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(71) Applicant (*for all designated States except US*): **TOTAL PETROCHEMICALS RESEARCH FELUY** [BE/BE];
Zone Industrielle C, B-7181 Seneffe (Feluy) (BE).

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **CHARLIER, Pascal** [BE/BE]; Rue de la Resistance 82, B-1080 Evere (BE).

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(54) Title: CORONA TREATED POLYETHYLENE FILMS

(57) Abstract: The present invention relates to a method for obtaining a heat seal between two polyethylene surfaces, at least one of which being corona treated.



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Corona treated polyethylene films

The present invention relates to a method for obtaining a heat seal between two polyethylene surfaces, at least one of which being corona treated.

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Polyethylene is a thermoplastic commodity widely used in consumer products. While its mechanical, chemical and processing properties make it the material of choice in a wide range of applications, its chemical inertness and low surface energy pose problems in applications that require printing, coating, bonding or
10 adhesion with other substrates. This is especially the case for example in packaging applications when information regarding contents must be conveyed or surface decoration is required for aesthetic reasons. For these applications it is therefore necessary to subject the polyethylene to a surface-modifying treatment that increases the surface energy.

15

The most common method to increase the surface energy of a plastic surface is corona treatment, also known as corona discharge treatment. During the corona treatment, the film passes through a highly charged electrical field that bombards the surface of the film in the presence of oxygen. This bombardment
20 converts the oxygen into ozone, which oxidizes the surface of the film, creating sites for anchorage of adhesives, inks or coatings. The corona treatment is usually performed at a point within the take up section of a blown or a cast film production prior to the steps of printing or coating the film.

25

A drawback of corona treatment is that the treatment affects the seal strength of the treated surface of the film. This is observed when an attempt is made either to heat seal two corona treated surfaces or to seal the treated side to itself as in a pouch. This is also the case if an attempt is made to seal the treated surface to an untreated surface. In each case, even if a seal is formed,
30 the seal is too weak. The seal tends to break if the film surface is used as a sealable surface for example in the production of bags or heavy-duty sacks and the like.

EP 1 810 992 relates to polyethylene blends of metallocene catalysed very low density polyethylene and linear low density polyethylene and films thereof. The surface of the films can be modified by corona discharge treatment.

5 WO 97/13640 relates to multilayer films comprising a first layer, which comprises a first homogeneous ethylene/alpha-olefin copolymer, a second layer, which comprises a polyolefin and a third layer, which comprises a second homogeneous ethylene/alpha-olefin copolymer. Preferably, the first and second homogeneous ethylene/alpha-olefin copolymers have a density of less than
10 about 0.915 g/cm³. One outer layer of the film comprises an antifog agent on the outer surface thereof. This document also discloses a packaging process using the film. The film is especially suitable for the packaging of oxygen-sensitive products such as lettuce. Preferably, the package has printing on the outside of the film.

15

WO 01/03921 discloses an oriented multilayer film comprising a base layer containing a thermoplastic polymer, at least one tie layer and at least one outer layer containing a metallocene catalysed polyethylene. One or more of the exposed layers of the multilayer film structures may be surface treated to
20 render the films to be more receptive to printing inks, adhesives, coatings and the like. The surface treatment may be carried out by corona discharge treatment. Further, one or both of the outermost surfaces of the film structure may be coated with various compositions such as primers, coatings.

25 It is an object of the present invention to enhance the seal strength between two polyethylene surfaces, at least one of which polyethylene surfaces being corona treated.

The term "heat sealing" as used herein refers to the technique of sealing by
30 heat and pressure together.

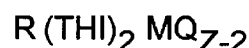
The term "polyethylene surface" as used herein refers either to the surface of a monolayer film or to the surface layer of a multilayer film wherein said surface is a polyethylene.

5 The present invention provides a method for obtaining a heat seal between two polyethylene surfaces, the method comprising the steps of:

- a) providing a first polyethylene surface, wherein the polyethylene is produced with a metallocene catalyst,
- 10 b) providing a second polyethylene surface, wherein the polyethylene is produced with a metallocene catalyst,
- c) corona treating at least one of the polyethylene surfaces and
- d) heat sealing the first polyethylene surface and the second polyethylene surface together.

15 By corona treating at least one of the polyethylene surfaces, it is meant for example that at least the first polyethylene surface is corona treated. The first corona treated polyethylene surface and the second polyethylene surface are further heat sealed together.

