(19)

(12)





(11) **EP 2 058 106 B1**

EUROPEAN PATENT SPECIFICATION

- (45) Date of publication and mention of the grant of the patent:13.06.2012 Bulletin 2012/24
- (21) Application number: 07792345.6
- (22) Date of filing: 10.08.2007

(51) Int Cl.: *B29C 55/28* ^(2006.01) *B65D 65/40* ^(2006.01) *B29K 77/00* ^(2006.01)

B32B 27/34 ^(2006.01) C08J 5/18 ^(2006.01) B29L 7/00 ^(2006.01)

- (86) International application number: PCT/JP2007/065700
- (87) International publication number: WO 2008/020569 (21.02.2008 Gazette 2008/08)
- (54) Biaxially oriented nylon film, laminate wrapping material and process for production of biaxially oriented nylon film

Biaxial orientierte Polyamidfolie, Laminateinwickelmaterial und Verfahren zur Herstellung einer biaxial orientierten Polyamidfolie

Film de nylon biaxialement orienté, matière d'emballage laminée et procédé de production du film de nylon biaxialement orienté

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, -	14.08.2006JP 200622105114.08.2006JP 200622105214.08.2006JP 2006221053	(74)	Representative: Clar Gill Jennings & Eve The Broadgate Tow 20 Primrose Street	ery LLP ver
. ,	publication of application: 009 Bulletin 2009/20		London EC2A 2ES	(GB)
		(56)	References cited:	
,	al application: 09.3 / 2 455 209		EP-A2- 0 335 411 JP-A- 06 106 619 JP-A- 2001 064 415	JP-A- 03 126 523 JP-A- 10 036 665
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104-003	33 (JP)			

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Description

TECHNICAL FIELD

⁵ **[0001]** The present invention relates to biaxially-oriented nylon film, a laminated packing material and a manufacturing method for the biaxially-oriented nylon film.

BACKGROUND ART

¹⁰ **[0002]** Biaxially-oriented nylon film (hereinafter also referred to as ONy film), which is excellent in strength, impact resistance and anti-pinhole property, is frequently used for packaging a product such as a heavy product or liquid product on which a great load is applied.

[0003] There has been conventionally known a technique to use nylon for a packing material used in such a forming as a deep-drawing, a stretch forming or the like (see e.g. Patent Document 1, Patent Document 2).

- Specifically, Patent Document 1 discloses resin sheet for cold forming that includes: a base material layer that contains a polystyrene-based resin; and a functional layer that is single-layered or two-layered on both surfaces or one surface of the base material layer. In addition, according to Patent Document 1, as the functional layer, an abrasion resistance layer that contains a nylon resin is provided on an exterior layer of the resin sheet for cold forming.
- According to such resin sheet for cold forming, a cool-formed article that is excellent in impact resistance and shaperetaining property can be obtained. By providing the abrasion resistance layer containing the nylon resin on the exterior layer of the sheet, the exterior layer of the sheet can be prevented from being damaged during cool-forming. As described in Patent Document 1, as compared with hot-forming, cool-forming is excellent in that a size of an apparatus

can be reduced with a heater being omitted and that a continuous forming at high speed can be realized.

[0004] On the other hand, Patent Document 2 discloses composite sheet for deep-drawing that is formed by laminating plural pieces of sheet that includes a seal layer, a middle layer and an outer layer. In the sheet, the seal layer includes a polypropylene-based resin layer, the middle layer includes an oxygen-barrier resin layer, a nylon-based resin layer and a polyethylene-based resin layer, and the outer layer is made from a hygroscopic material.

According to such composite sheet for deep-drawing, the composite sheet can be given a mechanical strength by providing the nylon-based resin layer in the middle layer. With this arrangement, an occurrence of a pinhole during deepdrawing at approximately 150 degrees C can be prevented.

- EP 0335411 discloses a method of and an apparatus for manufacturing biaxially oriented film. A tubular original film which has been extruded by an extruding die is biaxially oriented by heat and air injected to the inside portion thereof being conveyed to nip rolls each having an individual circumferential speed. The temperature of heat to be applied to the film is controlled on the basis of the detected film thickness for the purpose of obtaining a uniform film thickness
- ³⁵ distribution. Furthermore, the film can be made uniform by adjusting the outer diameter of the bubble-shaped oriented film by adjusting the distance between two sets of nip rolls on the basis of the measured width of the film. In addition, when the thus-oriented film is subjected to a heat treatment, temperature of heat is arranged to be a pre-determined temperature as to prevent adhesion of the films.
- JP 2001 064415 further discloses a film and a method of producing a film excellent in especially sliding property under a high humidity and a high temperature while retaining the transparency of polyamide film excellent in strength properties. JP 03 126523 discloses a method of and an apparatus for biaxially orienting a crystalline thermoplastic resin film and subsequently thermally processing the film with first and second heating devices, in which the temperatures of respective heaters for biaxially orienting the film are separately controlled, the first heating device being operated by a tubular method or a tenter method, and the second heating device being operated under a tenter method and above the
- 45 temperature in the first heating device, whereby a melting and sticking of the film is prevented and the bowing ratio is decreased.

JP 06 106619 is directed to heat treating without fusion bonding and providing good straight cutting properties by melt extruding a mixture of Nylon 6 and metaxyleneadipamide, folding a colored raw fabric film, carrying out the heat treatment in the first stage, cutting both ends open and separating the film into two and carrying out the heat treatment in the second stage.

[0005]

[Patent Document 1] JP-A-2004-74795 [Patent Document 2] JP-A-2004-98600

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DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

- 5 [0006] However, since there is no detailed description in Patent Document 1 with respect to the nylon-based resin layer provided on the exterior layer of the resin sheet for cold-forming, the resin sheet may not show a favorable formability, strength or anti-pinhole property for cold-forming, depending on the nylon resin layer used therein. In such a case, a molded article of a sharp shape may not be obtained, and a pinhole may be formed in the sheet during cool-forming. [0007] In Patent Document 2, although there is a detailed description with respect to a material used for forming the
- nylon-based resin layer, there is no detailed description with respect to a material disculor forming the
 nylon-based resin layer, there is no detailed description with respect to mechanical property such as an elongation ratio of the nylon-based resin layer. In addition, although referring to deep-forming at approximately 150 degrees C, Patent Document 2 does not refer to cool-forming. Accordingly, as in Patent Document 1, a favorable molded article may not be obtained by cool-forming.

[0008] An object of the present invention is to provide, as a main base material for packing material used in coolforming etc., biaxially-oriented nylon film that is excellent in formability, strength and anti-pinhole property, a laminated packing material including the same and a manufacturing method of the biaxially-oriented nylon film.

MEANS FOR SOLVING THE PROBLEMS

- **[0009]** According to a finding on which the present invention is based, biaxially-oriented nylon film (ONy film) that is excellent in formability, strength and anti-pinhole property can be obtained when predetermined conditions are satisfied with respect to an elongation ratio until a rupture in each four directions (an MD direction, a TD direction, a 45 degrees direction and a 135 degrees direction) obtained in a tensile test of the ONy film and to a tensile stress σ_1 at a point where the elongation ratio becomes 50 percent and tensile stress σ_2 at an yield point in a stress-strain curve obtained in the
- 25 tensile test of the film.

[0010] In short, according, to the present invention, biaxially-oriented nylon film described as follows is provided. Biaxially-oriented nylon film according to an aspect of the present invention is biaxially-oriented nylon film made from nylon 6, wherein an elongation ratio of the film measured in a tensile test in each of a direction in which the film is moved, a direction of a film width, a 45 degree direction and a 135 degree direction until a film rupture is 70 percent or more,

- ³⁰ the elongation ratio being measured under conditions of: a sample width being 15 mm; a distance between gauge points being 50 mm; and a tensile speed being 100 mm/min a stress ratio A (σ_1/σ_2) between a tensile stress σ_1 and a tensile stress σ_2 in a stress-strain curve obtained in the tensile test of the film is 2 or more in each of the four directions, the tensile stress σ_1 being a value at a point where the elongation ratio becomes 50 percent while the tensile stress σ_2 being a value at an yield point,
- 35 the film is made from a film forming material that contains a virgin material and a thermal hysteresis material, the virgin material being formed of nylon 6 and metaxylylene adipamide, the thermal hysteresis material being obtained by melt-kneading nylon 6 and metaxylylene adipamide and by setting the metaxylylene adipamide to have a melt point of 233 to 238 degrees C, and

a hydrothermal shrinkage factor of the film is 3 to 20 percent in each of the direction in which the film is moved and the direction of the film width when the film is retained in hot liquid of 95 degrees C for thirty minutes.

[0011] According to the aspect of the present invention, since the elongation ratio until the rupture in each of a direction in which the film is moved, a direction of a film width, a 45 degree direction and a 135 degree direction is 70 percent or more and the stress ratio A in the stress-strain curve of the ONy film is 2 or more in each of the directions, the ONy film is excellent in formability, strength and anti-pinhole property, which is specifically favorable in cold-forming. According

to a laminated packing material formed to contain such ONy film, no pinhole is formed in the ONy film during cold deep-drawing or the like, thereby manufacturing a molded article of a sharp shape.
[0012] In the present invention, cold-forming refers to forming that is conducted under an atmosphere at a temperature less than a glass transition point (Tg) of a resin. Preferably in cool-forming, using a cool-forming machine for forming aluminum foil, a sheet material is forced into a female die by a male die to be pressed at high speed. In this manner,

⁵⁰ without being heated, the sheet material can experience such a plastic deformation as molding, bending, shearing and drawing.

[0013] In the biaxially-oriented nylon film according to the aspect of the present invention, it is preferable that a crystallinity degree of the film is in a range of 20 to 38 percent.

[0014] According to the aspect of the present invention, since the crystallinity is in the range of 20 to 38 percent, the film exhibits a favorable elongation property during forming.

