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(54) **MONOFILAMENTS OR STRETCHED TAPES FROM METALLOCENE-PRODUCED POLYETHYLENE**

MONOFILAMENTE UND GESTRECKTE BÄNDER AUS METALLOCENKATALISIERTEM POLYETHYLEN

MONOFILAMENTS ET RUBANS PRODUITS D'UN POLYETHYLENE CATALYSE PAR METALLOCENE

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**EP-A- 0 483 780 EP-A- 0 608 137**  
**EP-A1- 0 943 633 EP-A2- 0 899 278**  
**WO-A-99/65949 US-B1- 6 512 029**

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- **PATENT ABSTRACTS OF JAPAN vol. 1999, no. 12, 29 October 1999 (1999-10-29) -& JP 11 200176 A (HAGIWARA KOGYO KK), 27 July 1999 (1999-07-27)**
- **PATENT ABSTRACTS OF JAPAN vol. 1999, no. 01, 29 January 1999 (1999-01-29) -& JP 10 273848 A (MORISHITA KAGAKU KOGYO KK), 13 October 1998 (1998-10-13)**
- **KOKKO E ET AL.: "Influence of the Catalyst and Polymerization Conditions on the Long-Chain Branching of Metallocene-Catalyzed Polyethenes", JOURNAL OF APPLIED POLYMER SCIENCE, JOHN WILEY AND SONS INC. NEW YORK, US, vol. 38, no. 2, 21 January 2000 (2000-01-21), pages 376-388, ISSN: 1099-0518, DOI: 10.1002/(SICI)1099-0518(20000115)38:2<376::AID-POLA12>3.0.CO;2-5**
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## Description

**[0001]** This invention relates to the field of monofilaments and stretched tapes prepared with metallocene-produced polyethylene.

**[0002]** Monofilaments are uniaxially oriented wire-like polymer strands having a circular cross section. They are manufactured by melt spinning process and their size ranges from 0.1 to 2.5 mm in diameter, depending upon the end use application. Polyethylene, polypropylene, nylon and polyesters are commonly used as raw materials for making monofilaments.

**[0003]** Stretched tapes are prepared from a primary film produced either by a blown or by a cast film process. The film can be cut into tapes and then oriented or reversely, oriented and then cut into tapes. The orientation is carried out by stretching the film or tapes while passing through an air oven or on a hot plate at a temperature below the melting point. The stretching is carried out by passing the film or tapes over two sets of rollers placed respectively before and after the air oven/hot plate and operating at different speeds, the speed of the second set of rollers being larger than that of the first set of rollers.

**[0004]** The polymer preferably used in the market for these applications is a high density polyethylene (HDPE) prepared with a Ziegler-Natta catalyst, said HDPE having a MI2 smaller than 1 g/10min such as for example Solvay Eltex A4009MFN1325 resin or Basell Hostalen GF 7740 F1, GF7740 F2, GF7740 F3, GF7750 M2 grades or the polyethylene resins disclosed in GB-0023662. The molecular weight distribution MWD of these resins is quite broad which means that the resins may include very long as well as very short chains.

**[0005]** JP 11-201,176 A discloses a shrinkable packaging material obtained by weaving a flat yam comprising an ethylene- $\alpha$ -olefin copolymer having a 0.90 - 0.93 g/cm<sup>3</sup> density and produced by using a metallocene catalyst.

**[0006]** Semi-crystalline polyethylene (PE) and polypropylene (PP) have also been used as materials for monofilaments stretched tapes and raffia, such as disclosed for example in FR-A-2814761, JP-2001342209 or JP-2001220405. Throughout this description, raffia is defined as woven monofilaments or woven stretched tapes. The stretched tapes and monofilaments prepared with polyethylene exhibit a higher elongation at rupture, a greater flexibility and a lower tendency to fibrillation than those prepared from polypropylene. These properties are advantageous for example in the production of woven tape fabrics. The products prepared from polyethylene however suffer from the disadvantage their tenacity is much lower than that of the products prepared from polypropylene. Tenacity increases as a function of molecular weight, density, degree of orientation of the chains/crystallites and increases with narrowing of the molecular weight distribution. Impact strength increases with decreasing density, increasing molecular weight and decreasing molecular weight distribution.

**[0007]** There is thus a need for monofilaments or stretched tapes, unwoven or woven into raffia having a better balance of properties.

