

Description

The present invention relates to stretchable cling film compositions based on ethylene (co)polymer, and to films produced therefrom.

The preparation of plastic films having cling and stretch properties at ambient temperature is already known, the compositions from which such films are fabricated comprising a polymer or copolymer of ethylene, and a cling agent. The polymer or copolymer of ethylene used in these compositions is generally selected from amongst low density polyethylenes and copolymers of ethylene and vinyl esters obtained by the free radical catalysed polymerisation of ethylene or copolymerisation of ethylene and vinyl ester, linear low density polyethylene obtained by the copolymerisation of ethylene and at least one other alpha-olefin by means of a Ziegler-type catalyst system or a Phillips-type catalyst system, or else mixtures of two or more of these polymers or copolymers of ethylene. The cling-agent, i.e. the agent providing the film with self-adhesive properties, used in these compositions is generally selected from copolymers of ethylene and propylene of the elastomer type, liquid polybutenes, polyisobutenes, atactic polypropylenes, or amorphous hydrocarbon polymers, generally consisting of hydrogenated polycyclic resins, such as the resins obtained by hydrogenation of polycyclopentadiene, polyterpene or coumarin/indene.

The cling films produced from such compositions desirably have stretch characteristics and mechanical properties, for example elongation at break, tearing strengths and breaking strengths permitting stretching at ambient temperature. Moreover, these films should have good cling properties, and should be capable of being used in automated packaging operations.

However, it is observed that films produced from such compositions generally have two main disadvantages. The first of these resides in the greasy surface qualities of these films, especially when the cling agent is polybutene or polyisobutene. The greasy surface quality may disturb the performance of automated packaging operations, and may also cause a deterioration in the packaged objects. The second disadvantage shown by these compositions resides in a considerable drop in cling properties, i.e. adhesion or resistance to detachment of the films, when the ambient temperature rises. This disadvantage becomes particularly severe when articles wrapped in the film are subject to heating or are stored or transported to countries where the ambient temperature is relatively high.

To reduce or eliminate the greasy surface quality of these films, it has been proposed to add monoglycerides and/or diglycerides of fatty acids to the cling film compositions. It is found that the films obtained in fact have a better surface appearance, but their cling performance is appreciably reduced.

It is an object of the present invention to provide improved compositions for manufacturing stretchable cling film.

Accordingly the present invention provides a composition based on ethylene polymer suitable for the manufacture of stretchable cling film, characterised in that the composition comprises from 80 to 99% by weight of at least one polymer or copolymer of ethylene having a density less than or equal to 0.935 and a total of from 1 to 20% by weight, based on the total composition, of components (a) and (b) comprising

(a) at least one cling agent selected from polybutene, polyisobutene and atactic polypropylene and

(b) at least one crystalline wax having one or more melting points (as measured by differential scanning calorimetry) between 50° and 200°C and a number average molecular weight between 250 and 15000 and wherein the quantity of the crystalline wax lies in the range 0.01 to 50% by weight of the total weight of (a) and (b) together.

The polymer or copolymer of ethylene employed in the compositions according to the present invention may be chosen from amongst a wide variety of polymers. For example, they can be polyethylenes of low density, preferably comprised between 0.920 and 0.930, obtained by free radical polymerisation of ethylene, or copolymers of ethylene and a vinyl carboxylate ester or an alkyl ester of an unsaturated carboxylic acid obtained by free radical copolymerisation. The carboxylate part of the vinyl carboxylate ester is preferably derived from an aliphatic, saturated carboxylic acid having from 2 to 30 carbon atoms. Examples of suitable comonomers include vinyl propionate, vinyl hexanoate, vinyl octanoate, vinyl behenate, isopropenyl acetate, ethyl acrylate and butyl acrylate. Vinyl acetate is preferred.

These copolymers preferably contain at least 89% by weight and most preferably from 91 to 95% by weight of ethylene, their density preferably being in the range 0.917 and 0.933. They can be obtained for example by copolymerising ethylene and the comonomer under conventional high temperature, high pressure conditions.

The polymer or copolymer of ethylene used in the composition according to the present invention is preferably linear low density polyethylene obtained by copolymerising ethylene and at least one other alpha-olefin, in the presence of a Ziegler-type catalyst system or a Phillips type catalyst. Examples of linear low density polyethylenes are copolymers of ethylene and another alpha-olefin which can comprise from 3 to 12 carbon atoms, such as propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene, or terpolymers of ethylene, propylene or 1-butene, and another alpha-olefin having from 5 to 12 carbon atoms. These linear low density polyethylenes generally contain from 80 to 98%, preferably from 85 to 97% by weight of ethylene, and have a density between 0.880 and 0.935, preferably between 0.900 and 0.930. They may be produced, for example, by copolymerisation at a pressure below 6 MPa, especially between 0.1 and 5 MPa, either at a temperature between about 40 and 110°C in an inert liquid hydrocarbon medium in which the copolymer produced is in suspension, or at a temperature between about 110 and 300°C in an

inert liquid hydrocarbon in which the copolymer is produced in solution.