20 Preferably, the metallocene catalysed polyethylene used in the present invention is produced with a metallocene having the general formula



wherein

25 THI is a tetrahydrogenated indenyl group which may be substituted or not,

R is a substituted or unsubstituted C₁-C₄ alkylidene radical, a dialkyl germanium, a dialkyl silicon, a diaryl silicon, a di-alkoxysilane, a diphenoxysilane, or an alkyl phosphine or amine radical bridging two tetrahydrogenated indenyl groups,

30 Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radical having from 1-20 carbon atoms, hydrocarboxy

radical having 1-20 carbon atoms or halogen and can be the same or different from each other,

M is a group IVb, Vb or VIb transition metal, and

Z is the valence of the transition metal.

5

Preferably, THl is an unsubstituted tetrahydrogenated indenyl group.

Preferably, M is a group IVb transition metal, more preferably M is zirconium.

10

Preferably, Q is an alkyl radical having from 1-4 carbon atoms or a halogen, more preferably Q is methyl or chlorine.

Preferably, R is a substituted or unsubstituted C₁-C₄ alkylidene radical, more preferably ethylidene or isopropylidene.

15

Preferably, the metallocene catalyst used is a bridged bis (tetrahydro-indenyl) zirconium dichloride, more preferably ethylene bis (tetrahydro-indenyl) zirconium dichloride.

20

The melt index of the metallocene catalysed polyethylene can be regulated by the amount of hydrogen injected in the reactor. The melt index (MI₂) of the polyethylene ranges from 0.2 g/10 min to 10 g/10 min when measured according to ASTM D 1238, conditions 190°C/2.16 kg.

25

The metallocene catalysed polyethylene may have a density of at least 0.900 g/cm³, preferably of at least 0.918 g/cm³, more preferably of at least 0.923 g/cm³. It has a density of at most 0.965 g/cm³, preferably of at most 0.960 g/cm³, more preferably of at most 0.950 g/cm³, even more preferably of at most 0.940 g/cm³. Preferably, the metallocene catalysed polyethylene has a density

30

As known in the art, the desired density is obtained by copolymerisation of ethylene with a suitable amount of a comonomer selected from the group

consisting of propylene, 1-butene, 1-hexene, 1-octene and 4-methyl-1-pentene, the preferred comonomer being 1-butene, 1-hexene, 1-octene, the most preferable comonomer being 1-hexene.

- 5 The metallocene catalysed polyethylene may have a monomodal molecular weight distribution. The molecular weight distribution is defined by a parameter, known as the dispersion index (D), which is the ratio between the average molecular weight by weight (Mw) and the average molecular weight by number (Mn). Preferably, the metallocene catalysed polyethylene used in the present invention has a molecular weight distribution of less than 4, preferably between 10 2 and 3, more preferably between 2.2 to 2.7. The molecular weights are determined by gel permeation chromatography (GPC).

15 The metallocene catalysed polyethylene is also characterised by a long chain branching structure.

Preferably, the mPE resin used in the present invention has a rheological long-chain branching index, LCBI, such as defined by R.N. Shroff and H. Mavridis in *Macromolecules* 2001, 34, 7362-7367 by the equation:

$$20 \quad \text{LCBI} = \frac{\eta_0^{0.179}}{4.8 [\eta]} - 1$$

where η_0 is the limiting, zero-shear viscosity at 190°C and $[\eta]$ is the intrinsic viscosity in trichlorobenzene at 135°C.

The LCBI is calculated from the best fitting by least squares analysis of the rheological curve (complex viscosity versus frequency) as described in US-A- 25 6114486 with the following generalized Cross equation, i.e. $\eta = \eta_0 / (1 + (\dot{\gamma} t_0)^n)$ wherein n is the power law index of the material characterizing the shear thinning behaviour of the material, t_0 is the characteristic relaxation time of the material, η_0 is the zero-shear viscosity, η and $\dot{\gamma}$ are the measured viscosity and shear rate data respectively. The dynamic rheological analysis is performed at 30 190°C under nitrogen and the strain amplitude is 10%. Results are reported according to ASTM D 4440.

Preferably, the LCBI of the metallocene catalysed polyethylene used in the present invention is at least 0.14, more preferably at least 0.50, even more preferably at least 1, most preferably at least 2.

- 5 Corona treatment of polymer film surfaces is well known. It is an electrical process that uses ionized air to increase the surface energy of plastic surface in order to allow improved wettability and adhesion of inks, coatings and adhesives. The treated surface demonstrates improved printing and coating quality. Usually, corona treatment is carried out such as to provide a surface
10 tension of 35 to 50 mN/m.

According to one embodiment, only one metallocene catalysed polyethylene surface is corona treated.

- 15 According to another embodiment, both metallocene catalysed polyethylene surfaces are corona treated.