[0015] In the biaxially-oriented nylon film according to the aspect of the present invention, the film is made from a film forming material that contains a virgin material and a thermal hysteresis material, the virgin material being formed of nylon 6 (hereinafter also referred to as Ny6) and metaxylylene adipamide (hereinafter also referred to as MXD6), the

thermal hysteresis material being obtained by melt-kneading Ny6 and MXD6 and by setting the MXD6 to have a melt point of 233 to 238 degrees C, and a hydrothermal shrinkage factor of the film is 3 to 20 percent in each of the MD direction and the TD direction of the film when the film is retained in hot liquid of 95 degrees C for thirty minutes.

[0016] According to the aspect of the present invention, since the hydrothermal shrinkage factor of the film when the film is retained in the hot liquid of 95 degrees C for thirty minutes is in the range of 3 to 20 percent, the film exhibits a favorable elongation property during forming. According to a laminated packing material formed to contain such ONy film, since MXD6 is contained in the ONy film,

According to a laminated packing material formed to contain such ONy film, since MXD6 is contained in the ONy film, the laminated packing material exhibits an excellent heat resistance. Accordingly, when the packing material having been formed by laminating an ONy film layer and a sealant layer is heated by a seal bar to be seal-treated, the packing material data and here to the seal here whereby a forward a sealant layer is heated by a seal bar to be seal-treated, the packing material data and here to the seal here whereby a forward is a sealant layer is heated by a seal bar to be seal-treated, the packing material data and here to the seal here whereby a forward is a sealant layer is heated by a seal bar to be seal-treated.

10 material does not adhere to the seal bar, whereby a favorable seal-treatment can be realized. Further, according to the packing material, since the ONy film layer contains the thermal hysteresis material, an occurrence of an intra-layer separation inside the ONy film layer can be prevented, whereby a molded article that is excellent in impact resistance can be obtained.

[0017] In the biaxially-oriented nylon film according to the aspect of the present invention, it is preferable that the Ny6

¹⁵ and the MXD6 are contained in the virgin material by ratios of 60 to 85 parts by mass and 15 to 40 parts by mass respectively, and a content of the thermal hysteresis material is 5 to 40 percent by mass of the total amount of the film forming material.

[0018] In the biaxially-oriented nylon film according to the aspect of the present invention, it is preferable that the Ny6 and the MXD6 are contained in the thermal hysteresis material by ratios of 60 to 85 parts by mass and 15 to 40 parts by mass respectively.

[0019] In the biaxially-oriented nylon film according to the aspect of the present invention, it is preferable that a ratio (A_{max}/A_{min}) between a maximum stress ratio A_{max} and a minimum stress ratio A_{min} of the stress ratios A obtained with respect to the four directions is 2 or less.

[0020] In the biaxially-oriented nylon film according to the aspect of the present invention, it is preferable that a tensilerupture strength of the film in each of the four directions measured in the tensile test of the film is 18MPa or more.

[0021] A laminated packing material according to another aspect of the present invention is a laminated packing material that includes the above-described biaxially-oriented nylon film.

[0022] A method of manufacturing biaxially-oriented nylon film according to still further aspect of the present invention is a manufacturing method of biaxially-oriented nylon film made from a film forming material that contains nylon 6, the method including steps of biaxially-oriented raw film made from the pylon 6 under a condition where an

- 30 method including steps of: biaxially-orienting unoriented raw film made from the nylon 6 under a condition where an oriented ratio of the film in each of a direction in which the film is moved and a direction of a film width becomes 2.8 times or more; and heat-treating the raw film at a temperature between 160 and 200 degrees C to manufacture biaxially-oriented nylon film, wherein a crystallinity degree of the film is in a range of 20 to 38 percent, an elongation ratio of the film measured in a tensile test in each of the direction in which the film is moved, the direction of the film width, a 45
- ³⁵ degree direction and a 135 degree direction until a film rupture is 70 percent or more, the elongation ratio being measured under conditions of: a sample width being 15 mm; a distance between gauge points being 50 mm; and a tensile speed being 100mm/min, a stress ratio A (σ_1/σ_2) of a tensile stress σ_1 and a tensile stress σ_2 in a stress-strain curve obtained in the tensile test of the film is 2 or more in each of the four directions, the tensile stress σ_1 being a value at a point where the elongation ratio becomes 50 percent while the tensile stress σ_2 being a value at an yield point,
- 40 the film is made from a film forming material that contains a virgin material and a thermal hysteresis material, the virgin material being formed of nylon 6 and metaxylylene adipamide, the thermal hysteresis material being obtained by melt-kneading nylon 6 and metaxylylene adipamide and by setting the metaxylylene adipamide to have a melt point of 233 to 238 degrees C, and
- a hydrothermal shrinkage factor of the film is 3 to 20 percent in each of the direction in which the film is moved and the direction of the film width when the film is retained in hot liquid of 95 degrees C for thirty minutes.

BRIEF DESCRIPTION OF DRAWINGS

[0023]

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Fig. 1 is a graph showing an example of a stress-strain curve obtained when a tensile test is conducted on ONy film according to a first and third embodiments of the present invention; and

Fig. 2 is an illustration schematically showing a biaxially-orienting apparatus for manufacturing the ONy film according to the first and third embodiments of the present invention.

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EXPLANATION OF CODES

[0024]

11: raw film, 16: bubble, 18: oriented film

BEST MODE FOR CARRYING OUT THE INVENTION

5 <First Embodiment>

[0025] A first embodiment will be described in detail below.

[Arrangement of Biaxially-Oriented Nylon Film]

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[0026] Biaxially-oriented nylon film (ONy film) according to the present embodiment is formed by biaxially-orienting unoriented raw film made from nylon 6 (hereinafter called, Ny6) and heat-treating the oriented raw film at a predetermined temperature. By biaxially-orienting the unoriented raw film as described above, ONy film excellent in impact resistance can be obtained.

¹⁵ The chemical formula of the Ny6 is represented by Formula 1 below. [0027]

[Formula 1] H-[NH-(CH₂)5-CO]n-OH

- 20 [0028] In the present embodiment, an elongation ratio, a stress ratio A and a tensile-rupture stress of the ONy film in each four directions (MD direction, TD direction, 45 degree direction and 135 degree direction) until a tensile rupture of the film are obtained based on a stress-strain curve obtained through a tensile test (a sample width of 15 mm, a distance between gauges points of 50 mm and a tensile speed of 100 mm/min) conducted on the ONy film. An example of the stress-strain curve obtained through the tensile test is shown in Fig. 1.
- ²⁵ In Fig. 1, the vertical scale shows a tensile stress σ (MPa) of the ONy film while the horizontal scale shows a strain ε of the ONy film ($\varepsilon = \Delta 1 / 1$, in which I represents an initial length of the film and $\Delta 1$ represents an increment in the film length). By conducting the tensile test on the ONy film, the tensile stress σ is increased in such a manner as to substantially satisfy a direct function in accordance with an increase in the strain ε , such that an increasing trend of the tensile σ at a predetermined strain ε_1 is greatly changed. In the present embodiment, the point (ε_1 , σ_2) is defined as an yield point.
- ³⁰ When the strain ε is further increased, the tensile stress σ is also increased accordingly. When the strain ε is increased up to a predetermined strain ε_2 , the film is ruptured. Stress-strain curves corresponding respectively to the four directions (MD direction, TD direction, 45 degrees direction and 135 degrees direction) are obtained per one piece of the ONy film. **[0029]** In the ONy film according to the present embodiment, the elongation ratios in the four directions (the MD direction, the TD direction, the 45 degrees direction and the 135 degrees direction) until the film rupture in the tensile
- ³⁵ test are required to be 70 percent or more. In other words, as in the stress-strain curve shown in Fig. 1, the strain ε_2 at the time of the film rupture is required to be 0.7 or more. With this arrangement, the ONy film can be stretched in a balanced manner, thereby improving a drawing-formability of the ONy film when the ONy film is formed to be a laminate material. When the elongation ratio in one of the four directions is less than 70 percent, the film can be easily ruptured in a cold deep-drawing operation, whereby a good formability is not obtained.
- 40 It is more preferable that a value obtained by dividing a maximum elongation ratio by a minimum elongation ratio out of the elongation ratios in the four directions is 2.0 or less. With this arrangement, the ONy film can be stretched in a further balanced manner.

In addition, it is preferable that the elongation ratios of the ONy film in the four directions are 75 percent or more and that the value obtained by dividing the maximum elongation ratio by the minimum elongation ratio out of the elongations ratios in the four directions is 2.0 or less, whereby a further excellent formability can be obtained.

- ⁴⁵ ratios in the four directions is 2.0 or less, whereby a further excellent formability can be obtained. **[0030]** In the ONy film according to the present embodiment, a stress ratio A (σ_1/σ_2) between the tensile stress σ_1 when the elongation ratio becomes 50 percent (strain ε = 0.5) and the tensile stress σ_2 at the yield point in the stressstrain curve exemplarily shown in Fig. 1 is required to be 2 or more (more preferably 2.2 or more) in each of the four directions. With this arrangement, a formation of a pinhole during the cold deep-drawing operation can be reliably
- ⁵⁰ prevented, whereby a molded article of a sharp shape can be manufactured. When the stress ratio A is less than 2 in one of the directions, a film thickness may be uneven with the film being partially thinned, whereby the film may be ruptured. A ratio (A_{max}/A_{min}) between a maximum stress ratio A_{max} and a minimum stress ratio A_{min} out of the stress ratios A in the four directions is preferably 2.0 or less (more preferably 1.8 or less). With this arrangement, the film can be stretched in a balanced manner during a cold forming operation, whereby a molded article with a uniform thickness can be
- ⁵⁵ manufactured. When the ratio A_{max}/A_{min} is more than 2.0, the film thickness may be uneven with the film being partially thinned, whereby the film may be ruptured.

[0031] Further, in the ONy film according to the present embodiment, a tensile-rupture strength (σ_3) in each of the four directions is preferably 180 MPa or more in the stress-strain curve exemplarily shown in Fig. 1. With this arrangement,

a sufficient processing strength can be obtained, whereby the ONy film can be more invulnerable to rupture in the cold deep-forming operation or the like. At this time, a value obtained by dividing a maximum strength by a minimum strength out of the tensile-rupture strengths in the four directions is preferably 2.0 or less, whereby a well-balanced processing strength can be obtained.