However, it is preferred to employ linear low density polyethylene prepared by copolymerising ethylene and at least one other alpha-olefin in a gas-fluidised bed, using a Ziegler type catalyst system comprising as catalyst a halogenated compound of a transition metal belonging to Groups IV, V or VI of the Periodic Table of Elements, and as co-catalyst an organo metallic compound of a metal belonging to Groups I to III of this Table. Such Ziegler-type catalyst systems are well known in the art.

Also suitable for use as the ethylene copolymer are linear low density polyethylenes prepared by the copolymerisation of ethylene and at least one other alpha-olefin using as catalyst, chromium oxide supported on a refractory oxide and activated by thermal treatment e.g. catalysts of the well-known Phillips type. The copolymerisation can be carried out under solution, slurry or gas phase conditions.

In the compositions according to the present invention, two or more of the defined polymers or copolymers of ethylene such as those mentioned above may be used simultaneously in admixture. Thus, for example, one may use a mixture consisting of a low density polyethylene or a copolymer of ethylene and vinyl ester of a saturated carboxylic acid or alkyl ester of an unsaturated carboxylic acid, and a linear low density polyethylene, the mixture containing for example 10 to 99% by weight, and preferably 60 to 99% by weight of linear low density polyethylene.

The polymers or copolymers of ethylene employed in the composition of the present invention suitably have a melt index ($MI_{2.16}$) measured at 190°C under a 2.16kg load between 0.1 and 10 g/10 minutes, preferably between 0.2 and 5 g/10 minutes. They suitably have a molecular weight distribution between 2 and 15 and preferably between 3 and 8, the distribution being calculated by the ratio of the weight average molecular weight M_w to the number average molecular weight M_n determined by gel Permeation chromatography. They preferably have a flow parameter n between 15 and 400, most preferably between 20 and 200, n being the ratio of the melt index $MI_{21.6}$ measured at 190°C under a 21.6 kg load to the melt index $MI_{2.16}$. By differential scanning calorimetry, after post-curing at 200°C, maintenance at this temperature for 20 minutes, cooling at a rate of 16°C per minute and heating at a rate of 16°C per minute, the polymers or copolymers of ethylene used in the compositions according to the present invention preferably have one or more melting points between 100 and 130°C, preferably between 110 and 128°C, and most preferably a single melting point comprised between 115°C and 123°C, corresponding to a crystalline phase having a special distribution of the crystallite dimensions. This melting point or points is preferably accompanied by a melting range spread between approximately 100 and 120°C, corresponding to a relatively large amorphous phase. The fusion enthalpy of the polymers or copolymers of ethylene employed in the composition of the present invention is preferably between 40 and 170 J/g, most preferably between 60 and 120 J/g. Their degree of crystallinity, deduced from the measurements of fusion enthalpy, can be, for example, between 15 and 60%, preferably between 20 and 45%.

The compositions based on ethylene polymer according to the present invention comprise from 1 to 20% by weight of components (a) and (b) consisting of at least one cling agent (a) and at least one crystalline wax (b). A content of (a) + (b) of less than 1% by weight would not impart the desired cling properties to the films obtained from such compositions. On the other hand a content of over 20% by weight would deleteriously affect the mechanical properties of the films. The content by weight is preferably comprised between 2 and 15% by weight when the cling agent is a polybutene or polyisobutene and between 5 and 20% when the cling agent is atactic polypropylene.

The polybutene can, for example, be produced by cationic polymerisation of 1-butene or 2-butenes or of a mixture of 1-butene and 2-butenes, or by copolymerisation of isobutene with 1-butene and/or 2-butenes, especially by means of a Friedel-Crafts type catalyst, such as aluminium trichloride, boron trifluoride, tin or titanium tetrachlorides. One may also use a polyisobutene produced by polymerising isobutene by means of a cationic catalyst.

The polybutenes or polyisobutenes which are suitable for preparing the compositions according to the invention have a number average molecular weight between 500 and 10000, preferably between 700 and 5000. By way of example, polybutenes sold by BP CHIMIE under the trade names NAPVIS D 3 (Reg.TM), NAPVIS D 10 (Reg.TM), NAPVIS D 30 (Reg.TM), NAPVIS D 200 (Reg.TM) or mixtures thereof may be employed. These also have a viscosity at 100°C comprised between 10 and 10⁶ centistokes, ($\cdot 10^{-6} m^2 \cdot s^{-1}$) preferably comprised between 50 and 5×10^4 centistokes ($\cdot 10^{-6} m^2 \cdot s^{-1}$) this viscosity being measured according to the NF-T-60100 or the ASTM-D-445 standards.

It is also possible to employ atactic polypropylene as a cling agent. Atactic polypropylene or copolymers of propylene and ethylene having a density comprised between 0.85 and 0.91, a weight average molecular weight between 500 and 50000, preferably between 1000 and 10000, and more especially between 1000 and 5000, and showing a complete absence of crystallinity as determined by differential scanning calorimetric analysis are particularly suitable.

The presence of crystalline wax in the compositions according to the invention improves the cling properties of the films obtained from these new compositions and also preserves or improves the excellent mechanical properties of these films.

The proportion of crystalline wax is between 0.01 and 50% by weight and preferably between 0.1 and 10% by weight of the total amount of the cling agent and the crystalline wax. Too low a proportion of crystalline wax would not impart improved cling properties to these films, especially at a relatively high ambient temperature, nor reduce or eliminate the greasy surface quality of these films. On the other hand,

too large a proportion of crystalline wax would reduce the cling properties of the films.