**[0008]** It is an object of the present invention to prepare monofilament or stretched tape products having high tenacity.

**[0009]** It is another object of the present invention to prepare monofilament or stretched tape-products having high impact strength.

**[0010]** It is also an object of the present invention to prepare monofilament or stretched tape products having high elongation at rupture.

**[0011]** It is a further object of the present invention to prepare monofilament or stretched tape products having a soft touch.

**[0012]** It is yet another object of the present invention to prepare monofilament or stretched tape products having great flexibility.

**[0013]** Accordingly the present invention provides monofilaments or stretched tapes, unwoven or woven into raffia prepared from metallocene-produced polyethylene (mPE) resin having long chain branches, and a density of from 0.930 to 0.950 g/cm<sup>3</sup>, wherein the metallocene component is a bis-indenyl represented by the general formula



wherein (Ind) is an indenyl or an hydrogenated indenyl, substituted or unsubstituted, R'' is a structural bridge between the two indenyls to impart stereorigidity that comprises a C<sub>1</sub>-C<sub>4</sub> alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical, which bridge is substituted or unsubstituted; Q is a hydrocarbyl radical having from 1 to 20 carbon atoms or a halogen, and M is a group IVb transition metal or vanadium.

**[0014]** The preferred metallocene catalyst component is based on a tetrahydroindenyl component or on a constrained geometry component, more preferably on a tetrahydroindenyl component.

**[0015]** The invention also provides a process for preparing the above mentioned raffia or stretched tapes with a metallocene-produced polyethylene that comprises the steps of:

- a) providing a metallocene-produced medium density polyethylene resin having long chain branches, wherein the

metallocene component is a bis-indenyl represented by the general formula



wherein (Ind) is an indenyl or an hydrogenated indenyl, substituted or unsubstituted, R'' is a structural bridge between the two indenyls to impart stereorigidity that comprises a C<sub>1</sub>-C<sub>4</sub> alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical, which bridge is substituted or unsubstituted; Q is a hydrocarbyl radical having from 1 to 20 carbon atoms or a halogen, and M is a group IVb transition metal or vanadium;

b) producing a film from the polyethylene resin of step a)

c) orienting the film obtained from step b) by stretching;

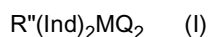
d) cutting the stretched film of step c) into strips;

e) optionally, annealing the stretched tapes.

**[0016]** Alternatively, the primary film can first be cut into strips and then oriented by stretching.

**[0017]** The present invention also provides a process for preparing the above mentioned raffia or stretched tapes that comprises the steps of

a) providing a metallocene-produced medium density polyethylene resin having long chain branches wherein the metallocene component is a tetrahydroindenyl bis-indenyl represented by the general formula



wherein (Ind) is an indenyl or a hydrogenated indenyl, substituted or unsubstituted, R'' is a structural bridge between the two indenyls to impart stereorigidity that comprises a C<sub>1</sub>-C<sub>4</sub> alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical, which bridge is substituted or unsubstituted; Q is a hydrocarbyl radical having from 1 to 20 carbon atoms or a halogen, and M is a group IVb transition metal or vanadium;

b) producing a film from the polyethylene resin of step a)

c) cutting the film obtained from step b) into strips;

d) orienting the strips of film of step c) by stretching;

e) optionally annealing the stretched tapes.

**[0018]** The film can be either a blown film or a cast film. Film production is easier with processed material having high melt strength such as polyethylene having long chain branches and/or very long linear chains. Metallocene catalyst systems based on tetrahydroindenyl components or on constrained geometry components are particularly useful for preparing polyethylene resins having long branches.

**[0019]** In the production of blown films, the resins prepared with a tetrahydroindenyl catalyst component provide a very stable bubble thereby leading to films having a uniform thickness and presenting no or very little creases. Uneven thickness and creases are points of weakness when the film is cut into tapes and stretched.

**[0020]** In the production of cast films, the resins prepared with a tetrahydroindenyl catalyst component have a stable elongational viscosity leading to a stable and regular thickness.

**[0021]** It is further observed that resins having long branches keep good mechanical properties, such as traction resistance and tenacity, at densities smaller than those of linear resins having equivalent mechanical properties. Working at low densities has the advantage of providing material that has improved flexibility, low fusion temperature and good processability.