⁵ It is preferable that the tensile-rupture strengths of the ONy film in the four directions are 200MPa or more and that the value obtained by dividing the maximum strength by the minimum strength out of the tensile-rupture strengths in the four directions is preferably 1.8 or less, whereby a better-balanced processing strength can be obtained.

[Manufacturing Method of ONy Film]

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[0032] The above-described ONy film can be obtained by biaxially-orienting the unoriented raw film made from Ny6 under a condition where an oriented ratio in each of the MD direction and the TD direction becomes 2.8 times or more and by heat-treating the oriented raw film at a temperatures between 205 and 215 degrees C.

As a method of biaxial orienting, a simultaneous biaxial-orienting or a sequential biaxial-orienting such as a tubular ¹⁵ method or a tenter method can be employed. However, in light of a strength balance between a lengthwise direction and a widthwise direction, it is preferable to perform the simultaneous biaxial-orienting according to the tubular method. [0033] Specifically, the ONy film according to the present embodiment can be manufactured as follows.

After Ny6 pellets are melt-kneaded in an extruder at 270 degrees C, a molten material is extruded from a die in a shape of cylindrical film. By subsequently quenching the extruded molten material by water, a raw film is prepared.

- 20 Then, as exemplarily shown in Fig. 2, after inserted between a pair of nip rollers 12, the raw film 11 is heated by a heater 13 while a gas is injected into the raw film 11. The raw film 11 is applied with air 15 from an air ring 14 at a drawing start point to be distended to form a bubble 16. By pulling the raw film 11 using a pair of nip rollers 17 provided at a downstream side, the simultaneous biaxial orienting in the MD direction and the TD direction according to the tubular method is performed. At this time, the oriented ratio in each of the MD direction and the TD direction is required to be 2.8 times or
- ²⁵ more. When the oriented ratio is less than 2.8 times, an impact strength is deteriorated, which is practically unfavorable. Subsequently, the oriented film is put into a tenter heat treat furnace (not shown) to be heat-fixed at 205 to 215 degrees C, whereby ONy film 18 according to the present embodiment is obtained. When a heat-treating temperature is higher than 215 degrees C, due to an excessive growth of a bowing phenomenon, an anisotropy in a width direction is increased while a crystallinity degree is excessively increased, whereby the strength is deteriorated. On the other hand, when the
- 30 heat-treating temperature is lower than 205 degrees C, due to an excessive increase in a film shrinkage factor, the film may be easily shrunk during a secondary processing.

[Arrangement of Laminated Packing Material]

- ³⁵ **[0034]** A laminated packing material according to the present embodiment is formed by laminating onto at least one surface of the ONy film another laminate base material of one layer or of two layers or more. Specifically, the other laminate base material may be exemplarily a film that includes an aluminum layer or the like. Generally, a laminated packing material including the aluminum layer is not suitable for cool forming because the alu-
- minum layer can be easily ruptured due to necking during a cool forming operation. In this regard, in the laminated packing material according to the present embodiment, since the ONy film is excellent in a formability, impact resistance and anti-pinhole property, the aluminum layer can be prevented from being ruptured during a cool stretch-expanding operation or a cool deep-drawing operation, thereby preventing a pinhole formation in the packing material. Accordingly, even when the total thickness of the packing material is small, a molded article of a sharp shape with high strength can be obtained.
- 45 [0035] The total thickness of the laminated packing material according to the present embodiment (i.e., a sum of thicknesses of the ONy film and the other laminate base material) is preferably 200 μm or less. When the total thickness is more than 200 μm, corner portions of the packing material may not be easily formed by cool forming, whereby a molded article of a sharp shape may not be obtained.
- **[0036]** The thickness of the ONy film in the laminated packing material according to the present embodiment is preferably 5 to 50 μm, more preferably 10 um to 30 μm. When the thickness of the ONy film is less than 5 μm, impact resistance of the laminated packing material may be deteriorated, whereby a sufficient cool formability may not be obtained. On the other hand, when the thickness of the ONy film is more than 50 μm, impact resistance of the laminated packing material may not be further improved even though the total thickness of the packing material is increased, which is unfavorable.
- ⁵⁵ **[0037]** As the aluminum layer used in the laminated packing material according to the present embodiment, aluminum foil formed from pure aluminum or from a soft material of aluminum-iron alloy may be used. In order to improve laminate property, the aluminum foil preferably experiences a pretreatment such as an undercoating treatment by silane coupling agent or titanium coupling agent, a corona discharge treatment and the like, such that the pretreated aluminum foil is

laminated onto the ONy film.

A thickness of the aluminum layer is preferably 20 to 100 μ m. With this arrangement, a shape of the molded article can be well-maintained, and oxygen, moisture and the like can be prevented from being permeated through the packing material.

- ⁵ When the thickness of the aluminum layer is less than 20 µm, the aluminum layer may be easily ruptured during the cool forming of the laminated packing material. Even when the aluminum layer is not ruptured, a pinhole or the like may be easily formed. Thus, oxygen, moisture and the like may be permeated through the packing material. On the other hand, when the thickness of the aluminum layer is more than 100 µm, neither the rupture during the cool forming nor a formation of the pinhole is notably prevented even though the total thickness of the packing material is increased, which
- 10 is unfavorable.

<Second Embodiment>

[0038] A second embodiment will be described in detail below.

¹⁵ In the description of the second embodiment, what has been already described in the preceding first embodiment will not be repeated.

[Arrangement of Biaxially-Oriented Nylon Film]

20 **[0039]** Biaxially-oriented nylon film (ONy film) according to the present embodiment is formed by biaxially-orienting unoriented raw film made from a material containing Ny6 and heat-treating the oriented raw film at a predetermined temperature, as in the first embodiment.

Unlike the first embodiment, the ONy film preferably has a crystallinity degree of 20 to 38 percent, more preferably 24 to 36 percent. With this arrangement, ONy film that is excellently stretchable during a forming operation as compared

- ²⁵ with general ONy film can be obtained, whereby the rupture of the ONy film and the formation of the pinhole can be prevented during, for example, the cool forming operation. When the crystallinity degree of the film is less than 20 percent, there is no particular difference in the stretchability during the forming operation between the ONy film and general ONy film. On the other hand, when the crystallinity degree of the film is more than 38 percent, a cool drawing-formability and an impact strength may be deteriorated.
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[Manufacturing method of ONy Film]

[0040] The ONy film according to the present embodiment can be obtained by biaxially-orienting the unoriented raw film made from the material containing Ny6 under the condition where the oriented ratio in each of the MD direction and the TD direction becomes 2.8 times or more and by heat-treating the oriented raw film, as in the first embodiment.

the TD direction becomes 2.8 times or more and by heat-treating the oriented raw film, as in the first embodiment. However, although the heat-treating is performed at the temperature between 205 and 215 degrees C in the first embodiment, the heat-treating is performed at a temperature between 160 and 200 degrees C in the present embodiment. Specifically, the oriented film is put into a tenter heat treat furnace (not shown) to be heat-fixed at 160 to 200 degrees C, whereby ONy film 18 according to the present embodiment is obtained.

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[Arrangement of Laminated Packing Material]

[0041] The laminated packing material according to the present embodiment is prepared in the same manner as in the first embodiment, a description of which is omitted.

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<Third Embodiment>

[0042] An embodiment third embodiment of the present invention will be described in detail below. In the description of the third embodiment, what has been already described in the preceding embodiments will not be repeated.

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[Arrangement of Biaxially-Oriented Nylon Film]

[0043] Biaxially-oriented nylon film (ONy film) according to the present embodiment is formed by biaxially-orienting unoriented raw film made from a material containing: a virgin material formed from Ny6 and MXD6; and a thermal hysteresis material formed by melt-kneading Ny6 and MXD6, and by heat-treating the oriented raw film at a predetermined temperature. By biaxially-orienting the unoriented raw film as described above, ONy film excellent in impact resistance can be obtained.

[0044] The chemical formula of the Ny6 is represented by Formula 2 below while the chemical formula of the MXD6 is represented by Formula 3 below. [0045]

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[Formula 2] H-[NH-(CH₂)₅-CO]n-OH

[0046]

[Formula 3]

 $H \neq NHCH_2$ CH2NHCO-(CH2)4-CO]n-OH

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[0047] The above-mentioned virgin material generally means a material other than a mixture material having a history where the Ny6 and the MXD6 have been mixed to be melt-kneaded. For instance, even when the Ny6 or the MXD6 in a material individually has a melt-kneading history (e.g., a recycled product), the material is the virgin material as long as the Ny6 and the MXD6 are not mixed to be melt-kneaded.

In light of the impact strength and the heat resistance of the ONy film, the Ny6 and the MXD6 are preferably contained in the virgin material by a ratio of 60 to 85 parts by mass (Ny6): 15 to 40 parts by mass (MXD6). When the MXD6 in the virgin material is less than 15 parts by mass, the heat resistance is deteriorated. Accordingly, when the laminated packing

²⁵ material, in which suitable sealant film is laminated onto the ONy film, is seal-treated, the laminated packing material may adhere to a seal bar. On the other hand, when the MXD6 is more than 40 parts by mass, the impact strength is so much deteriorated as to impair practical usability.

[0048] The above-mentioned thermal hysteresis material means a material containing Ny6 and MXD6, the material having passed through an extruder. In the present invention, as the MXD 6, MXD6 whose melt point is maintained within

- ³⁰ a range of 233 to 238 degrees C (preferably within a range of 235 to 237 degrees C) is used, the melt point being measured with a differential scanning calorimetry (DSC). The thermal hysteresis material may be prepared by recycling the ONy film obtained in the present invention. Since the thermal hysteresis material serves as a compatible solubilizer that has an affinity for both the Ny6 and the MXD6, an intra-layer separation of the ONy film can be prevented by adding the thermal hysteresis material to the ONy film.
- ³⁵ The intra-layer separation means a phenomenon where a separation is induced inside the ONy film when the ONy film onto which suitable sealant film has been laminated is used under such severe conditions as in the cool forming. The mechanism of the intra-layer separation has not been completely specified. However, it is speculated that the Ny6 and the MXD6 are layer-oriented in the ONy film and the intra-layer separation occurs between layers.
- The melt point of the MXD6 in the thermal hysteresis material means a melt point measured before the thermal hysteresis material is melt-kneaded with the virgin material. When the melt point of the MXD6 in the thermal hysteresis material is less than 233 degrees C, the impact strength of the ONy film is deteriorated. When the melt point of the MXD6 in the thermal hysteresis material is 238 degrees C or more, the intra-layer separation may not be favorably prevented. **[0049]** A content of the thermal hysteresis material is preferably 5 to 40 percent by mass of the total amount of the

(0049) A content of the thermal hysteresis material is preferably 5 to 40 percent by mass of the total amount of the ONy film forming material. When the thermal hysteresis material is less than 5 percent by mass, the intra-layer separation can be easily induced when the ONy film is used under such severe conditions as in the cool forming after the ONy film is formed into a laminated film. When the thermal hysteresis material is more than 40 percent by mass, the impact strength of the ONy film may be deteriorated.