By differential scanning calorimetry (DSC), after post-curing at 200°C, maintenance at this temperature for 20 minutes, cooling at a rate of 16°C per minute and heating at a rate of 16°C per minute, the crystalline waxes employed in these compositions according to the invention preferably have one or more melting points between 50 and 200°C, most preferably between 60 and 160°C. Such crystalline waxes possess a crystalline phase having a distribution of the crystallite dimensions which is particularly well suited to the nature of the ingredients of the compositions according to the invention. The fusion enthalpy of this crystalline wax is generally comprised between 60 and 300 J/g, preferably comprised between 80 and 200 J/g.

The crystalline waxes suitable for preparing the compositions according to the invention preferably have a number average molecular weight measured by osmometry or by gel permeation chromatography, between 250 and 15000, most preferably between 300 and 10000, and more especially between 300 and 5000.

These crystalline waxes may be chosen from amongst a wide variety of waxes including both natural and synthetic waxes. Amongst the natural waxes one may employ animal waxes such as beeswax; vegetable waxes such as Carnauba, the principal constituent of which is the ester of cerotic acid and myricyl alcohol, having a molecular weight of 830; paraffin waxes of petroleum origin isolated from waxy distillate, appearing under microscopic examination in the form of long needles; and also microcrystalline waxes of petroleum origin separated from distillation residues by means of solvents, appearing under microscopic examination in the form of small irregular slightly elongated crystals.

Amongst synthetic waxes one may use, for example, microcrystalline waxes obtained by Fischer-Tropsch synthesis, having number average molecular weight generally between 400 and 1000, waxes of high density polyethylene or of low density polyethylene obtained by direct polymerisation of ethylene or by degradation of high molecular weight polyethylene, these polyethylene waxes having number average molecular weights between 300 and 15000, preferably between 400 and 5000, hydrogenated castor oil waxes whose main component is the triglyceride of hydrogenated ricinoleic acid of molecular weight 938, or waxes consisting of aliphatic amides of high molecular weights, having for example a melting point of about 145°C.

The compositions according to the invention may be prepared by known methods of blending or mixing, for example using a Banbury-type mixer, a tilting drum, a continuous or batch mixer or a single-screw or twin-screw extruder. The compositions can also be made by pre-mixing the cling agent with the crystalline wax at a temperature close to the melt temperature of the crystalline wax or above it, the mixture thus obtained occurring at ambient temperature (20°C) in the form of a gel. This pre-mix can be blended or mixed with the polymer or copolymer of ethylene, to obtain compositions according to the invention, either at ambient temperature, or at a temperature of 50 to 200°C. If desired, one may add to the compositions according to the invention additives normally employed with polymers or copolymers of ethylene, such as antioxidant, stabilising agents, compounds absorbing ultra-violet radiation, antistatic agents, dyes or pigments.

Single-layer or multi-layer stretchable cling films may be obtained from compositions according to the invention by extrusion-blowing using an annular die and at a temperature generally comprised between 180 and 280°C, with a blow-up ratio which may be for example between 1.5 and 4. Films may also be obtained by extrusion-casting through a slot die, in this case the surface of the film in contact with the chill roll generally having stronger cling properties. The films may have a thickness for example between 10 and 150µm approximately. They have non-greasy surface qualities and good cling properties (high resistance to detachment), these properties being relatively insensitive to temperature. The films also possess excellent mechanical properties.

The resistance to detachment of the films, characterising the cling, is determined by using test pieces prepared by placing together strips of film 5cm wide, over a length of 3cm, (i.e. a surface area of 15 cm²) and under a pressure of 830g/cm² for 30 minutes. These test pieces are then subjected to a drawing force at a rate of 250 millimetres per minute, the distance between jaws initially being 50 millimetres. The force of drawing necessary for detachment is measured (in Newtons) and also the elongation (in millimetres) of the test piece before the two strips separate.

The tearing resistance of the films is measured in the machine direction and the transverse direction determined according to the ASTM-D-1922 standard and expressed in grams for films 25 microns thick.

The invention is illustrated by the following Examples:

Example 1

A cling film composition (A) is obtained by mixing:

(a) 96.5% by weight of a linear low density polyethylene, obtained by copolymerising ethylene and 1-butene under gas fluidised bed conditions, having a content by weight of units derived from 1-butene of 7.5%, a density of 0.918 (at 20°C), a melt index (MI_{2.16}) of 0.9, a flow parameter (n) of 25, a molecular weight distribution (M_w/M_n) of 4.5, a single melting point determined by differential calorimetric analysis of 123°C and a fusion enthalpy of 96 J/g;

(b) 3.5% by weight of a mixture consisting of 99% by weight of a polybutene sold by BP CHIMIE under the trade name NAPVIS D 30 (Reg.TM), having a number average molecular weight of 1350 and a viscosity

at 100°C of 650 centistokes, and 1% by weight of a crystalline wax obtained by Fischer-Tropsch synthesis sold by SASOL (South Africa), under the trade name SASOLWAX H2 (Reg.TM). This crystalline wax has a number average molecular weight of 600 determined by osmometry, two melting points determined by DSC of 78° and 103°C and a fusion enthalpy of 193 J/g.

