuous process after transverse stretching using a tenter stretching machine. The heat treatment may be carried out with the film being diminished (relaxed) in width by 20% or less, preferably by 3-10%, or with the film being set to the same width as when transversely stretched or set to a larger width than when transversely stretched. The heat treatment may be carried out at temperatures below 150°C, preferably at about 80-130°C, optionally with the film being diminished in width by 20% or less, preferably by 3-10%, for example, using a tenter stretching machine. The film is subjected to thermal contraction in order to prevent natural contraction.

[0015] The multilayer film of the present invention is suitable for use as a film for forming a vapor deposited balloon. Stated more specifically, a vapor deposited layer of aluminium oxide, silicon dioxide or any other metal (e.g., aluminum foil) may be formed over the whole or partial surface of the outermost polyamide resin layer of the film of the invention. The metal deposited layer may be formed on any part of the surface of the outermost layer. However, it is preferable that the film be cut into strips and a metal vapor deposited layer be formed on one side of the centerline in width, with the other side being a transparent film. This is convenient because with use of such a film, one can very easily form a balloon having a transparent half side and a non-transparent metal deposited layer formed on the other half side. Moreover, by using the film, one can easily form a spherical balloon having a transparent appearance in one hemisphere and a non-transparent metal deposited layer formed on the other hemisphere.

[0016] Preferably, the balloon film of the present invention has the following physical properties:

- Haze (measured according to ASTM D-1003): 1.0-7.0%, preferably 2.0-5.0%;
- Tensile strength: MD (800-1500 kg/cm²), TD (800-1500 kg/cm²);
- Tensile elongation: MD (80-180%), TD (80-180%);
(tensile strength and tensile elongation both measured according to JIS K-6732);
- Thermal shrinkage (measured in warm water at 100°C for 30 seconds): MD (0-5.0%), TD (0-5.0%);
- Puncture strength: NY surface (0.5 kg or more);
LL surface (0.5 kg or more) (measured according to JIS P-8116);
- Impact strength: NY surface (5.0 kg • cm or more);
LL surface (5.0 kg • cm or more) (measured with a punching impact tester using a small ball);
- Seal strength (pressure = 2kg/cm² time = 1 second):
120°C (1.0 kg/cm or more), 130°C (1.0 kg/cm or more),
140°C (1.5 kg/cm or more), 150°C (1.5 kg/cm or more),
160°C (1.5 kg/cm or more), 170°C (1.5 kg/cm or more);
- Oxygen permeability: 100 cc/m² • 24h • 20°C×65%RH or less (measured according to ASTM D-3985);
- Wet tension strength: NY surface (45 dyn/cm or more) (measured according to JIS K-6768);
- Slipperiness: between NY-NY surfaces (both the coefficient of static friction and the coefficient of dynamic friction being 0.3 to 0.6);
between LL-LL surfaces (both the coefficient of static friction and the coefficient of dynamic friction being 0.3 to 0.8) (measured according to ASTM D-1894).

[0017] The balloon of the present invention can be formed by heat sealing portions of seal layer(s) of the balloon film(s) together to form into a desired shape such as sphere, ellipse or the like in a desired size.

BEST MODE FOR CARRYING OUT THE INVENTION

[0018] The present invention will be described below in more detail with reference to Examples and Comparative Examples.

[Curling Evaluation Method]

[0019] Measurement temperature and humidity: 20°C and 50%RH

- (1) a film, 100 mm x 100 mm, is diagonally cut to make incisions,
- (2) the width and height of the film are measured after rolling up the film in the machine direction and in the transverse direction.

Criteria:

[0020] The larger the width is, the smaller curling property the film has (the quality is good).

[0021] The greater the height is, the smaller curling property the film has (the quality is good).

[0022] This is because a film having higher curling property is rolled up tightly, thus having a smaller width and a lower height.

Example 1

5

[0023] The laminate film having a five-layer structure was formed using the following starting materials.