According to one embodiment, the corona treated polyethylene surface is the surface of a monolayer film.

20

According to another embodiment, the corona treated polyethylene surface is the surface layer of a multilayer film, the surface layer having been corona treated on its upper side. By multilayer film, it is meant a film having from 2 to 7 layers or even more. For example, the film may have a three-layer structure

- 25 A/C/A wherein "A" may be either of the same composition or may be of different composition provided that when "A" is corona treated, then "A" is a metallocene catalysed polyethylene. The core layer C can be either a tie layer such as for example a layer of ethylene vinyl acetate or can be any polyolefins such as polyethylene, polypropylene or mixture thereof. One can cite for example a high
30 density polyethylene resin which imparts the stiffness to the film.

One or more inner layers may also be present between layers A and C. One can cite for example a gas barrier layer containing for example ethylene vinyl

alcohol (EVOH). The multilayer structure may also include a laminate. The multilayer film is made by coextruding the resins of the different layers. Preferably, the multilayer film is produced by a coextrusion blown film process.

- 5 In the present invention, the sealing occurs between two polyethylene surfaces, the polyethylene of each surface being produced with a metallocene catalyst, and at least one polyethylene surface is corona treated before the sealing. Preferably both polyethylene surfaces are metallocene catalysed polyethylene such as previously defined.

10

The polyethylene surface, which is not corona treated and to which the corona treated polyethylene surface is sealed to, may be the polyethylene surface of either a monolayer or a multilayer film.

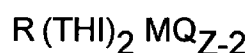
- 15 The sealing temperature of the polyethylene surfaces may range from 120°C to 160°C.

- The present invention further provides a packaging comprising a heat seal obtained by the method of the invention. As packaging, one can cite for
20 example bags or heavy-duty sacks.

According to one embodiment, the heat seal occurs between the polyethylene surfaces of two films.

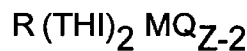
- 25 According to another embodiment, a film is first folded over itself and the corona treated polyethylene surface is either sealed to itself or sealed to the backside surface of the film, provided that the backside surface of the film is made of a metallocene catalysed polyethylene, preferably a polyethylene produced with the catalyst having the general formula

30



wherein THI, R, Q, M and Z have the meaning stated above.

The present invention also provides the use of a corona treated polyethylene as a heat sealing surface to a second polyethylene surface characterised in that both polyethylenes are metallocene catalysed polyethylenes, preferably both polyethylenes being produced with the metallocene catalyst having the general
5 formula



wherein THI, R, Q, M and Z have the meaning stated above.

10 Examples

1. Materials

The following resins were used:

- 15 * A metallocene polyethylene resin was prepared by using ethylene bis (4,5,6,7,tetrahydro-1-indenyl) zirconium dichloride. Said catalyst was activated and supported. The resin had a density of 0.923 g/cm³, a MI₂ of 0.9 g/10min, a molecular weight distribution of 2, a long chain branching index (LCBI) of 0.60 and a surface tension of 32 mN/m. The resin was used
- 20 - on one hand as such and identified hereinafter "M" and
 - on the other hand previously corona treated on one side and identified hereinafter "Mc". The surface tension of the corona treated resin was 40 mN/m.
- 25 * A commercially available low-density polyethylene produced by a high pressure polymerisation process sold by Total Petrochemicals having a density of 0.924 g/cm³, a MI₂ of 0.8 g/10min, a molecular weight distribution of 5.6 and a surface tension of 30 mN/m known under the reference 1008FE24. The resin was used:
- 30 - on one hand as such and identified "L" and

- on the other hand previously corona treated on one side and identified hereinafter "Lc". The surface tension of the corona treated resin was 36 mN/m.

- 5 * A commercially available high-density polyethylene sold by Total Petrochemicals under the reference HL717 having a density of 0.958 g/cm³, a MI₂ of 0.26 g/10min, a molecular weight distribution of 12 and a long chain branching index (LCBI) of 0.4.

10 2. Films preparation

Four blown coextruded three-layers A/B/A films (F1-F4) were prepared and characterised by

- 15 - either two identical surface layers (A) made of "M" (F2) and "L" (F4) or two different surface layers, one made of "Mc" and the other one made of "M" (F1) or one made of "Lc" and the other one made of "L" (F3),
- one core layer (B) made of HL717.

The thickness of each layer A is 10µm. The thickness of layer B is 20µm.