To the composition (A) are added:

0.1% by weight of calcium stearate 0.02% by weight of an antioxidant of the hindered phenol type sold by CIBAGEIGY under the trade name IRGANOX 1076 (Reg.TM) and 0.08% by weight of a stabilising agent sold by CIBA-GEIGY under trade name IRGAFOS 168 (Reg.TM).

Films 35µm thick are produced from this composition by extrusion-blowing using an annular die. The characteristics of the films are evaluated after a period of 24 hours. The results summarised in Table I show that the films obtained from composition (A) have non-greasy surface qualities and have both excellent cling properties at 23°C, characterised by high values of their resistance to detachment and their elongation before break, and very satisfactory mechanical properties.

Example 2 (Comparative)

Composition (B) is identical to composition (A) described in Example 1, except that crystalline wax is not used. Composition (B) has calcium stearate, IRGANOX 1076 (Reg.TM) added to it in the same proportions as for composition (A).

Films are produced as in Example 1. The results, summarised in Table I, show that the films obtained from composition (B) have greasy surface qualities and have mediocre cling at 23°C, characterised by relatively low values for their resistance to detachment and their elongation before break.

Example 3 (Comparative)

Composition (C) is obtained by mixing:

(a) 95.75% by weight of a linear low density polyethylene identical to that used in an Example 1.

(b) 3.5% by weight of a polybutene identical to that used in Example 1.

(c) 0.75% by weight of a product containing mono glycerides and diglycerides of oleic acid sold by ATLAS CHEMICAL (France) under the trade name ATMER 121 (Reg.TM).

Composition (C) has calcium stearate, IRGANOX 1076 (Reg.TM) and IRGAFOS 168 (Reg.TM) added to it in the same proportions as composition (A) of Example 1. Films are produced as in Example 1.

The results, summarised in Table I, show that the films obtained from composition (C) have non-greasy surface qualities but have mediocre cling properties at 23°C, characterised by relatively low values for their resistance to detachment and their elongation before break.

Example 4

Composition (D) is obtained by mixing:

(a) 96.5% by weight of a linear low density polyethylene obtained by gas fluidised bed copolymerisation of ethylene and 1-butene, having a content by weight of units derived from 1-butene of 5.5%, a density of 0.928 (at 20°C), a melt index (MI2.16) of 4.2, a flow parameter (n) of 22, a MWD (Mw/Mn) of 3.2, a single melting point determined by DSC of 126°C and a fusion enthalpy of 125 J/g.

(b) 3.5% by weight of a mixture consisting of 99% by weight of a polybutene identical to that used in Example 1 and 1% by weight of a crystalline wax identical to that used in Example 1.

Composition (D) has calcium stearate, IRGANOX 1076 (Reg.TM) and IRGAFOS 168 (Reg.TM) added to it in the same proportions as to composition (A) in Example 1.

Films are produced as in Example 1. The results, summarised in Table I, show that the films obtained from composition (D) have non-greasy surface qualities and have both excellent cling properties at 23°C, characterised by high values for their resistance to detachment and elongation before break, and very satisfactory mechanical properties.

Example 5 (Comparative)

Composition (E) is identical to composition (D) described in Example 4, except for the fact that it does not contain any crystalline wax.

Composition (E) has calcium stearate, IRGANOX 1076 (Reg.TM) and IRGAFOS 168 (Reg.TM) added to it in the same proportions as in composition (A) of Example 1.

Films are produced as in Example 1. The results, summarised in Table I, show that the films obtained from composition (E) have greasy surface qualities and have mediocre cling properties at 23°C, characterised by relatively low values for their resistance to detachment and their elongation before break.

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Example 6 (Comparative)

Composition (F) is obtained by mixing:

(a) 95.75% by weight of a linear low density polyethylene identical to that used in Example 4.

(b) 3.5% by weight of a polybutene identical to that used in Example 1.

5 (c) 0.75% by weight of a product comprising mono glycerides and diglycerides of oleic acid, identical to that used in Example 3.

Composition (F) has calcium stearate, IRGANOX 1076 (Reg.TM) and IRGAFOS 168 (Reg.TM) added to it in the same proportions as in composition (A) of Example 1.

10 Films are produced as in Example 1. The results, summarised in Table I, show that the films obtained from composition (F) have non-greasy surface qualities but have mediocre cling properties at 23°C, characterised by relatively low values for their resistance to detachment and their elongation before break.

Example 7

15 Composition (G) is obtained by mixing:

(a) 96.5% by weight of a linear low density polyethylene identical to that used in Example 1.

(b) 3.5% by weight of a mixture consisting of 99% by weight of a polybutene sold by BP Chimie (France) under trade name NAPVIS D 10 (Reg.TM), ($10^{-3}\text{m}^2\cdot\text{s}^{-1}$) having a number average molecular weight of 970 and a viscosity at 100°C of 220 centistokes ($10^{-6}\text{m}^2\cdot\text{s}^{-1}$) and 1% by weight of a crystalline wax
20 identical to that used in Example 1.

Composition (G) has calcium stearate, IRGANOX 1076 (Reg.TM) and IRGAFOS 168 (Reg.TM) added to it in the same proportions as in composition (A) of Example 1.