**[0022]** Orientation of the primary film or of the cut tapes is carried out by stretching while passing through an air oven or over a hot plate, maintained at a temperature below the melting temperature. Stretching of the primary film or of the cut tapes is done by passing said film or tapes over two sets of rollers (godet rollers) placed respectively before and after the air oven/hot plate, and operating at different speeds. The stretch ratio S<sub>2</sub>/S<sub>1</sub> is defined by the ratio of the speed of roller 2, S<sub>2</sub> to the speed of roller 1, S<sub>1</sub> wherein S<sub>2</sub> is larger than S<sub>1</sub>.

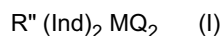
**[0023]** Stretching at such high temperature results in chain/crystals orientation with a simultaneous increase of crystallinity. These structural changes lead to an increase of tensile strength and concurrently to a reduction of elongation. The tensile strength increases with increasing stretch ratio and with increasing stretching temperature. It is preferred that the stretching temperature is as close as possible to but smaller than the melting temperature. For high density polyethylene, typical values for the stretch ratio are of from 5.0 to 7.0. The typical stretching temperatures depend upon the melting temperature of the polyethylene resins: they must be lower than but as close as possible to the melting temperature. Typically, they are from 5 to 70 °C lower than the melting temperature of the resin, preferably they are from 10 to 50 °C lower than the melting temperature of the resin.

**[0024]** Preferably, the drawn tapes are annealed immediately after the stretching operation in order to minimise shrink-

age that could occur as a result of residual stresses in the oriented tapes. Annealing is done by heating the stretched tapes while they are being transferred from the second goddet rollers onto a third roller having a speed S3 that is smaller than the speed of roller 2, S2. Preferably, speed S3 is about 95 % of speed S2. The annealing ratio AR is defined as (S2-S3)/S2 at a temperature slightly inferior to the stretching temperature. Typically, the annealing temperature is from

5 to 10 °C lower than the stretching temperature.  
**[0025]** Polymers that do not include either very long linear chains or long chain branched molecules have a better stretchability. For example, the low density polyethylene (LDPE) having long chain branches cannot be stretched beyond a certain degree, whereas the purely linear polyethylene chains usually obtained with a Ziegler-Natta catalyst have a high degree of stretchability.

10 **[0026]** The metallocene used to prepare the high density polyethylene is a bis-indenyl represented by the general formula:



15 wherein (Ind) is an indenyl or an hydrogenated indenyl, substituted. or unsubstituted, R'' is a structural bridge between the two indenyls to impart stereorigidity that comprises a C<sub>1</sub>-C<sub>4</sub> alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical, which bridge is substituted or unsubstituted; Q is a hydrocarbyl radical having from 1 to 20 carbon atoms or a halogen, and M is a group IVb transition metal or Vanadium.

20 **[0027]** In formula (I), each indenyl or hydrogenated indenyl compound may be substituted in the same way or differently from one another at one or more positions in the cyclopentadienyl ring, the cyclohexenyl ring and the bridge.

**[0028]** In formula (I), each substituent on the indenyl may be independently chosen from those of formula XR<sub>v</sub> in which X is chosen from group IVA, oxygen and nitrogen and each R is the same or different and chosen from hydrogen or hydrocarbyl of from 1 to 20 carbon atoms and v+1 is the valence of X. X is preferably C. If the cyclopentadienyl ring is substituted, its substituent groups must be so bulky as to affect coordination of the olefin monomer to the metal M. Substituents on the cyclopentadienyl ring preferably have R as hydrogen or CH<sub>3</sub>. More preferably, at least one and most preferably both cyclopentadienyl rings are unsubstituted.

25 **[0029]** In a preferred embodiment, both indenyls are unsubstituted and the most preferred catalyst component is a tetrahydroindenyl.

30 **[0030]** R'' is preferably a C1-C4 alkylene radical (as used herein to describe a difunctional radical, also called alkylidene), most preferably an ethylene bridge (as used herein to describe a difunctional radical, also called ethylidene), which is substituted or unsubstituted.

**[0031]** The metal M is preferably zirconium, hafnium, or titanium, most preferably zirconium.

**[0032]** Each Q is the same or different and may be a hydrocarbyl or hydrocarboxy radical having 1 to 20 carbon atoms or a halogen. Suitable hydrocarbyls include aryl, alkyl, alkenyl, alkylaryl or arylalkyl. Each Q is preferably halogen.