(1) Starting materials:

10 **[0024]**

- Polyamide resin layer (hereinafter referred to as layer "A") = nylon 6 (80 wt.%) and amorphous nylon (20 wt.%).
- Polyolefin layer (hereinafter referred to as layer "B") = an LLDPE based adhesive resin
- Adhesive resin layer (hereinafter referred to as layer "C") = an LLDPE based adhesive resin
- 15 • Seal layer (hereinafter referred to as layer "D") = LLDPE

(2) Production method

[0025] The layer components (A/B/A/C/D) were coextruded from a T-die to form a flat five-layer film on a chilled roll with cooling water being circulated. The film was then stretched three times in the machine direction using a roll stretching machine at 80°C and stretched 3.8 times in the transverse direction using a tenter stretching machine in an atmosphere at 120°C. Subsequently, with the width of the film being reduced by about 4% using the tenter stretching machine, the film was thermally fixed in an atmosphere at 200°C. The film obtained had a thickness of A/B/A/C/D = 4/2/4/2/8 (μm).

25 **[0026]** Table 1 shows physical properties of the film.

Example 2

[0027] A laminate film having a five-layer structure consisting of A/B/A/C/D = 4/2/4/2/8 (μm) in thickness was formed in the same manner as in Example 1 except that the following starting materials were used. Table 1 shows physical properties of the film.

- Layer A = nylon 6 (80 wt.%) and amorphous nylon (20 wt.%)
- Layer B = LLDPE based adhesive resin (50 wt.%) + LLDPE (50 wt.%)
- 35 Layer C = LLDPE based adhesive resin
- Layer D = LLDPE

Example 3

[0028] A laminate film having a five-layer structure consisting of A/B/A/C/D = 6/3/6/2/18 (μm) in thickness was formed in the same manner as in Example 1 except that the following starting materials were used. Table 1 shows physical properties of the film.

- Layer A = nylon 6 (80 wt.%) and amorphous nylon (20 wt.%)
- 45 Layer B = LLDPE based adhesive resin
- Layer C = LLDPE based adhesive resin
- Layer D = LLDPE

[0029] Physical properties of the films obtained in Examples 1-3 were determined according to the following methods:

- Haze: measured according to ASTM D-1003;
- Tensile strength and tensile elongation: measured according to JIS K-6732;
- Slipperiness (static friction/dynamic friction): measured according to ASTM D-1894;
- 55 • Thermal shrinkage: measured in warm water at 100°C for 30 seconds;
- Puncture strength: measured according to JIS P-8116;
- Impact strength: measured with a punching impact tester using a small ball;

EP 1 080 762 A1

- Seal strength: measured at a pressure of 2kg/cm² for 1 second;
- Oxygen permeability: measured according to ASTM D-3985;
- Wet tension strength: measured according to JIS K-6768;

5

Table 1

10

15

20

25

30

35

40

45

50

	Example 1	Example 2	Example 3
Average thickness (μm):	20.7	20.5	35.0
Haze (%):	2.5	3.2	6.5
Tensile strength (kg/cm ²)			
MD	960	854	819
TD	1397	1260	1140
Tensile elongation (%)			
MD	160	154	150
TD	85	95	92
Slipperiness (static friction/dynamic friction)			
NY-NY	0.58/0.51	0.49/0.42	0.46/0.38
LL-LL	0.62/0.51	0.50/0.42	0.40/0.36
Thermal shrinkage (%)			
MD	2.3	1.8	1.4
TD	1.3	0.8	0.5
Puncture strength (kg)			
NY surface	0.67	0.72	0.95
LL surface	0.60	0.62	0.75
Impact strength (kg • cm)			
NY surface	8.3	9.0	9.8
LL surface	9.0	9.5	10.8
Seal strength (kg/cm)			
120°C	1.2	1.2	1.9
130°C	2.1	2.3	3.4
140°C	2.2	2.2	3.5
150°C	2.3	2.3	3.6
160°C	2.3	2.3	3.7
170°C	2.3	2.2	3.7
Oxygen permeability (cc/m ² • 24h • 20°C×65%RH)	43	42	40
Wet tension strength (dyn/cm)			
LL surface	36	36	36
NY surface	50	50	50