25 Films are produced as in Example 1. The results, summarised in Table II, show that the films obtained from composition (G) have very good cling properties at 23°C and good cling properties at 50°C.

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TABLE I

Example	Composition	Resistance to detachment at 23°C (N)	Elongation before break at 23°C (mm)	Surface quality	Resistance to tearing (film 25mm thick)	
					machine direction (g)	transverse direction (g)
1	(A)	21.1	191	non-greasy	136	400
2 (Comparative)	(B)	20.3	165	greasy	140	360
3 (Comparative)	(C)	15.7	104	non-greasy	230	480
4	(D)	20.2	182	non-greasy	130	400
5 (Comparative)	(E)	19.3	154	greasy	140	360
6 (Comparative)	(F)	15.5	98	non-greasy	280	470

TABLE II

Example	Composition	Resistance to detachment at 23°C (N)		Elongation before break (mm)	
		at 23°C	at 50°C	at 23°C	at 50°C
7	(G)	19.3	12.2	183	129



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Claims for the Contracting States: BE CH DE FR GB IT LI NL SE

1. A composition based on ethylene polymer and suitable for the manufacture of stretchable cling film characterised in that the composition comprises from 80 to 99% by weight of at least one polymer or copolymer of ethylene having a density less than or equal to 0.935, and a total of from 1 to 20% by weight, based on the total composition, of components (a) and (b) comprising

(a) at least one cling agent selected from liquid polybutene, polyisobutene and atactic polypropylene and

(b) at least one crystalline wax having one or more melting points, (as determined by differential scanning calorimetry) between 50° and 200°C and a number average molecular weight between 250 and 15000 and wherein the quantity of the crystalline wax lies in the range 0.01 to 50% by weight of the total weight of (a) and (b) together.

2. A composition according to claim 1, characterised in that the polymer or copolymer of ethylene has a melt index, measured at 190°C under a 2.16kg load, in the range 0.1 and 10g/10 minutes.

3. A composition according to claim 1, characterised in that the polymer or copolymer of ethylene is selected from low density polyethylene, a copolymer of ethylene and a vinyl carboxylate ester or a copolymer of ethylene with an alkyl ester of an unsaturated carboxylic acid obtained by polymerisation under high pressure and at high temperature, by means of a radical-forming catalyst, or from linear low density polyethylene obtained by the copolymerisation of ethylene and at least one other alpha-olefin, by means of a Ziegler type catalyst system or a phillips type catalyst.

4. Compositions according to claim 1, characterised in that the cling agent is a polybutene or polyisobutene have a number average molecular weight in the range 500 and 10000, preferably in the range 700 and 5000.

5. A composition according to claim 1, characterised in that the cling agent is atactic polypropylene having a number average molecular weight in the range 500 and 50000, preferably in the range 1000 and 10000.

6. A composition according to claim 1, characterised in that the crystalline wax is selected from microcrystalline waxes obtained by Fischer-Tropsch synthesis, having a number average molecular weight in the range 400 and 1000, waxes of high density polyethylene or of low density polyethylene, obtained by direct polymerisation or by degradation of polyethylene of high molecular weight, these polyethylene waxes having a number average molecular weight in the range 300 and 15000, hydrogenated castor oil waxes or waxes consisting of aliphatic amides of high molecular weight.

7. Process for the preparation of a composition according to any one of claims 1 to 6, characterised in that the cling agent and the crystalline wax are mixed before being added to the polymer or copolymer of ethylene.

8. Stretchable cling film characterised in that it is obtained by extrusion-blowing or cast-extrusion from a composition according to any one of claims 1 to 5.

Claims for the Contracting State: AT

1. A process for preparing a composition based on ethylene polymer and suitable for the manufacture of stretchable cling film characterised in that the process comprises mixing together from 80 to 99% by weight of at least one polymer or copolymer of ethylene having a density less than or equal to 0.935, and a total of from 1 to 20% by weight, based on the total composition, of components (a) and (b) comprising

(a) at least one cling agent selected from liquid polybutene, polyisobutene and atactic polypropylene and

(b) at least one crystalline wax having one or more melting points, (as determined by differential scanning calorimetry) between 50° and 200°C and a number average molecular weight between 250 and 15000 and wherein the quantity of the crystalline wax lies in the range 0.01 to 50% by weight of the total weight of (a) and (b) together.

2. A process according to claim 1, characterised in that the polymer or copolymer of ethylene has a melt index, measured at 190°C under a 2.16kg load, in the range 0.1 and 10g/10 minutes.

3. A process according to claim 1, characterised in that the polymer or copolymer of ethylene is selected from low density polyethylene, a copolymer of ethylene and a vinyl carboxylate ester or a copolymer of ethylene with an alkyl ester of an unsaturated carboxylic acid obtained by polymerisation under high pressure and at high temperature, by means of a radical-forming catalyst, or from linear low density polyethylene obtained by the copolymerisation of ethylene and at least one other alpha-olefin, by means of a Ziegler type catalyst system or a Phillips type catalyst.

4. A process according to claim 1, characterised in that the cling agent is a polybutene or polyisobutene have a number average molecular weight in the range 500 and 10000, preferably in the range 700 and 5000.