In light of the impact strength and a prevention of the intra-layer separation, the Ny6 and the MXD6 is preferably contained in the thermal hysteresis material by a ratio of 60 to 85 parts by mass (Ny6): 15 to 40 parts by mass (MXD6) When a

- 50 content ratio of the MXD6 in the thermal hysteresis material is less than 15 parts by mass (i.e., a content ratio of the Ny6 is more than 85 parts by mass), the intra-layer separation of the ONy film may not be favorably prevented. When the content ratio of the MXD6 in the thermal hysteresis material is more than 40 parts by mass (i.e., the content ratio of the Ny6 is less than 60 parts by mass), the impact strength of the ONy film may be deteriorated.
- [0050] The ONy film according to the present embodiment is required to have a hydrothermal shrinkage factor of 3 to 20 percent in the MD direction and the TD direction of the film respectively (preferably 6 to 20 percent) when the film is retained in hot liquid of 95 degrees C for thirty minutes. With this arrangement, ONy film that is excellently stretchable during the forming operation as compared with general ONy film can be obtained, whereby the rupture of the ONy film and the formation of the pinhole can be prevented during, for example, the cool forming operation. When the hydrothermal

shrinkage factor of the film is less than 3 percent, there is no particular difference in the stretchability during the forming operation between the ONy film and general ONy film. On the other hand, when the hydrothermal shrinkage factor of the film is more than 20 percent, a delamination may occur between the ONy film and the other film layer when the other film layer is laminated to the ONy film to form the laminated packing material.

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[Manufacturing Method of ONy Film]

[0051] The ONy film according to the present embodiment can be obtained by biaxially orienting the unoriented raw film made from the material containing the virgin material and the thermal hysteresis material by a predetermined mixture ratio under the condition where the oriented ratio in each of the MD direction and the TD direction becomes 2.8 times or more and by heat-treating the oriented raw film at a temperature between 160 and 200 degrees C. The virgin material and the thermal hysteresis material are made from the Ny6 and the MXD6.

As a method of biaxial orienting, a simultaneous biaxial-orienting or a sequential biaxial-orienting such as a tubular method or a tenter method can be employed. However, in light of a strength balance between a lengthwise direction

- ¹⁵ and a widthwise direction, it is preferable to perform the simultaneous biaxial-orienting according to the tubular method. In order to prepare the Ny6 and the MXD6 contained in the virgin material, it is preferable to use and dry-blend pelleted Ny6 and pelleted MXD6. In addition, it is preferable to use pelleted thermal hysteresis material. For example, the pellets may be prepared by cutting the biaxially-oriented nylon film obtained according to the present embodiment into small pieces and compressing the cut film. With this arrangement, the thermal hysteresis material can be favorably dry-blended with the Ny6 pellets and the MXD6 pellets.
- [0052] Specifically, the ONy film according to the present embodiment can be manufactured as follows.
 After the Ny6 pellets, the MXD6 pellets and the pelleted thermal hysteresis material are melt-kneaded in an extruder at 270 degrees C, a molten material is extruded from a die in a shape of cylindrical film. The extruded molten material is subsequently quenched by water, whereby a raw film is obtained.
- Then, as exemplarily shown in Fig. 2, after inserted between the pair of nip rollers 12, the raw film 11 was heated by the heater 13 while a gas was injected into the raw film 11. The raw film 11 was applied with the air 15 from the air ring 14 at the drawing start point to be distended to form the bubble 16. By pulling the raw film 11 using the pair of nip rollers 17 provided at the downstream side, the simultaneous biaxial orienting in the MD direction and the TD direction according to the tubular method was performed. At this time, the oriented ratio in each of the MD direction and the TD direction is
- ³⁰ required to be 2.8 times or more. When the oriented ratio is less than 2.8 time, an impact strength is deteriorated, which is practically unfavorable. Subsequently, the oriented film is put into a tenter heat treat furnace (not shown) to be heat-fixed at 160 to 200 degrees C, whereby ONy film 18 according to the present embodiment is obtained.
- ³⁵ [Arrangement of Laminated Packing Material]

[0053] The laminated packing material according to the present embodiment is prepared in the same manner as in the first embodiment, a description of which is omitted.

- However, the laminated packing material according to the present invention contains the MXD 6 in the ONy film layer as well as the components of the laminated packing material according to the first embodiment, thereby exhibiting an excellent heat resistance. Accordingly, when the packing material includes a sealant layer, the packing material does not adhere to the seal bar when heated by the seal bar to be seal-treated, whereby a favorable seal-treatment is realized. According to the packing material, since the ONy film layer contains the thermal hysteresis material, no intra-layer separation occurs inside the ONy film layer during the cool forming operation, so that a molded article that is excellent
- ⁴⁵ in impact resistance can be obtained.

<Modification>

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[0054] Although the best arrangements etc. for implementing the present invention has been described in the first to ⁵⁰ third embodiments, the present invention is not limited thereto. In other words, while the present invention has been described with reference to the specific embodiments, various modifications may be made to the above described embodiments by those of ordinary skill in the art without departing from the spirit and scope of the invention.

Therefore, the description that limits the materials, the layer arrangements and the like is only an example to make the invention easily understood, but is not intended to limit the invention, so that the invention includes the description using a name without a part of or all of the limitation on the material etc.

[0055] For example, although the tubular method is employed as the method of biaxial orienting in the first to third embodiments, the tenter method may be used. In addition, the method of orienting may be performed by the simultaneous biaxial orienting or by the sequential biaxial orienting.

The ONy film may be added with any necessary additives as desired. Such additives exemplarily include an anti-blocking agent (such as inorganic filler), a water repellant (such as ethylene-bis-stearate ester) or a lubricant (such as calcium stearate).

Although the laminated packing material in which the aluminum layer etc. is laminated to the ONy film is exemplified in the above described embodiments, the arrangement is not limited thereto. In the laminated packing material according to the average and the average of the second second

to the present invention, various functional layers such as a sealant layer, an antistatic layer, a print layer, a barrier layer, a reinforcing layer and the like may be laminated.

[Example]

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[0056] Next, the first to third embodiments will be described in detail by reference to examples and comparative examples. It should be noted that the present invention is not limited to or by the examples described below.

<Examples of First Embodiment>

[Examples 1, 2 (not part of the present invention)]

(Manufacturing of Oriented Film)

- 20 [0057] After Ny6 pellets were melt-kneaded in an extruder at 270 degrees C, a molten material was extruded from a die in a shape of cylindrical film. The extruded molten material was subsequently quenched by water, whereby a raw film was obtained. As the Ny6, nylon 6 manufactured by Ube Industries, Ltd. [UBE NYLON 1023FD (trade name), relative viscosity: ηr = 3.6] was used.
- Then, as shown in Fig. 2, after inserted between the pair of nip rollers 12, the raw film 11 was heated by the heater 13 while a gas was injected into the raw film 11. The raw film 11 was applied with the air 15 from the air ring 14 at the drawing start point to be distended to form the bubble 16. By pulling the raw film 11 using the pair of nip rollers 17 provided at the downstream side, the simultaneous biaxial orienting in the MD direction and the TD direction according to the tubular method was performed. The oriented ratios at the time of the orienting were respectively 3.0 times (in the MD direction) and 3.2 times (in the TD direction).
- ³⁰ Subsequently, the oriented film was put into a tenter heat treat furnace (not shown) and heat-fixed at 210 degrees C, whereby ONy film 18 (hereinafter, also referred to as ONy film 18) according to the present examples was obtained. The ONy film was 15 μm thick in Example 1 while the ONy film was 25 μm thick in Example 2.

[Evaluation Method]

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(Tensile Test)

[0058] A tensile test of the ONy film 18 was conducted with a tester manufactured by Instron Corporation (Tester Type: 5564) under conditions: a sample with of 15mm, a distance between fasteners of 50mm; and a tensile speed of 100mm/min. Measurements were conducted on the ONy film 18 with respect to the MD direction, the TD direction, the 45 degrees direction and the 135 degrees direction. Based on the stress-strain curves obtained with respect to the directions of the ONy film, respective rupture elongation ratios (percent) in the directions, a ratio between a maximum value and a minimum value of the rupture elongation ratios, the respective stress ratios A in the directions (A = σ_1/σ_2 , in which σ_1 represents a tensile stress when the elongation rate is 50 percent while σ_2 represents a tensile stress at the

45 yield point) and the ratio between the maximum value A_{max} and the minimum value A_{min} of the stress ratios A were obtained.

(Drawing Formability)

50 [0059] Drawing formability of the laminated packing material including the ONy film 18 was evaluated.

Specifically, the laminated packing material was prepared by: using the ONy film 18 according to each of Examples 1 and 2 as a front base material film; using L-LDPE film (UNILAX LS-711C (trade name), manufactured by Idemitsu Unitech CO., LTD, thickness of 120 µm) as a sealant film; and dry-laminating the ONy film 18 and the L-LDPE film. As an adhesive for dry-laminating, a blend of TAKELAC A-615 and TAKENATE A-65 (both of which are manufactured by Mitsui

⁵⁵ Takeda Chemicals, Inc.) was used (blend ratio: 16/1). The laminated packing material after the films were dry-laminated experienced an aging treatment at 40 degrees C for three days.
 The laminated packing materials manufactured as described above experienced a cold deep-drawing (at a normal temperature), in which a rectangular die in plan view (5mm-by-10mm) was used. Each of the laminated packing materials

experienced the deep-drawing ten times, and the number of occurrences of a defect such as a pinhole, a crack and the like was examined. When no defect occurred in any of ten times deep-drawing, the laminated packing material was rated as A. When such a defect occurred one to two times out of ten times, the laminated packing material was rated as B, when three to five times, rated as C, and when six times or more, rated as D.