20

The following films were thus produced:

F1: Mc/HL717/M,

F2: M/HL717/M,

F3: Lc/HL717/L and

25 F4: L/HL717/L.

3. Films sealing

Films 150 mm long and 100 mm wide were heat sealed to each other during

30 2.5 seconds at a pressure of 40 N at different temperature, by steps of 10°C. The films were maintained during 40 hours at 23°C, 50% humidity. The seal

strength was measured on a 15 mm width sample at 200 mm/min according to the ASTM F88-00 method.

4. Examples and comparative examples

5

Example 1: the corona treated polyethylene surface of the film F1, wherein the polyethylene is produced with a metallocene catalyst, was heat sealed to the metallocene catalysed polyethylene surface of the film F2 (example identified hereafter as Mc/M).

10

Comparative example 1: the corona treated polyethylene surface of the film F1, wherein the polyethylene is produced with a metallocene catalyst, was heat sealed to the low density polyethylene surface of the film F4 (comparative example identified hereafter as Mc/L).

15

Comparative example 2: the corona treated low density polyethylene surface of the film F3 was heat sealed to the metallocene catalysed polyethylene surface of the film F2 (comparative example identified hereafter as Lc/M).

20 Comparative example 3: the corona treated low density polyethylene surface of the film F3 was heat sealed to the low density polyethylene surface of the film F4 (comparative example identified hereafter as Lc/L).

25 Example 2: the corona treated polyethylene surface of the film F1, wherein the polyethylene is produced with a metallocene catalyst, was heat sealed to itself (example identified hereafter as Mc/Mc).

30 Comparative example 4: the corona treated low density polyethylene surface of the film F3 was heat sealed to the corona treated metallocene catalysed polyethylene surface of the film F1 (comparative example identified hereafter as Lc/Mc).

Comparative example 5: the corona treated low density polyethylene surface of the film F3 was heat sealed to itself (comparative example identified as Lc/Lc).

5. Film properties

The seal strength between the sealant surfaces was measured by the force (in Newtons) necessary for separating those surfaces. The results of tables I and II have been respectively plotted in figures I and II.

Table 1

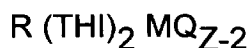
Sealing temperature (°C)	Seal strength (N)			
	Example 1 (Mc/M)	Comparative example 1 (Mc/L)	Comparative example 2 (Lc/M)	Comparative example 3 (Lc/L)
120	14.6	9.1	9.2	9.2
130	15.0	12.4	12.8	11.5
140	14.9	12.1	12.4	11.9
150	15.2	12.5	12.4	12.7
160	16.2	12.5	12.5	13.3

Table 2

Sealing temperature (°C)	Seal strength (N)		
	Example 2 (Mc/Mc)	Comparative example 4 (Lc/Mc)	Comparative example 5 (Lc/Lc)
120	12.5	8.9	8.9
130	13.6	12.3	11.1
140	13.9	12.6	11.8
150	14.4	12.9	11.9
160	14.1	12.7	12.3

Claims

1. A method for obtaining a heat seal between two polyethylene surfaces,
the method comprising the steps of:
 - 5 a) providing a first polyethylene surface, wherein the polyethylene is
 produced with a metallocene catalyst and has a density of from
 0.918 to 0.965 g/cm³,
 - b) providing a second polyethylene surface, wherein the
 polyethylene is produced with a metallocene catalyst and has a
10 density of from 0.918 to 0.965 g/cm³,
 - c) corona treating at least the first polyethylene surface and
 - d) heat sealing the first corona treated polyethylene surface and the
 second polyethylene surface together.
- 15 2. A method according to claim 1 wherein the first polyethylene surface and
 the second polyethylene surface are both corona treated.
3. A method according to claim 1 or 2 characterised in that the corona
 treated polyethylene surface is produced with a metallocene catalyst
20 having the general formula



wherein

- 25 THI is a tetrahydrogenated indenyl group which may be
 substituted or not,
- R is a substituted or unsubstituted C₁-C₄ alkylidene radical, a
 dialkyl germanium, a dialkyl silicon, a diaryl silicon, a di-
 alkoxysilane, a diphenoxysilane, or an alkyl phosphine or amine
 radical bridging two tetrahydrogenated indenyl groups,
- 30 Q is a hydrocarbonyl radical such as aryl, alkyl, alkenyl, alkylaryl, or
 arylalkyl radical having from 1-20 carbon atoms, hydrocarboxy

radical having 1-20 carbon atoms or halogen and can be the same or different from each other,

M is a group IVb, Vb or VIb transition metal, and

Z is the valence of the transition metal.

5

4. A method according to claim 3, wherein THI is an unsubstituted tetrahydrogenated indenyl group.

10

5. A method according to claim 3, wherein M is a group IVb transition metal.

6. A method according to claim 3, wherein M is zirconium.

15

7. A method according to claims 1 to 6, wherein the metallocene is a bridged bis (tetrahydro-indenyl) zirconium dichloride.