5. A process according to claim 1, characterised in that the cling agent is atactic polypropylene having a number average molecular weight in the range 500 and 50000, preferably in the range 1000 and 10000.

6. A process according to claim 1, characterised in that the crystalline wax is selected from microcrystalline waxes obtained by Fischer-Tropsch synthesis, having a number average molecular weight in the range 400 and 1000, waxes of high density polyethylene or of low density polyethylene, obtained by



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direct polymerisation or by degradation of polyethylene of high molecular weight, these polyethylene waxes having a number average molecular weight in the range 300 and 15000, hydrogenated castor oil waxes or waxes consisting of aliphatic amides of high molecular weight.

7. A process according to any one of claims 1 to 6, characterised in that the cling agent and the crystalline wax are mixed before being added to the polymer or copolymer of ethylene.

8. A process for the production of stretchable cling film characterised in that it is obtained by extrusion-blowing or last-extrusion from a composition produced according to a process as claimed in any one of claims 1 to 7.

10 Patentansprüche für die Vertragsstaaten: BE CH DE FR GB IT LI NL SE

1. Zusammensetzung, basierend auf Ethylenpolymer und geeignet für die Herstellung von ausdehnbarer, haftender Folie, dadurch gekennzeichnet, daß sich die Zusammensetzung aus 80 bis 99 Gew.-% von mindestens einem Polymer oder Copolymer des Ethylens mit einer Dichte geringer als oder
15 gleich 0,935, und einer Gesamtmenge von 1 bis 20 Gew.-%, basierend auf der Gesamtzusammensetzung, der Komponenten (a) und (b) zusammensetzt, beinhaltend

(a) mindestens ein Haftmittel, ausgewählt unter flüssigem Polybuten, Polyisobuten und ataktischem Polypropylen und

(b) mindestens ein kristallines Wachs mit einem oder mehreren Schmelzpunkten von 50° bis 200°C, (bestimmt durch Differential Scanning Calorimetry) und einem Zahlenmittel-Molekulargewicht von 250 bis 20
15.000 und worin die Menge des kristallinen Wachses im Bereich von 0,01 bis 50 Gew.-% des gemeinsamen Gesamtgewichtes von (a) und (b) beträgt.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Polymer oder Copolymer des Ethylens einen Schmelzindex im Bereich von 0,1 bis 10 g/10 Minuten, gemessen bei 190°C unter einer
25 Belastung von 2,16 kg, aufweist.

3. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Polymer oder Copolymer des Ethylens unter Polyethylen mit niedriger Dichte, einem Copolymer von Ethylen und einem Vinylcarboxylatester oder einem Copolymer von Ethylen mit einem Alkylester einer ungesättigten Carbonsäure, erhalten durch Polymerisation unter hohem Druck und bei hoher Temperatur mittels eines Radikale
30 bildenden Katalysators, oder unter linearem Polyethylen mit niedriger Dichte, erhalten durch die Copolymerisation von Ethylen und mindestens einem anderen alpha-Olefin mittels eines Katalysatorsystems vom Ziegler-Typ oder eines Katalysators vom Phillips-Typ, ausgewählt ist.

4. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Haftmittel ein Polybuten oder Polyisobuten mit einem Zahlenmittel-Molekulargewicht im Bereich von 500 bis 10.000, vorzugsweise
35 im Bereich von 700 bis 5.000, ist.

5. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Haftmittel ataktisches Polypropylen mit einem Zahlenmittel-Molekulargewicht im Bereich von 500 bis 50.000, vorzugsweise im Bereich von 1.000 bis 10.000, ist.

6. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das kristalline Wachs unter
40 mikrokristallinen Wachsen mit einem Zahlenmittel-Molekulargewicht im Bereich von 400 bis 1.000, die durch Fischer-Tropsch-Synthese erhalten werden, Wachsen von Polyethylen mit hoher Dichte oder von Polyethylen mit niedriger Dichte, die durch direkte Polymerisation oder durch Abbau von Polyethylen mit hohem Molekulargewicht erhalten werden, welche Polyethylenwachse ein Zahlenmittel-Molekulargewicht im Bereich von 300 bis 15.000 besitzen, hydrierten Castorölwachsen oder Wachsen, die aus aliphatischen
45 Amiden mit hohem Molekulargewichts bestehen, ausgewählt ist.

7. Verfahren zur Herstellung einer Zusammensetzung nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Haftmittel und das kristalline Wachs vermischt werden bevor sie zu dem Polymer oder zu dem Copolymer von Ethylen zugegeben werden.

8. Ausdehnbare, haftende Folie, dadurch gekennzeichnet, daß sie durch Extrusionsblasen oder Gieß-
50 Extrusion aus einer Zusammensetzung nach einem der Ansprüche 1 bis 5 erhalten wird.