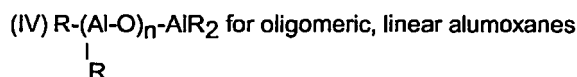
35 **[0033]** Among the preferred metallocenes used in the present invention, one can cite bis tetrahydro-indenyl compounds and bis indenyl compounds as disclosed for example in WO 96/35729 or bis(cyclopentadienyl) compounds. The most preferred metallocene catalyst is isopropylidene-bis(4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride.

40 **[0034]** The metallocene may be supported according to any method known in the art. In the event it is supported, the support used in the present invention can be any organic or inorganic solids, particularly porous supports such as talc, inorganic oxides, and resinous support material such as polyolefin. Preferably, the support material is an inorganic oxide in its finely divided form.

**[0035]** The addition on the support, of an agent that reacts with the support and has an ionising action, creates an active site.

45 **[0036]** Preferably, alumoxane is used to ionise the catalyst during the polymerization procedure, and any alumoxane known in the art is suitable.

**[0037]** The preferred alumoxanes comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula :



And



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wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C<sub>1</sub>-C<sub>8</sub> alkyl group and preferably methyl. Methylalumoxane is preferably used.

[0038] One or more aluminiumalkyl(s) can be used as cocatalyst in the reactor. The aluminiumalkyl is represented by the formula AlR<sub>x</sub> can be used wherein each R is the same or different and is selected from halides or from alkoxy or alkyl groups having from 1 to 12 carbon atoms and x is from 1 to 3. Especially suitable aluminiumalkyl are trialkylaluminium, the most preferred being triisobutylaluminium (TIBAL).

[0039] Further, the catalyst may be prepolymerised prior to introducing it in the reaction zone and/or prior to the stabilization of the reaction conditions in the reactor.

[0040] The polyethylene resin of the present invention has a density ranging from 0.930 to 0.950 g/cm<sup>3</sup>, preferably, from 0.930 to 0.940 g/cm<sup>3</sup> and most preferably about 0.935 g/cm<sup>3</sup>. The melt index MI2 is within the range 0.1 to 5 g/10 min, preferably in the range 0.2 to 1.5 g/10 min.

[0041] The density is measured following the method of standard test ASTM D 1505 at 23 °C and the melt index MI2 is measured following the method of standard test ASTM D 1238 at 190 °C and under a load of 2.16 kg.

[0042] The metallocene-prepared polyethylenes produce very strong stretched tapes and raffia products, mainly because of their narrow molecular weight distribution and because they have long chain branches. The final products have improved tensile and elongation properties and simultaneously they have improved flexibility and processing properties.

### Example.

[0043] Several resins have been tested for preparing raffia products.

[0044] Resin R1 is a medium density polyethylene resin prepared with isopropylidene (tetrahydroindenyl) zirconium dichloride. It had a density of 0.934 g/cm<sup>3</sup> and a melt index MI2 of 0.9 g/10 min. It was additivated as follows:

- 94.5 wt% of resin R1;
- 4 % red masterbatch PE 44930 from Clariant;
- 1 % polymer processing aid AMF 702 from Schuman;
- 0.5 % antibloc masterbatch B1981 from Clariant. Resin R2 was a commercial resin prepared with a Ziegler-Natta catalyst system: (GF7740 F1 from Hostalen). It had a density of 0.946 g/cm<sup>3</sup> and a melt index MI2 of 0.5 g/10min.

[0045] These two resins were treated under the same conditions for blown film production, and for stretching.

- Melt die temperature: 220 °C.
- Thickness of primary film: 60 microns;
- Orientation temperature: varied progressively from 80 to 120 °C.
- Stretch ratio: 7:1

[0046] The final products, whether unwoven or woven (nets) obtained from the metallocene-produced resin R1 had a high tenacity, an excellent elongation at rupture and a very high break strength. It also had a soft touch and a high flexibility.

[0047] The properties of the stretched tapes obtained from resins R1 and R2 are summarised in Table I.

**TABLE I.**

|                            | R1   | R2   |
|----------------------------|------|------|
| Tenacity at rupture cN/Tex | 24.9 | 22.1 |
| Elongation at rupture %    | 33.2 | 29.3 |
| Strength at rupture cN     | 593  | 525  |
| Titre Tex                  | 23.8 | 20.8 |

[0048] The elongation, the strength and the tenacity at rupture of the stretched tapes have been measured following the method of standard test ISO-2062 (1993).