8. A method according to claim 1, wherein the polyethylene surface, which is not corona treated is produced with a metallocene catalyst having the general formula mentioned in claim 3.

20

9. A packaging comprising a heat seal obtained by the method of any one of the preceding claims.

25

10. Use of a corona treated polyethylene having a density of from 0.918 to 0.965 g/cm³ as a heat sealing surface to a second polyethylene surface having a density of from 0.918 to 0.965 g/cm³ characterised in that both polyethylenes are metallocene catalysed polyethylenes.

30

Fig.1

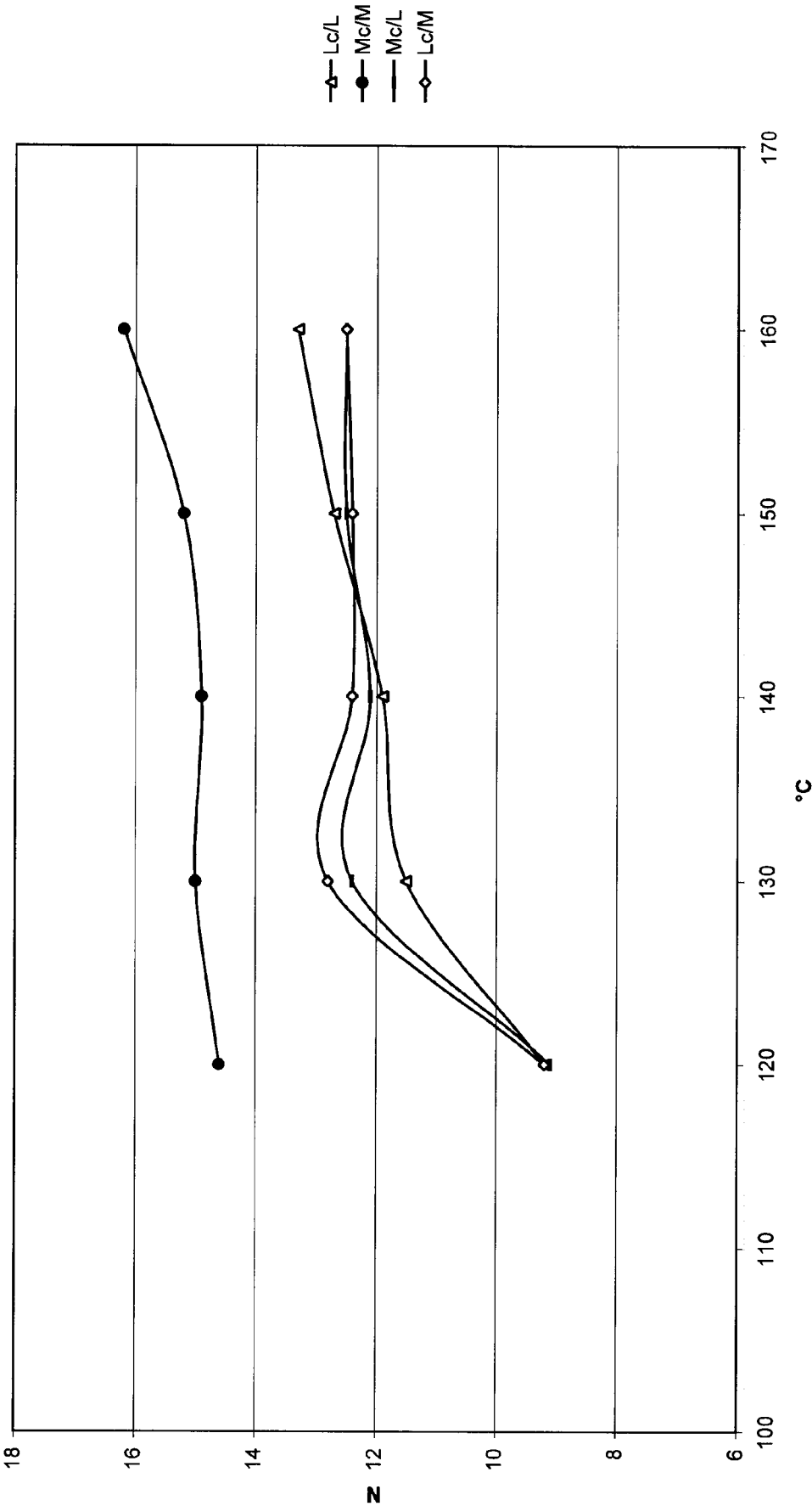


Fig.2