Patentansprüche für den Vertragsstaat: AT

1. Verfahren zur Herstellung einer Zusammensetzung, basierend auf Ethylenpolymer und geeignet für
55 die Herstellung von ausdehnbarer, haftender Folie, dadurch gekennzeichnet, daß das Verfahren des gemeinsamen Vermischen von 80 bis 99 Gew.-% von mindestens einem Polymer oder Copolymer des Ethylens mit einer Dichte geringer als oder gleich 0,935, und einer Gesamtmenge von 1 bis 20 Gew.-%, basierend auf der Gesamtzusammensetzung, der Komponenten (a) und (b) umfaßt, beinhaltend

(a) mindestens ein Haftmittel, ausgewählt unter flüssigem Polybuten, Polyisobuten und ataktischem
60 Polypropylen und

(b) mindestens ein kristallines Wachs mit einem oder mehreren Schmelzpunkten von 50° bis 200°C, (bestimmt durch Differential Scanning Calorimetry) und einem Zahlenmittel-Molekulargewicht von 250 bis 15.000 und worin die Menge des kristallinen Wachses im Bereich von 0,01 bis 50 Gew.-% des gemeinsamen Gesamtgewichtes von (a) und (b) beträgt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Polymer oder Copolymer des
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Ethylens einen Schmelzindex im Bereich von 0,1 bis 10 g/10 Minuten, gemessen bei 190°C unter einer Belastung von 2,16 kg, aufweist.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Polymer oder Copolymer des Ethylens unter Polyethylen mit niedriger Dichte, einem Copolymer von Ethylen und einem Vinylcarboxylat-
5 ester oder einem Copolymer von Ethylen mit einem Alkylester einer ungesättigten Carbonsäure, erhalten durch Polymerisation unter hohem Druck und bei hoher Temperatur mittels eines Radikale bildenden Katalysators, oder unter linearem Polyethylen mit niedriger Dichte, erhalten durch die Copolymerisation von Ethylen und mindestens einem anderen alpha-Olefin mittels eines Katalysatorsystems vom Ziegler-Typ oder eines Katalysators vom Phillips-Typ, ausgewählt ist.

10 4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Haftmittel ein Polybuten oder Polyisobuten mit einem Zahlenmittel-Molekulargewicht im Bereich von 500 bis 10.000, vorzugsweise im Bereich von 700 bis 5.000, ist.

5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Haftmittel ataktisches Polypropylen mit einem Zahlenmittel-Molekulargewicht im Bereich von 500 bis 50.000, vorzugsweise im Bereich von
15 1.000 bis 10.000, ist.

6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das kristalline Wachs unter mikrokristallinen Wachsen mit einem Zahlenmittel-Molekulargewicht im Bereich von 400 bis 1.000, die durch Fischer-Tropsch-Synthese erhalten werden, Wachsen von Polyethylen mit hoher Dichte oder von Polyethylen mit niedriger Dichte, die durch direkte Polymerisation oder durch Abbau von Polyethylen mit
20 hohem Molekulargewicht erhalten werden, welche Polyethylenwachse ein Zahlenmittel-Molekulargewicht im Bereich von 300 bis 15.000 besitzen, hydrierten Castorölwachsen oder Wachsen, die aus aliphatischen Amiden mit hohem Molekulargewichts bestehen, ausgewählt ist.

7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Haftmittel und das kristalline Wachs vermischelt werden bevor sie zu dem Polymer oder zu dem Copolymer von Ethylen
25 zugegeben werden.

8. Verfahren zur Herstellung einer ausdehnbaren, haftenden Folie, dadurch gekennzeichnet, daß sie durch Extrusionsblasen oder Gieß-Extrusion aus einer gemäß einem Verfahren nach einem der Ansprüche 1 bis 7 hergestellten Zusammensetzung erhalten wird.

30 Revendications pour les Etats contractants : BE CH DE FR GB IT LI NL SE

1. Composition à base d'un polymère d'éthylène et convenant pour la fabrication d'une pellicule étirable et auto-adhérente, composition caractérisée en ce qu'elle comprend de 80 à 99 % en poids d'au moins un polymère ou copolymère de l'éthylène, ayant une densité inférieure ou égale à 0,935, et au total
35 d' 1 à 20 % en poids, sur la base de la composition totale, de composants (a) et (b) comprenant

(a) au moins un agent d'auto-adhérence, choisi parmi du polybutène liquide, du polyisobutène et du polypropylène atactique, et

(b) au moins une cire cristalline ayant un ou plusieurs points de fusion (ce que l'on détermine par calorimétrie à balayage différentiel) entre 50 °C et 200 °C et un poids moléculaire moyen en nombre
40 compris entre 250 et 15 000, la quantité de la cire cristalline se situant entre 0,01 et 50 % en poids, sur la base du poids total de (a) et de (b) ensemble.

2. Composition selon la revendication 1, caractérisée en ce que le polymère ou copolymère de l'éthylène a un indice de fluidité (indice d'écoulement à l'état fondu), mesuré à 190 °C sous une charge de 2,16 kg, compris entre 0,1 et 10 g/10 min.

45 3. Composition selon la revendication 1, caractérisée en ce que le polymère ou copolymère de l'éthylène est choisi parmi du polyéthylène basse densité, un copolymère de l'éthylène et d'un carboxylate de vinyle ou un copolymère de l'éthylène avec un ester alkylque d'un acide carboxylique insaturé obtenu par polymérisation, sous pression élevée et à température élevée, à l'aide d'un catalyseur formateur de radicaux, ou parmi du polyéthylène linéaire à basse densité obtenu par la copolymérisation de l'éthylène et
50 d'au moins une autre alpha-oléfine, à l'aide d'un système de catalyseur de type Ziegler ou d'un catalyseur de type Phillips.