[0049] The titre is measured in tex or g/km: this is a measure of the linear mass of a filament or fibre.

[0050] The properties of the woven stretched tapes or raffia are displayed in Table II.

TABLE II.

|                         | R1   | R2   |
|-------------------------|------|------|
| Elongation at rupture % | 30.6 | 29.4 |
| Strength at rupture cN  | 997  | 811  |

**[0051]** The raffia products prepared according to the present invention has thus improved properties with respect to those of the prior art.

**[0052]** The elongation and strength at rupture of the raffia have been measured following the method of standard test ISO-5081 (1977).

### Claims

1. Monofilaments or stretched tapes, unwoven or woven into raffia prepared from a metallocene-produced polyethylene resin having long chain branches and a density of from 0.930 to 0.950 g/cm<sup>3</sup>, wherein the metallocene component is a bis-indenyl represented by the general formula

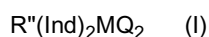


wherein (Ind) is an indenyl or a hydrogenated indenyl, substituted or unsubstituted, R'' is a structural bridge between the two indenyls to impart stereoridity that comprises a C1-C4 alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical, which bridge is substituted or unsubstituted; Q is a hydrocarbyl radical having from 1 to 20 carbon atoms or a halogen, and M is a group IVb transition metal or vanadium.

2. The monofilaments or stretched tapes of claim 1 wherein the density of the polyethylene resin is of from 0.930 to 0.940 g/cm<sup>3</sup> and preferably of about 0.935 g/cm<sup>3</sup> and the melt index MI2 is within the range 0.1 to 5 g/10 min, preferably in the range 0.2 to 1.5 g/10 min.

3. A process for preparing the stretched tapes of claim 1 or claim 2 that comprises the steps of:

a) providing a metallocene-produced medium density polyethylene resin having long chain branches wherein the metallocene component is a bis-indenyl represented by the general formula

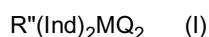


wherein (Ind) is an indenyl or a hydrogenated indenyl, substituted or unsubstituted, R'' is a structural bridge between the two indenyls to impart stereoridity that comprises a C1-C4 alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical, which bridge is substituted or unsubstituted; Q is a hydrocarbyl radical having from 1 to 20 carbon atoms or a halogen, and M is a group IVb transition metal or vanadium;

- b) producing a film from the polyethylene resin of step a)  
 c) orienting the film obtained from step b) by stretching;  
 d) cutting the stretched film of step c) into strips  
 e) optionally, annealing the stretched tapes.

4. A process for preparing the stretched tapes of claim 1 or claim 2 that comprises the steps of:

a) providing a metallocene-produced medium density polyethylene resin having long chain branches wherein the metallocene component is a bis-indenyl represented by the general formula



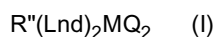
wherein (Ind) is an indenyl or a hydrogenated indenyl, substituted or unsubstituted, R'' is a structural bridge between the two indenyls to impart stereoridity that comprises a C1-C4 alkylene radical, a dialkyl germanium or silicon or siloxane, or a alkyl phosphine or amine radical, which bridge is substituted or unsubstituted; Q is a hydrocarbyl radical having from 1 to 20 carbon atoms or a halogen, and M is a group IVb transition metal or

- vanadium;  
 b) producing a film from the polyethylene resin of step a)  
 c) cutting the film obtained from step b) into strips;  
 d) orienting the strips of film of step c) by stretching;  
 e) optionally, annealing the stretched tapes.

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5. The process of claim 3 or 4 wherein the stretching temperature is of from 10 to 70 °C lower than the melting temperature of the resin.
  6. The process of claim 5 wherein the stretching temperature is of from 15 to 50 °C lower than the melting temperature of the resin
  7. The process of any one of claims 3 to 6 wherein the annealing temperature, if annealing is performed, is of from 5 to 10 °C lower than the stretching temperature.