55

Comparative Example 1

[0030] A laminate film having a three-layer structure consisting of A/C/D = 10/2/10 (μm) in thickness was formed in

EP 1 080 762 A1

the same manner as in Example 1 except that the following starting materials were used. The curing of the film obtained was measured. Table 2 shows the results.

Layer A = nylon 6 (80 wt.%) and amorphous nylon (20 wt.%)

Layer C = LLDPE based adhesive resin

Layer D = LLDPE

Test Example 1

[0031] The films obtained in Example 1 and Comparative Example 1 were tested for curling. Table 2 shows the results.

Table 2

	Width (mm)		Length (mm)	
	MD	TD	MD	TD
Example 1	8-10	7-9	10-12	15-17
Comp. Ex.1	5	5	5	5

Example 4

[0032] The film obtained in Example 1 was cut into strips having a width of 100 cm. A metal vapor deposited layer of aluminum was formed to a thickness of 400Å on one half of the surface of layer (A), i.e., on one side of the centerline in width. The obtained strips of the balloon film were formed into a spherical shape by heat sealing portions of seal layers of the strips together. By feeding therein helium gas at 1.2 atm., a balloon having a non-transparent metal deposited layer was formed. The balloon thus obtained had a good design effect and floated in the air for 7 days.

Claims

1. A film for forming a vapor deposited balloon, which comprises a five-layer structure composed of a polyamide resin layer, a polyolefin layer, a polyamide resin layer, an adhesive resin layer and a seal layer.
2. The film for forming a vapor deposited balloon according to claim 1 wherein the polyamide resin layer is a mixed resin layer comprising 5 to 30 wt.% of an amorphous polyamide resin and 95 to 70 wt.% of an aliphatic polyamide resin and/or a semiaromatic polyamide resin.
3. A film for forming a vapor deposited balloon, which is produced by forming a metal deposited layer over the whole or partial surface of the outermost polyamide resin layer of the film according to claim 1.
4. A film for forming a vapor deposited balloon, which has a transparent appearance on one side and comprises a metal deposited layer formed on the other side.
5. A balloon comprising the film for forming a vapor deposited balloon according to claim 1.
6. A method for producing a vapor deposited balloon, which comprises heat sealing portions of the seal layer(s) of vapor deposited balloon film(s) of claim 1 together to form into a desired shape such as sphere, ellipse or the like in a desired size.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/02333

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁶ A63H27/10		
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) Int.Cl. ⁶ A63H27/10		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-1999 Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI (DIALOG)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 7-284570, A (Dainippon Printing Co., Ltd.), 31 October, 1995 (31. 10. 95), Full text ; all drawings (Family: none)	1-6
Y	JP, 3-109092, A (Okura Industrial Co., Ltd.), 9 May, 1991 (09. 05. 91), Full text (Family: none)	1-6
Y	JP, 6-182058, A (K.K. Raifu), 5 July, 1994 (05. 07. 94), Full text ; Fig. 1 (Family: none)	1-6
Y	JP, 9-94357, A (Kuraray Co., Ltd.), 8 April, 1997 (08. 04. 97), Full text (Family: none)	1-6
Y	JP, 6-171043, A (Mitsubishi Kasei Corp.), 21 June, 1994 (21. 06. 94), Full text ; Fig. 1 (Family: none)	1-6
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> 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 "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 11 August, 1999 (11. 08. 99)	Date of mailing of the international search report 17 August, 1999 (17. 08. 99)	
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer	
Facsimile No.	Telephone No.	

Form PCT/ISA/210 (second sheet) (July 1992)