4. Composition selon la revendication 1, caractérisée en ce que l'agent d'auto-adhérence est un polybutène ou polyisobutène ayant un poids moléculaire moyen en nombre compris entre 500 et 10 000, de préférence entre 700 et 5 000.

55 5. Composition selon la revendication 1, caractérisée en ce que l'agent d'auto-adhérence est du polypropylène atactique, ayant un poids moléculaire moyen en nombre compris entre 500 et 50 000, de préférence entre 1 000 et 10 000.

60 6. Composition selon la revendication 1, caractérisée en ce que la cire cristalline est choisie parmi des cires microcristallines obtenues par synthèse de Fischer-Tropsch, ayant un poids moléculaire moyen en nombre compris entre 400 et 1000, des cires de polyéthylène haute densité ou de polyéthylène basse densité, obtenues par polymérisation directe ou par dégradation de polyéthylène à poids moléculaire élevé, ces cires de polyéthylène ayant un poids moléculaire moyen en nombre compris entre 300 et 15 000, des cires d'huile de ricin hydrogénées ou des cires consistant en des amides aliphatiques à poids moléculaire élevé.

65 7. Procédé pour la préparation d'une composition selon l'une quelconque des revendications 1 à 6,



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caractérisé en ce que l'agent d'auto-adhérence et la cire cristalline sont mélangés avant d'être ajoutés au polymère ou copolymère de l'éthylène.

8. Pellicule étirable et auto-adhérente, caractérisée en ce qu'elle est obtenue par extrusion-soufflage ou par coulée-extrusion, à partir d'une composition selon l'une quelconque des revendications 1 à 5.

Revendications pour l'Etat contractant: AT

1. Un processus de préparation d'une composition à base de polymère éthylénique et convenant à la fabrication d'un film ou feuil adhésif étirable, caractérisé en ce que le processus comporte le mélange de 80 à 99% en poids d'au moins un polymère ou copolymère éthylénique possédant une densité inférieure ou égale à 0,935, et un total de 1 à 20% en poids, basé sur la composition totale, des éléments constitutifs (a) et (b) comportant

(a) au moins un agent d'adhésivité, polybutène, polyisobutène ou polypropylène atactique en phase liquide et

(b) au moins une cire cristalline possédant un point de fusion ou davantage, (détermination par calorimétrie différentielle programmée) entre 50° et 200°C et une masse moléculaire moyenne située entre 250 et 15000, et dans laquelle la quantité de cire cristalline se situe dans la plage de 0,01 à 50% en poids du poids total de (a) et (b) ensemble.

2. Un processus, selon la revendication 1, caractérisé en ce que le polymère ou le copolymère éthylénique présente un indice de fusion, mesuré à 190°C sous une charge de 2,16 kg, dans la plage de 0,1 à 10 g/10 mn.

3. Un processus, selon la revendication 1, caractérisé en ce que le polymère ou le copolymère éthylénique est sélectionné à partir d'un polyéthylène de faible densité, d'un copolymère éthylénique et d'un ester de carboxylate vinylique ou d'un copolymère éthylénique avec un ester d'alkyle d'un acide carboxylique non saturé obtenu par polymérisation sous haute pression et à haute température, à l'aide d'un catalyseur formant des radicaux, ou à partir d'un polyéthylène linéaire de basse densité obtenu par copolymérisation d'éthylène et d'au moins une autre alpha-oléfine, au moyen d'un système catalyseur de type Ziegler ou d'un catalyseur de type Phillips.

4. Un processus selon la revendication 1, caractérisé en ce que l'agent d'adhésivité est un polybutène ou un polyisobutène possédant un poids moléculaire moyen (nombre) dans la plage de 500 à 10000, entre 700 et 5000 de préférence.

5. Un processus selon la revendication 1, caractérisé en ce que l'agent d'adhésivité est un polypropylène atactique possédant un poids moléculaire moyen (nombre) dans la plage de 500 à 50000, entre 1000 et 10000 de préférence.

6. Un processus selon la revendication 1, caractérisé en ce que la cire cristalline est sélectionnée parmi des cires microcristallines obtenues par la synthèse de Fischer-Tropsch, possédant un poids moléculaire moyen (nombre) dans la plage de 400 à 1000, des cires de polyéthylène haute pression ou de polyéthylène basse pression, obtenues par polymérisation directe ou par dégradation d'un polyéthylène de poids moléculaire élevé, ces cires de polyéthylène possédant un poids moléculaire moyen (nombre) dans la plage de 300 à 15000, des cires d'huile de ricin hydrogénée, ou des cires consistant en amides aliphatiques de poids moléculaire élevé.

7. Un processus selon l'une quelconque des revendications 1 à 6, caractérisé en ce que l'agent d'adhésivité et la cire cristalline sont mélangés avant d'être ajoutés au polymère ou au copolymère éthylénique.

8. Un processus de production de film adhésif étirable caractérisé en ce qu'il est obtenu par extrusion-soufflage ou par coulée-extrusion à partir d'une composition produite conformément à un processus tel que revendiqué dans l'une quelconque des revendications 1 à 7.