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(Piercing Strength)

[0060] A measurement of a piercing strength was conducted by: piercing the ONy film 18 with a needle of $1 \text{mm} \phi$ at a piercing speed of 200mm/min; and measuring a strength (N) required for the needle to pierce the film.

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(Impact Strength)

[0061] A measurement of an impact strength was conducted with a film impact tester (manufactured by Toyo Seiki Seisaku-sho, Ltd.) by: striking fixed ONy film 18 of a ring shape with a semispherical pendulum (diameter of 1/2 inch); and measuring an impact strength (kg/cm) required for punching the film. Incidentally, the impact strength is represented in absolute value. The larger the value is, the more excellent impact resistance of the film is evaluated to be.

[Comparative Example 1]

20 [0062] After the Ny6 pellets were melt-kneaded in the extruder at 270 degrees C, the molten material was extruded from T-die. The extruded molten material was subsequently contact-cooled by a chill roller, whereby unoriented raw film was manufactured. Incidentally, as the extruder, a single-screwed extruder of 50mm φ was used.

Next, the unoriented raw film was stretched to three times the original size in the MD direction while being heated at 100 degrees C by a heating roller of a stretching device (compact biaxial stretching device, manufactured by Nikkou Seisaku-sho Corporation). Immediately thereafter, the unoriented raw film was stretched to 3.2 times the original size in the TD direction with both ends thereof being grasped by a tenter device.

Then, the oriented film was put into a tenter heat treat furnace (not shown) and heat-fixed at 210 degrees C, whereby Ny film that was biaxially stretched in a sequential manner (thickness: 15μ m) according to Comparative Example 1 was obtained.

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[Comparative Example 2]

[0063] After the Ny6 pellets were melt-kneaded in the extruder at 270 degrees C, the molten material was extruded from T-die. The extruded molten material was subsequently contact-cooled by a chill roller, whereby unoriented raw film was manufactured. Incidentally, as the extruder, a single-screwed extruder of 50mm ϕ was used.

Then, using a biaxially stretching device (manufactured by Nikkou Seisaku-sho Corporation), the unoriented raw film was stretched to 3.0 times the original size both in the MD and TD directions while being heated at 120 degrees C. Additionally, the oriented film was heat-fixed by an oven at 210 degrees C, whereby Ny film that was biaxially stretched in a simultaneous manner (thickness: 15 µm) according to Comparative Example 2 was obtained.

⁴⁰ **[0064]** The same evaluation test was conducted on Comparative Examples 1 and 2 as was conducted on Examples 1 and 2.

Table 1 shows results of the tensile tests conducted on Examples 1 and 2 and Comparative Examples 1 and 2. Table 2 shows evaluation results of the drawing formability, the piercing strength and the impact strength observed in each of Examples 1 and 2 and Comparative Examples 1 and 2.

45 **[0065]**

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55	50	45	40	35	30	25	20	15	10	თ

			Rupture Elongation Ratio (%)					Stress Ratio A					Rupture Strength [MPa]				
	Thicknes s [μm]	MD	TD	45 degree s	135 degree s	Ratio max/mi n	MD	TD	45 degrees	135 degrees	Ratio Amax/ Amin	MD	TD	45 degrees	135 degrees	Ratio max/min	
Example 1*)	15	14 1	11 4	133	130	1.24	2.5	3.38	2.64	2.86	1.35	251	283	267	278	1.13	
Example 2 ^{*)}	25	15 5	10 9	137	120	1.42	2.11	3.77	2.65	2.82	1.79	265	299	284	262	1.14	
Comparativ e Example 1	15	87. 5	79. 4	79.4	98.5	1.24	2.8	2.89	4.21	1.9	2.2	228	225	342	170	2.01	
Comparativ e Example 2	15	12 7	66. 9	78	112	1.9	1.55	5.13	4.13	1.9	3.31	210	346	316	223	1.65	
*) not part of t	he present ir	iventio	n														

[Table 1]

[0066]

5		Drawing Formability	Piercing Strength
0	Example 1 ^{*)}	В	10
	Example 2 ^{*)}	В	15.4
	Comparative Example 1	D	9.5
10	Comparative Example 2	D	9.5

[Table 2]

Impact Strength [kg/cm] 23 degrees C

12.5

Not Break 💥 8.1

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★The film was not ruptured although measured as in Example 1.
*) not part of the present invention

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[Evaluation Result]

[0067] As shown in Table 1, the ONy film 18 according to Examples 1 and 2 is excellent in each of the deep-drawing formability, the piercing strength and the impact strength as compared with Comparative Examples 1 and 2.

20 On the other hand, since Comparative Examples do not satisfy the above-described conditions, there are problems with properties of the ONy film 18 according to each of Comparative Examples.

Specifically, according to Comparative Example 1, the stress ratio A in the 135 degrees direction is less than 2, the ratio (A_{max}/A_{min}) of the stress ratio A is more than 2, and the rupture strength in the 135 degrees direction is less than 180MPa. Thus, the film according to Comparative Example 1 exhibits an inferior drawing formability, a relatively low piercing strength and an inferior impact strength.

On the other hand, according to Comparative Example 2, the rupture elongation ratio in the TD direction is less than 70 percent, the stress ratios A in the MD and 135 degrees directions are less than 2, and the ratio (A_{max}/A_{min}) of the stress ratio A is more than 2. Thus, the film according to Comparative Example 2 exhibits an inferior drawing formability and a relatively low piercing strength.

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<Examples of Second Embodiment>

[0068] Next, the second embodiment will be described in detail by reference to examples and comparative examples. In the examples of the second embodiment, what has been already described in the examples of the preceding embodiment will not be repeated.

[Examples 3 to 5 (not part of the present invention)]

(Manufacturing of Oriented Film)

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[0069] an extrusion of Ny6 pellets and an orientation of film were performed as in Examples 1 and 2.

Subsequently, the oriented film was put into a tenter heat treat furnace (not shown) and heat-fixed at 195 degrees C, whereby ONy film 18 (hereinafter, also referred to as ONy film 18) according to Example 3 was obtained. A crystallinity degree of the film according to Example 3 was 33 percent and the film thickness was 15 μ m.

45 ONy film 18 according to Example 4 was manufactured under the same conditions as in Example 3 except that the oriented film was heat-fixed at 160 degrees C by the tenter test treat furnace. A crystallinity degree of the film according to Example 4 was 21 percent and the film thickness was 15 μm.

ONy film 18 according to Example 5 was manufactured in substantially the same conditions as in Example 3. A thickness of the ONy film 18 was 25 μ m and a crystallinity degree of the ONy film 18 was 33 percent.

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[Evaluation Method]

[0070] A tensile test and evaluation methods of a drawing formability and a piercing strength in the present embodiment were the same as in the first embodiment, a description of which is omitted.

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(Impact Strength)

[0071] A measurement of an impact strength was conducted with the film impact tester (manufactured by Toyo Seiki

Seisaku-sho, Ltd.) by: striking fixed ONy film 18 of a ring shape with the semispherical pendulum (diameter of 1/2 inch); and measuring an impact strength (kg/cm) required for punching the film. Incidentally, the impact strength is represented in absolute value. The larger the value is, the more excellent impact resistance of the film is evaluated to be.

5 [Comparative Example 3]

[0072] ONy film 18 according to Comparative Example 3 was manufactured under the same conditions as in Example 3 except that the oriented film was heat-fixed at 210 degrees C in the tenter heat treat furnace. A crystallinity degree of the film according to Comparative Example 3 was 41 percent and the film thickness was 15 μ m.

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[Comparative Example 4]

[0073] ONy film 18 according to Comparative Example 4 was manufactured under the same conditions as in Example 3 except that the oriented film was heat-fixed at 210 degrees C in the tenter heat treat furnace. A crystallinity degree of the film according to Comparative Example 4 was 40 percent and the film thickness was 15 μm.

[Comparative Example 5]

[0074] ONy film 18 according to Comparative Example 5 was manufactured under the same conditions as in Example
 5 except that the oriented film was heat-fixed at 210 degrees C in the tenter heat treat furnace. A crystallinity degree of the film according to Comparative Example 5 was 41 percent and the film thickness was 25 μm.

[0075] The same evaluation test was conducted on Comparative Examples 3 to 5 as was conducted on Examples 3 to 5. Table 3 shows the heat-treating temperature, the crystallinity degree, a hydrothermal shrinkage factor (a hydrothermal shrinkage factor of the film in the MD and TD directions when the film was retained in hot liquid of 95 degrees C for thirty minutes) and the film thickness respectively in Examples 3 to 5 and Comparative Examples 3 to 5. Table 4 shows results of the tensile tests conducted on Examples 3 to 5 and Comparative Examples 3 to 5. Table 5 shows evaluation results of the drawing formability, the piercing strength and the impact strength (23 degrees C, -10 degrees C and -30 degrees C) observed in each of Examples 3 to 5 and Comparative Examples 3 to 5.