### Patentansprüche

- 35  
 40
1. Monofilamente oder verstreckte Bänder, ungewebt oder zu Bast gewebt, hergestellt aus einem metallocenproduzierten Polyethylenharz mit langkettigen Verzweigungen und einer Dichte von 0,930 bis 0,950 g/cm<sup>3</sup>, wobei die Metallocenkomponente ein Bis-indenyl ist, dargestellt durch die allgemeine Formel:



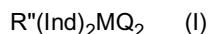
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wobei (Ind) ein Indenyl oder ein hydrogeniertes Indenyl, substituiert oder unsubstituiert, ist, wobei R'' eine Strukturbrücke zwischen den beiden Indenylen ist, die Stereorigidität verleiht und ein C1-C4-Alkyleriradikal, ein Dialkylgermanium- oder Silicium- oder Siloxan- oder ein Alkylphosphin- oder Aminradikal umfasst, wobei die Brücke substituiert oder unsubstituiert ist; wobei Q ein Hydrocarbylradikal mit 1 bis 20 Kohlenstoffatomen oder Halogen ist, und wobei M ein Übergangsmetall der Gruppe IVb oder Vanadium ist.

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2. Monofilamente oder verstreckte Bänder nach Anspruch 1, wobei die Dichte des Polyethylenharzes 0,930 bis 0,940 g/cm<sup>3</sup> und vorzugsweise ungefähr 0,935 g/cm<sup>3</sup> beträgt, und wobei der Schmelzindex MI2 im Bereich von 0,1 bis 5 g/10 min, vorzugsweise im Bereich von 0,2 bis 1,5 g/10 min; liegt.

3. Verfahren zum Herstellen der verstreckten Bänder nach Anspruch 1 oder 2, das die folgenden Schritte umfasst:

a) Bereitstellen eines metallocenproduzierten Polyethylenharzes mittlerer Dichte mit langkettigen Verzweigungen, wobei die Metallocenkomponente ein Bis-indenyl ist, dargestellt durch die allgemeine Formel



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wobei (Ind) ein Indenyl oder ein hydrogeniertes Indenyl, substituiert oder unsubstituiert, ist, wobei R'' eine Strukturbrücke zwischen den beiden Indenylen ist, die Stereorigidität verleiht und ein C1-C4-Alkylenradikal, ein Dialkylgermanium- oder Silicium- oder Siloxan- oder ein Alkylphosphin- oder Aminradikal umfasst, wobei die Brücke substituiert oder unsubstituiert ist; wobei Q ein Hydrocarbylradikal mit 1 bis 20 Kohlenstoffatomen oder Halogen ist, und wobei M ein Übergangsmetall der Gruppe IVb oder Vanadium ist;

- b) Herstellen eines Films aus dem Polyethylenharz von Schritt a)  
 c) Ausrichten des in Schritt b) erhaltenen Films durch Verstrecken;  
 d) Schneiden des verstreckten Films von Schritt c) in Streifen; und  
 e) optional Annelieren der verstreckten Bänder.

4. Verfahren zum Herstellen der verstreckten Bänder nach Anspruch 1 oder 2, das die folgenden Schritte umfasst:

a) Bereitstellen eines metallocenproduzierten Polyethylenharzes mittlerer Dichte mit langkettigen Verzweigungen, wobei die Metallocenkomponente ein Bis-indenyl ist, dargestellt durch die allgemeine Formel



wobei (Ind) ein Indenyl oder ein hydrogeniertes Indenyl, substituiert oder unsubstituiert, ist, wobei R" eine Strukturbrücke zwischen den beiden Indenylen ist, die Stereorigidität verleiht und ein C1-C4-Alkylenradikal, ein Dialkylgermanium- oder Silicium- oder Siloxan- oder ein Alkylphosphin- oder Aminradikal umfasst, wobei die Brücke substituiert oder unsubstituiert ist; wobei Q ein Hydrocarbylradikal mit 1 bis 20 Kohlenstoffatomen oder Halogen ist, und wobei M ein Übergangsmetall der Gruppe IVb oder Vanadium ist;

- b) Herstellen eines Films aus dem Polyethylenharz von Schritt a)
- c) Schneiden des in Schritt b) erhaltenen Films in Streifen;
- d) Ausrichten der Filmstreifen von Schritt c) durch Verstrecken; und
- e) optional Annelieren der verstreckten Bänder.

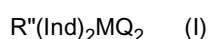
5. Verfahren nach Anspruch 3 oder 4, wobei die Verstrecktemperatur 10 bis 70 °C niedriger als die Schmelztemperatur des Harzes ist.

6. Verfahren nach Anspruch 5, wobei die Verstrecktemperatur 15 bis 50 °C niedriger als die Schmelztemperatur des Harzes ist.

7. Verfahren nach einem der Ansprüche 3 bis 6, wobei die Annelierungstemperatur, wenn ein Annelieren durchgeführt wird, 5 bis 10 °C niedriger als die Verstrecktemperatur ist.