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[0076]

			[Table 3]		
		Heat-Treating Temperature [°C]	Crystallinity Degree [%]	Hydrothermal Shrinkage Factor [%]	Thickness [µm]
35	Example 3 ^{*)}	195	33	5	15
	Example 4 ^{*)}	160	21	19	15
	Example 5 ^{*)}	195	33	5	25
40	Comparative Example 3	210	41	2	15
	Comparative Example 4	210	40	2	15
45	Comparative Example 5	210	41	2	25
	*)not part of the prese	ent invention	·		

[Table 3]

[0077]

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5 5 5 5 5 5 55 50 55 50 55 55

		Rupt	ure Elongat	ion Ratio (%	b)			Stress R	atio A		Rupture Strength [MPa]				
	MD	TD	45 degrees	135 degrees	Ratio max/min	MD	TD	45 degrees	135 degrees	Ratio Amax/ Amin	MD	TD	45 degrees	135 degrees	Ratio max/min
Example 3 ^{*)}	114	102	123	97	1.27	2.67	3.00	3.44	2.94	1.29	297	333	312	313	1.12
Example 4 ^{*)}	109	81	98	99	1.35	2.83	4.53	3.87	3.29	1.60	306	360	351	338	1.18
Example 5 ^{*)}	123	93	114	103	1.32	2.67	3.00	3.44	2.94	1.29	297	338	348	307	1.17
Comparative Example 3 Example 3	87.5	79.4	79.4	98.5	1.24	2.80	2.89	4.21	1.90	2.20	228	225	342	170	2.01
Comparative Example 4	141	114	133	130	1.24	2.50	3.38	2.64	2.86	1.35	251	283	267	278	1.13
Comparative Example 5	102	114	159	65	2.45	3.07	2.48	1.76	5.43	3.19	269	274	240	364	1.39
*)not part of the	e presen	t inventi	on												

[Table 4]

[0078]

			[Table 5]						
5		Drawing Formability	Piercing Strength [N]	Impact Strength [kg/cm]					
0		Drawing Formability		23°C	minus 10°C	minus 30°C			
	Example 3 *)	A	11.7	13.5	11.5	10.2			
	Example 4 *)	A	12	14.2	12.5	11.4			
10	Example 5 *)	A	17.4	Not Break 🔆	16.5	17.8			
	Comparative Example 3	D	9.5	8.1	6.5	5.8			
15	Comparative Example 4	С	10	12.5	10.2	7			
	Comparative Example 5	D	15.1	12.7	11	11.9			
20	✗"Not Break" means th [*])not part of the present	-	gh to withstand a rupture	е.					

[Table 5]

[Evaluation Result]

²⁵ **[0079]** As shown in Table 3, the ONy film 18 according to each of Examples 3 to 5 is excellent in each of the drawing formability, the piercing strength and the impact strength as compared with Comparative Examples 3 to 5. On the other hand, since Comparative Examples do not satisfy the above-described conditions, there are problems with properties of the ONy film 18 according to each of Comparative Examples.

Specifically, according to Comparative Example 3, the crystallinity degree is less than 20 percent, the stress ratio A in the 135 degrees direction is less than 2, the ratio (A_{max}/A_{min}) of the stress ratio A is more than 2, and the rupture strength in the 135 degrees direction is less than 180MPa. Thus, the film according to Comparative Example 3 has an inferior drawing formability, a relatively low piercing strength and an inferior impact strength.

According to Comparative Example 4, since the crystallinity degree is less than 20 percent, the film according to Comparative Example 4 has an inferior drawing formability.

- ³⁵ According to Comparative Example 5, the rupture elongation ratio in the 135 degrees direction is less than 70 percent, the value obtained by dividing the maximum elongation ratio by the minimum elongation ratio out of the elongation ratios in the four directions is more than 2, the stress ratio A in 45 degrees is less than 2 and the ratio (A_{max}/A_{min}) of the stress ratio A is more than 2. Thus, the film according to Comparative Example 5 has an inferior drawing formability.
- 40 <Examples of Third Embodiment>

[0080] Next, the Third embodiment, which is part of the present invention will be described in detail by reference to examples and comparative examples.

In the examples of the third embodiment, what has been already described in the examples of the preceding embodiments
 will not be repeated.

[Examples 6, 7 (part of the invention)]

(Manufacturing of Oriented Film)

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[0081] A mixture of Ny6 pellets and MXD6 pellets in which the pellets were mixed by a ratio of 70 parts by mass (Ny6) to 30 parts by mass (MXD6) was added with a thermal hysteresis material in a form of pellets by a ratio of 10 percent by mass of the total amount of the film forming material. In the thermal hysteresis material, the Ny6 and the MXD6 had been once melt-mixed by the aforesaid ratio of 70 parts by mass (Ny6) to 30 parts by mass (MXD6). After the dry-blended

⁵⁵ material was melt-kneaded in an extruder at 270 degrees C, a molten material was extruded from a die in a shape of cylindrical film. The extruded molten material was subsequently quenched by water, whereby a raw film was obtained. A melt point of the MXD6 was measured with a differential scanning calorimetry (DSC) (manufactured by PerkinElmer

Corporation) by raising a temperature from 50 degrees C to 280 degrees C at a speed of 10 degrees C per minute. In each of Examples, a value of the first run was employed as the melt point.

As the Ny6, nylon 6 (manufactured by Ube Industries, Ltd. [UBE nylon 1023FD (trade name), relative viscosity: $\eta r = 3.6$]) was used. As the MXD6, metaxylylene adipamide (manufactured by Mitsubishi Gas Chemical Company, INC., [MX nylon 6007 (trade mark), relative viscosity $\eta r = 2.7$]) was used.

- As the thermal hysteresis material, a material that had been extruded at 270 degrees C using a 40 ø EX single screw (manufactured by Yamaguchi Manufacture Works, LTD.) was used, the material containing the Ny6 and the MXD6 by the mixing ratio of 70 parts by mass to 30 parts by mass.
- Then, as shown in Fig. 2, after inserted between the pair of nip rollers 12, the raw film 11 was heated by the heater 13 while a gas was injected into the raw film 11. The raw film 11 was applied with the air 15 from the air ring 14 at the drawing start point to be distended to form the bubble 16. By pulling the raw film 11 using the pair of nip rollers 17 provided at the downstream side, the simultaneous biaxial orienting in the MD direction and the TD direction according to the tubular method was performed. The oriented ratios at the time of the orienting were respectively 3.0 times (in the MD direction) and 3.2 times (in the TD direction).
- ¹⁵ Subsequently, the oriented film was put into a tenter heat treat furnace (not shown) and heat-fixed at 200 degrees C, whereby ONy film 18 (hereinafter, also referred to as ONy film 18) according to Example 6 was obtained, the ONy film 18 having a thickness of 15 μm and a hydrothermal shrinkage factor of 3.4 percent.
- ONy film 18 according to Example 7 was manufactured under the same conditions as in Example 6 except that the thermal hysteresis material was added by 20 percent by mass of the total amount of the film forming material and that the oriented film was heat-fixed in the tenter heat treat furnace at 160 degrees C. A crystallinity degree of the film
- according to Example 7 was 19 percent and the film thickness was 15 μ m.

[Evaluation Method]

²⁵ **[0082]** A tensile test and an evaluation method of a drawing formability in the present embodiment were the same as in the first embodiment, a description of which is omitted.

(Inner Separation)

- 30 [0083] A laminated packing material was prepared in a manner as described in the section of the evaluation method of the drawing formability. Stripe specimens of 15 mm width were cut off from the laminated packing material. Each end thereof was boundary-separated by hands by several centimeters, such that a front base material film (ONy film 18) and a sealant film were separated. Subsequently, the film specimens each were set in a tension tester (Instron Universal Tester, Type: 1123) to experience a separation test for laminated portions at a speed of 300 mm per minute (90 degrees
- 35 separation).

Since a peel-strength is dramatically degraded when an intra-layer separation occurs inside the front base material film during the separation test, the occurrence of the intra-layer separation can be determined by observing whether or not such a behavior is present. For example, when the peel-strength radically decreases from approximately 7N/m (value when the separation test is started) to approximately 1 to 2N/m in the middle of the separation test, an occurrence of an intra-layer separation can be determined.

Then, film that had showed no behavior of intra-layer separation inside the front base material film was rated as "B" while film that had showed a behavior of intra-layer separation was rated as "D".

- (Seal Resistance)
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[0084] A laminated packing material was prepared in a manner as described in the section of the evaluation method of the drawing formability. The laminated packing material was seal-treated. The seal-treatment was conducted under the following conditions: a temperature of a seal bar was 200 degrees C; a seal with was 5mm (no teflon (Registered Trademark) tape was attached); a sealing time was 10 seconds; and a pressure by the seal bar was 2kg/cm². In evaluating

- 50 the seal resistance of laminated packing materials, laminated materials that had not adhered to the seal bar when sealtreated under the above-described conditions were rated as "B", laminated materials that had adhered to the seal bar at that time were rated as "C", and laminated materials that had adhered to the seal bar to experience an appearance whitening at that time were rated as "D".
- 55 [Comparative Example 6]

[0085] ONy film 18 according to Comparative Example 6 was manufactured under the same conditions as in Example 6 except that thermal hysteresis material was contained by 15 percent by mass of the total amount of the film forming

material and that the oriented film was heat-fixed at 210 degrees C in the tenter heat treat furnace. A hydrothermal shrinkage factor of the film according to Comparative Example 6 was 2.8 percent and the film thickness was 15 μ m.

[Comparative Example 7]

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[0086] ONy film 18 according to Comparative Example 7 was manufactured under the same conditions as in Example 6 except that only Ny6 was used in the film forming material and that the oriented film was heat-fixed at 195 degrees C in the tenter heat treat furnace. A hydrothermal shrinkage factor of the film according to Example 7 was 5 percent and the film thickness was 15 μ m.

¹⁰ **[0087]** The same evaluation test was conducted on Comparative Examples 6 and 7 as was conducted on Examples 6 and 7.