### Revendications

1. Monofilaments ou bandes étirées, non tissés ou tissés en un raphia, préparés à partir d'une résine de polyéthylène produite avec un métallocène ayant des ramifications à longue chaîne et une masse volumique de 0,930 à 0,950 g/cm<sup>3</sup>, dans lesquels le composant métallocène est un bis-indényle représenté par la formule générale :

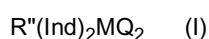


dans laquelle (Ind) est un indényle ou un indényle hydrogéné, substitué ou non substitué, R" est un pont structurel entre les deux indényles servant à conférer une stéréorigidité qui comprend un radical alkylène en C<sub>1</sub> à C<sub>4</sub>, un dialkyl-germanium ou silicium ou siloxane, ou un radical alkyl-phosphine ou amine, le pont étant substitué ou non substitué ; Q est un radical hydrocarbyle ayant de 1 à 20 atomes de carbone ou un halogène, et M est un métal de transition du Groupe IVb ou le vanadium.

2. Monofilaments ou bandes étirées selon la revendication 1, dans lesquels la masse volumique de la résine de polyéthylène est de 0,930 à 0,940 g/cm<sup>3</sup> et de préférence d'environ 0,935 g/cm<sup>3</sup> et l'indice de fusion MI2 est situé dans la plage allant de 0,1 à 5 g/10 min, de préférence dans la plage allant de 0,2 à 1,5 g/10 min.

3. Procédé pour préparer les bandes étirées de la revendication 1 ou de la revendication 2, qui comprend les étapes consistant à :

a) disposer d'une résine de polyéthylène moyenne densité produite avec un métallocène, ayant des ramifications à longue chaîne, le composant métallocène étant un bis-indényle représenté par la formule générale :



dans laquelle (Ind) est un indényle ou un indényle hydrogéné, substitué ou non substitué, R" est un pont structurel entre les deux indényles servant à conférer une stéréorigidité qui comprend un radical alkylène en C<sub>1</sub> à C<sub>4</sub>, un dialkyl-germanium ou silicium ou siloxane, ou un radical alkyl-phosphine ou amine, le pont étant substitué ou non substitué ; Q est un radical hydrocarbyle ayant de 1 à 20 atomes de carbone ou un halogène, et M est un métal de transition du Groupe IVb ou le vanadium ;

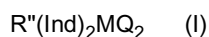
- b) produire un film à partir de la résine de polyéthylène de l'étape a) ;
- c) orienter le film obtenu dans l'étape b) par étirage ;
- d) découper en bandes le film étiré de l'étape c) ;
- e) éventuellement recuire les bandes étirées.

4. Procédé pour préparer les bandes étirées de la revendication 1 ou de la revendication 2, qui comprend les étapes consistant à :



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a) disposer d'une résine de polyéthylène moyenne densité produite avec un métallocène, ayant des ramifications à longue chaîne, le composant métallocène étant un bis-indényle représenté par la formule générale :



dans laquelle (Ind) est un indényle ou un indényle hydrogéné, substitué ou non substitué, R'' est un pont structurel entre les deux indényles servant à conférer une stéréorigidité qui comprend un radical alkylène en C<sub>1</sub> à C<sub>4</sub>, un dialkyl-germanium ou silicium ou siloxane, ou un radical alkyl-phosphine ou amine, le pont étant substitué ou non substitué ; Q est un radical hydrocarbyle ayant de 1 à 20 atomes de carbone ou un halogène, et M est un métal de transition du Groupe IVb ou le vanadium ;

b) produire un film à partir de la résine de polyéthylène de l'étape a) ;

c) découper en bandes le film obtenu dans l'étape b) ;

d) orienter les bandes de film obtenues dans l'étape c) par étirage ;

e) éventuellement recuire les bandes étirées.

5. Procédé selon la revendication 3 ou 4, dans lequel la température d'étirage est inférieure de 10 à 70°C au point de fusion de la résine.

6. Procédé selon la revendication 5, dans lequel la température d'étirage est inférieure de 15 à 50°C au point de fusion de la résine.

7. Procédé selon l'une quelconque des revendications 3 à 6, dans lequel la température de recuit, si un recuit est effectué, est inférieure de 5 à 10°C à la température d'étirage.

**REFERENCES CITED IN THE DESCRIPTION**

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