Table 6 shows the film forming material, the content of the thermal hysteresis material, the heat-treating temperature and the hydrothermal shrinkage factor of Examples 6 and 7 and Comparative Examples 6 and 7. Table 7 shows results of the tensile tests conducted on Examples 6 and 7 and Comparative Examples 6 and 7. Table 8 shows evaluation

results of the drawing formability, the inner-separation and the seal resistance observed in each of Examples 6 to 7 and Comparative Examples 6 to 7.
 [0088]

				[Table (6]		
20		Material [% by mass]	Thermal			
25		Ny6	MXD6	Hysteresis Material Content [% by mass]	Heat-Treating Temperature [°C]	Hydrothermal Shrinkage Factor [%]	Thickness [μm]
20	Example 6	70	30	10	200	3.4	15
	Example 7	70	30	20	160	19	15
30	Comparative Example 6	70	30	15	210	2.8	15
	Comparative Example 7	100	0	0	195	5	15

₃₅ [0089]

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5 40 3 20 10 5 55 50 40 35 20 15 10

		Rup	ture Elonga	tion Ratio (%	%)	Stress Ratio A						Rupture Strength [MPa]					
	MD	TD	45 degrees	135 degrees	Ratio max/min	MD	TD	45 degrees	135 degrees	Ratio Amax/ Amin	MD	TD	45 degrees	135 degrees	Ratio max/min		
Example 6	100	103	112	101	1.12	2.75	2.63	2.50	2.59	1.10	296	286	292	295	1.04		
Example 7	86	94	88	93	1.09	3.65	3.10	2.80	2.50	1.46	338	306	316	326	1.10		
Comparative Example 6	103	119	119	116	1.16	2.42	1.90	1.74	2.05	1.39	240	208	236	223	1.15		
Comparative Example 7	114	102	123	97	1.27	2.67	3.00	3.44	2.94	1.29	297	333	312	313	1.12		

[Table 7]

[0090]

	Drawing Formability	Intra-Layer Separation	Seal Resistance	
Example 6	A	В	В	
Example 7	A	В	В	
Comparative Example 6	D	В	В	
Comparative Example 7	A	В	D	

[Table 8]

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[Evaluation Result]

- [0091] As shown in Table 6, the ONy film 18 according to Examples 6 and 7 is excellent in each of the drawing formability, the inner-separation and the seal resistance as compared with Comparative Examples 6 to 7. On the other hand, since Comparative Examples do not satisfy the above-described conditions, there are problems with properties of the ONy film 18 according to each of Comparative Examples. Specifically, according to Comparative Example 6, since the stress ratios in the TD and 45 degrees directions are less than 2 percent, the film according to Comparative Example 6 is inferior in the drawing formability. The film according to Comparative Example 7, which does
- not contain MXD6 in the film forming material, is inferior in the seal resistance.

Industrial Applicability

[0092] The invention is applicable to biaxially-oriented nylon film, a laminated pa cking material and a manufacturing method for the biaxially-oriented nylon film, and can be utilized for packing material used in cool-forming etc.

Claims

- 30
- 1. Biaxially-oriented nylon film made from nylon 6, wherein an elongation ratio of the film measured in a tensile test in each of a direction in which the film is moved, a direction of a film width, a 45 degree direction and a 135 degree direction until a film rupture is 70 percent or more, the elongation ratio being measured under conditions of a sample width being 15 mm; a distance between gauge points being 50 mm; and a tensile speed being 100 mm/min
- being 50 mm; and a tensile speed being 100 mm/min a stress ratio A (σ_1/σ_2) between a tensile stress σ_1 and a tensile stress σ_2 in a stress-strain curve obtained in the tensile test of the film is 2 or more in each of the four directions, the tensile stress σ_1 being a value at a point where the elongation ratio becomes 50 percent while the tensile stress σ_2 being a value at an yield point,
- the film is made from a film forming material that contains a virgin material and a thermal hysteresis material, the virgin material being formed of nylon 6 and metaxylylene adipamide, the thermal hysteresis material being obtained by melt-kneading nylon 6 and metaxylylene adipamide and by setting the metaxylylene adipamide to have a melt point of 233 to 238 degrees C, and

a hydrothermal shrinkage factor of the film is 3 to 20 percent in each of the direction in which the film is moved and the direction of the film width when the film is retained in hot liquid of 95 degrees C for thirty minutes.

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- 2. The biaxially-oriented nylon film according to Claim 1, wherein a crystallinity degree of the film is in a range of 20 to 38 percent.
- 3. The biaxially-oriented nylon film according to Claim 1, wherein
 - nylon 6 and metaxylylene adipamide are contained in the virgin material by ratios of 60 to 85 parts by mass and 15 to 40 parts by mass respectively, and

a content of the thermal hysteresis material is 5 to 40 percent by mass of the total amount of the film forming material.

- 4. The biaxially-oriented nylon film according to Claim 1 or 3, wherein the nylon 6 and the metaxylylene adipamide are contained in the thermal hysteresis material by ratios of 60 to 85 parts by mass and 15 to 40 parts by mass respectively.
- 5. The biaxially-oriented nylon film according to any one of Claims 1 to 4, wherein a ratio (A_{max}/A_{min}) between a maximum stress ratio A_{max} and a minimum stress ratio A_{min} of the stress ratios A obtained with respect to the four

directions is 2 or less.

- 6. The biaxially-oriented nylon film according to any one of Claims 1 to 5, wherein a tensile-rupture strength of the film in each of the four directions measured in the tensile test of the film is 180 MPa or more.
- 7. A laminated packing material, comprising the biaxially-oriented nylon film according to any one of Claims 1 to 6.
- **8.** A manufacturing method of biaxially-oriented nylon film made from a film forming material that contains nylon 6, comprising:

biaxially-orienting unoriented raw film made from the nylon 6 under a condition where an oriented ratio of the film in each of a direction in which the film is moved and a direction of a film width becomes 2.8 times or more; and heat-treating the raw film at a temperature between 160 and 200 degrees C to manufacture biaxially-oriented nylon film, wherein

- a crystallinity degree of the film is in a range of 20 to 38 percent,
 an elongation ratio of the film measured in a tensile test in each of the direction in which the film is moved, the
 direction of the film width, a 45 degree direction and a 135 degree direction until a film rupture is 70 percent or
 more, the elongation ratio being measured under conditions of: a sample width being 15 mm; a distance between
 gauge points being 50 mm; and a tensile speed being 100 mm/min,
- ²⁰ a stress ratio A (σ_1/σ_2) of a tensile stress σ_1 and a tensile stress σ_2 in a stress-strain curve obtained in the tensile test of the film is 2 or more in each of the four directions, the tensile stress σ_1 being a value at a point where the elongation ratio becomes 50 percent while the tensile stress σ_2 being a value at an yield point,
- the film is made from a film forming material that contains a virgin material and a thermal hysteresis material, the virgin material being formed of nylon 6 and metaxylylene adipamide, the thermal hysteresis material being
 obtained by melt-kneading nylon 6 and metaxylylene adipamide and by setting the metaxylylene adipamide to have a melt point of 233 to 238 degrees C, and

a hydrothermal shrinkage factor of the film is 3 to 20 percent in each of the direction in which the film is moved and the direction of the film width when the film is retained in hot liquid of 95 degrees C for thirty minutes.

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Patentansprüche

1. Aus Nylon 6 hergestellte biaxial orientierte Nylonfolie, wobei

ein Dehnungsverhältnis der Folie, gemessen in einem Zugversuch in jeweils einer Richtung, in der die Folie bewegt
 ³⁵ wird, einer Richtung einer Folienbreite, einer Richtung von 45 Grad und einer Richtung von 135 Grad, bis zum
 Reißen einer Folie, 70 % oder mehr beträgt, wobei das Dehnungsverhältnis unter Bedingungen gemessen wird,
 unter denen eine Probenbreite 15 mm beträgt; ein Abstand zwischen den Messpunkten 50 mm beträgt und eine
 Zuggeschwindigkeit 100 mm/min beträgt,

ein Spannungsverhältnis A (σ_1/σ_2) zwischen einer Zugspannung σ_1 und einer Zugspannung σ_2 , in einer im Zugversuch der Folie erhaltenen Spannungs-DehnungsKurve in jeder der vier Richtungen, 2 oder mehr beträgt, wobei die Zugspannung σ_1 ein Wert an einem Punkt ist, an dem das Dehnungsverhältnis 50 % erreicht, während die Zugspannung σ_2 ein Wert an einem Streckgrenzpunkt ist,

die Folie aus einem folienbildenden Material hergestellt wird, das ein Frischmaterial und ein thermisches Hysterese-Material enthält, wobei das Frischmaterial aus Nylon 6 und Metaxylylenadipamid gebildet wird, wobei das thermische

- 45 Hysterese-Material durch Schmelzkneten von Nylon 6 und Metaxylylenadipamid und durch Einstellen des Metaxylylenadipamids dergestalt erhalten wird, dass es einen Schmelzpunkt von 233 bis 238 °C aufweist, und ein hydrothermaler Schrumpffaktor der Folie in jeweils der Richtung, in der die Folie bewegt wird, und der Richtung der Folienbreite, wenn die Folie 30 Minuten in einer heißen Flüssigkeit von 95 °C zurückgehalten wird, 3 bis 20 % beträgt.
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- 2. Biaxial orientierte Nylonfolie nach Anspruch 1, wobei ein Kristallinitätsgrad der Folie im Bereich von 20 bis 38 % liegt.
- **3.** Biaxial orientierte Nylonfolie nach Anspruch 1, wobei Nylon 6 und Metaxylylenadipamid in dem Frischmaterial in Verhältnissen von 60 zu 85 Masseteilen bzw. 15 zu 40 Masseteilen enthalten sind, und
- ein Gehalt des thermischen Hysterese-Materials 5 bis 40 Masse-% bezogen auf die Gesamtmenge des folienbildenden Materials beträgt.
 - 4. Biaxial orientierte Nylonfolie nach Anspruch 1 oder 3, wobei das Nylon 6 und das Metaxylylenadipamid in dem

thermischen Hysterese-Material in Verhältnissen von 60 zu 85 Masseteilen bzw. 15 zu 40 Masseteilen enthalten sind.

- Biaxial orientierte Nylonfolie nach einem der Ansprüche 1 bis 4, wobei ein Verhältnis (A_{max}/A_{min}) zwischen einem maximalen Spannungsverhältnis A_{max} und einem minimalen Spannungsverhältnis A_{min} der bezogen auf die vier Richtungen erhaltenen Spannungsverhältnisse A, 2 oder weniger beträgt.
- 6. Biaxial orientierte Nylonfolie nach einem der Ansprüche 1 to 5, wobei eine Zug-Reißfestigkeit der Folie, in jeder der im Zugversuch der Folie gemessenen vier Richtungen, 180 MPa oder mehr beträgt.
- 10 7. Laminiertes Verpackungsmaterial, umfassend die biaxial orientierte Nylonfolie nach einem der Ansprüche 1 bis 6.
 - 8. Herstellungsverfahren einer biaxial orientierten Nylonfolie, die aus einem folienbildenden Material hergestellt wird, das Nylon 6 enthält, umfassend:
- eine biaxial orientierende nicht orientierte Rohfolie, die aus Nylon 6 unter einer Bedingung hergestellt wird, unter der ein Verhältnis der orientierten Folie in jeweils einer Richtung, in der die Folie bewegt wird, und einer Richtung einer Folienbreite, 2,8-mal oder mehr erreicht; und
 Wärmebehandlung der Rohfolie bei einer Temperatur zwischen 160 und 200 °C zur Herstellung einer biaxial
- orientierten Nylonfolie, wobei
 ein Kristallinitätsgrad der Folie in einem Bereich von 20 bis 38 % liegt,
 ein Dehnungsverhältnis der Folie, gemessen in einem Zugversuch in jeweils der Richtung, in der die Folie
 bewegt wird, der Richtung der Folienbreite, einer Richtung von 45 Grad und einer Richtung von 135 Grad, bis
 zum Reißen der Folie, 70 % oder mehr beträgt, wobei das Dehnungsverhältnis unter Bedingungen gemessen
 wird, unter denen eine Probenbreite 15 mm beträgt; ein Abstand zwischen den Messpunkten 50 mm beträgt
 und eine Zuggeschwindigkeit 100 mm/min beträgt,
- ein Spannungsverhältnis A (σ_1/σ_2) einer Zugspannung σ_1 und einer Zugspannung σ_2 , in einer im Zugversuch der Folie erhaltenen Spannungs-Dehnungskurve in jeder der vier Richtungen, 2 oder mehr beträgt, wobei die Zugspannung σ_1 ein Wert an einem Punkt ist, an dem das Dehnungsverhältnis 50 % erreicht, während die Zugspannung σ_2 ein Wert an einem Streckgrenzpunkt ist,
- 30 die Folie aus einem folienbildenden Material hergestellt wird, das ein Frischmaterial und ein thermisches Hysterese-Material enthält, wobei das Frischmaterial aus Nylon 6 und Metaxylylenadipamid gebildet wird, wobei das thermische Hysterese-Material durch Schmelzkneten von Nylon 6 und Metaxylylenadipamid und durch Einstellen des Metaxylylenadipamids dergestalt erhalten wird, dass es einen Schmelzpunkt von 233 bis 238 °C aufweist, und
- ein hydrothermaler Schrumpffaktor der Folie in jeweils der Richtung, in der die Folie bewegt wird, und der Richtung der Folienbreite, wenn die Folie 30 Minuten in einer heißen Flüssigkeit von 95 °C zurückgehalten wird, 3 bis 20 % beträgt.

40 Revendications

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- 1. La présente invention concerne un film de nylon à orientation biaxiale composé de nylon 6, dans lequel
- un rapport d'allongement du film mesuré dans un essai de traction dans chacune d'une direction vers laquelle le film est déplacé, une direction d'une largeur du film, une direction de 45 degrés et une direction de 135 degrés
 ⁴⁵ jusqu'à ce qu'une rupture du film est de 70 pour cent ou davantage, le rapport d'allongement étant mesuré sous des conditions de : une largeur d'échantillon étant de 15 mm ; une distance entre les points de jaugeage étant de 50 mm ; et une vitesse de traction étant de 100 mm/min,

un rapport de contrainte A (σ_1/σ_2) entre une tension de traction σ_1 et une tension de traction σ_2 dans une courbe contrainte-déformation obtenue dans l'essai de traction du film est de 2 ou davantage dans chacune des quatre directions, la tension de traction σ_1 étant une valeur à un point où le rapport d'allongement devient 50 pour cent, la tension de contrainte σ_2 étant quant à elle une valeur à une limite d'élasticité,

le film est composé d'un matériau de formation de film qui contient un matériau vierge et un matériau d'hystérèse thermique, le matériau vierge étant formé de nylon 6 et de métaxylylène adipamide, le matériau d'hystérèse thermique étant obtenu par malaxage à l'état fondu du nylon 6 et du métaxylylène adipamide et par régulation du métaxylylène adipamide de manière à ce qu'il ait un point de fusion de 233 à 238 degrés C, et

un facteur de rétrécissement hydrothermique du film est de 3 à 20 pour cent dans chacune de la direction dans laquelle le film est déplacé et de la direction de la largeur du film lorsque le film est maintenu dans un liquide chaud de 95 degrés C pendant 30 minutes.

- 2. Film de nylon à orientation biaxiale selon la Revendication 1, dans lequel un degré de cristallinité du film se situe dans la plage de 20 à 38 pour cent.
- 3. Film de nylon à orientation biaxiale selon la Revendication 1, dans lequel le nylon 6 et le métaxylylène adipamide sont contenus dans le matériau vierge selon des rapports de 60 à 85 parties en masse et de 15 à 40 parties en masse respectivement, et un contenu du matériau d'hystérèse thermique est de 5 à 40 pour cent en masse de la quantité totale du matériau de formation de film.
- 10 4. Film de nylon à orientation biaxiale selon la Revendication 1 ou 3, dans lequel le nylon 6 et le métaxylylène adipamide sont contenus dans le matériau d'hystérèse thermique selon des rapports de 60 à 85 parties en masse et de 15 à 40 parties en masse respectivement.
- Film de nylon à orientation biaxiale selon l'une quelconque des Revendications 1 à 4, dans lequel un rapport
 (A_{max}/A_{min}) entre un rapport de contrainte maximale A_{maxi} et un rapport de contrainte minimale A_{mini} des rapports de contrainte A obtenus par rapport aux quatre directions est de 2 ou inférieur.
 - 6. Film de nylon à orientation biaxiale selon l'une quelconque des Revendications 1 à 5, dans lequel la résistance à la rupture en traction du film dans chacune des quatre directions mesurées dans le test de traction est de 180 MPa ou supérieure.
 - 7. Matériau d'emballage stratifié, comprenant le film de nylon à orientation biaxiale selon l'une quelconque des Revendications 1 à 6.
- **8.** Procédé de fabrication d'un film de nylon à orientation biaxiale composé d'un matériau de formation de film qui contient du nylon 6, comprenant :
 - un film brut non orienté à orientation biaxiale composé de nylon 6 sous une condition selon laquelle un rapport orienté du film dans chacune d'une direction dans laquelle le film est déplacé et une direction d'une largeur de film devient 2,8 fois ou supérieure ; et
 - le traitement thermique du film brut à une température comprise entre 160 et 200 degrés C pour fabriquer le film de nylon à orientation biaxiale, dans lequel

un degré de cristallinité du film se situe dans la plage de 20 à 38 pour cent,

- un rapport d'allongement du film mesuré dans un test de traction dans chacune de la direction vers laquelle le film est déplacé, la direction de la largeur du film, une direction de 45 degrés et une direction de 135 degrés jusqu'à ce qu'une rupture du film est de 70 pour cent ou davantage, le rapport d'allongement étant mesuré sous des conditions de : une largeur d'échantillon étant de 15 mm ; ; une distance entre les points de jaugeage étant de 50 mm ; et une vitesse de traction étant de 100 mm/min,
- ⁴⁰ un rapport de contrainte A (σ_1/σ_2) d'une tension de traction σ_1 et d'une tension de traction σ_2 dans une courbe ⁴⁰ contrainte-déformation obtenue dans l'essai de traction du film est de 2 ou davantage dans chacune des quatre directions, la tension de traction σ_1 étant une valeur à un point où le rapport d'allongement devient 50 pour cent, la tension de contrainte σ_2 étant quant à elle une valeur à une limite d'élasticité,

le film est composé d'un matériau de formation de film qui contient un matériau vierge et un matériau d'hystérèse
 thermique, le matériau vierge étant formé de nylon 6 et de métaxylylène adipamide, le matériau d'hystérèse
 thermique étant obtenu par malaxage à l'état fondu du nylon 6 et du métaxylylène adipamide et par régulation
 du métaxylylène adipamide de manière à ce qu'il ait un point de fusion de 233 à 238 degrés C, et

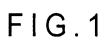
un facteur de rétrécissement hydrothermique du film est de 3 à 20 pour cent dans chacune de la direction dans laquelle le film est déplacé et de la direction de la largeur du film lorsque le film est maintenu dans un liquide chaud de 95 degrés C pendant 30 minutes.

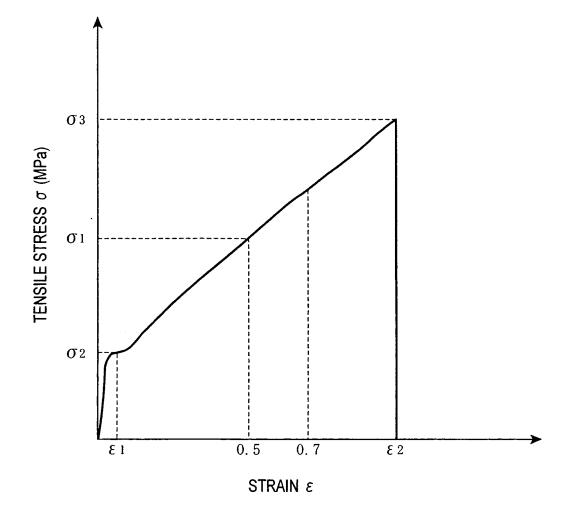
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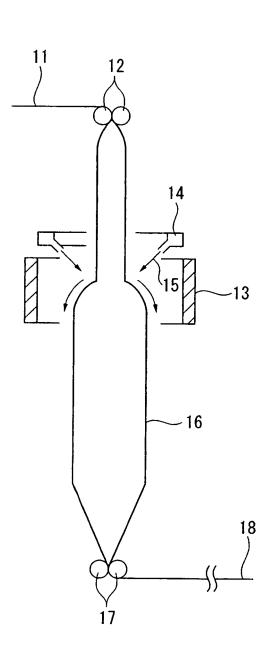
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REFERENCES CITED IN THE DESCRIPTION

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