

Clarke, Modet & Co.

COLOMBIA  
E-MAIL: clarkemo@colomnet.net.co  
SANTAFÉ DE BOGOTÁ, A.A. 92

33  
30

SUPERINDUSTRIA Y COMERCIO  
Radicación : 00032437 00000001  
Fecha (AMD): 2000-05-07 16:20:18  
Trámite : 002 PATENTES D 1 REGISTRO/ 329 COMPLEMEN  
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES  
Folios: 34

SEÑORES  
DIVISION DE NUEVAS CREACIONES  
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO  
E. S. D.

COD:08

Ref.: EXPEDIENTE N° 00032437 ✓  
FECHA SOLICITUD: Mayo 5, 2000  
PATENTE: COPOLIMEROS DE ETILENO Y ALFA-OLEFINAS Y PELÍCULAS  
PRODUCIDAS A PARTIR DE LOS MISMOS  
SOLICITANTE: BP CHEMICALS LIMITED

ASUNTO: PRESENTACION PRIORIDAD

DILIA RODRIGUEZ D'ALEMAN, en mi condición de apoderada de la sociedad  
solicitante, en esta oportunidad por el presente escrito me permito presentar:

1. Copia certificada de la prioridad Británica reivindicada N° 9910370.7 de  
Mayo 5 de 1999
2. Copia certificada de la prioridad Británica reivindicada N° 9927205.6 de  
Noviembre 17 de 1999
- Traducción al Español de las mencionadas prioridades

Estas prioridades están siendo presentadas dentro del término de 3  
meses que exige el Convenio de Paris, toda vez que la solicitud fué  
radicada el 5 de mayo de 2.000.

Ruego a usted continuar con el presente trámite.

Señor Jefe,

DILIA RODRIGUEZ D'ALEMAN  
CCR/srr  
P- 331



The  
Patent  
Office

Columbia



INVESTOR IN PEOPLE

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

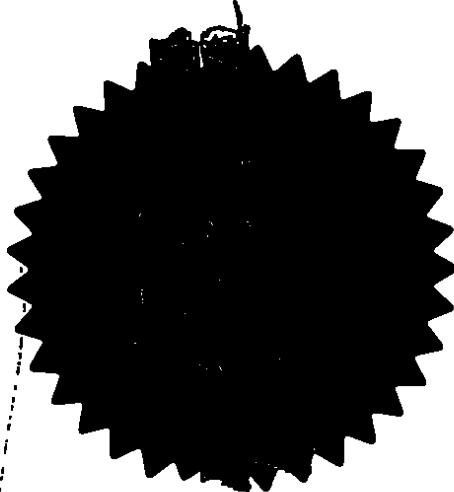
12331  
34  
31

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed *Ansower*

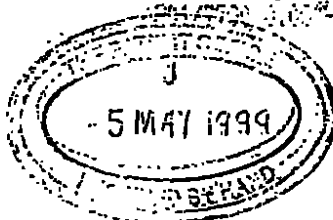
Dated 18 April 2000

TRADUCCION OFICIAL No. *200608*  
MILDA AGUILERA DE PIEDRAHITA  
INTERPRETE OFICIAL  
RES No 323 DEL MIN DE ECONOMIA

An Executive Agency of the Department of Trade and Industry

05 MAY 1999

32 35



# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

BPCL 9158

2. Patent application number

(The Patent Office will fill in this part)

9910370.7

3. Full name, address and postcode of the or of each applicant (underline all surnames)

BP CHEMICALS LIMITED  
Britannic House  
1 Finsbury Circus  
London  
EC2M 7BA

Patents ADP number (If you know it)

If the applicant is a corporate body, give the country/state of its incorporation

England, UNITED KINGDOM

4. Title of the invention

NOVEL COPOLYMERS AND FILMS THEREOF

5. Name of your agent (If you have one)

PREECE, Michael

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

BP INTERNATIONAL LIMITED  
Group Patents & Agreements  
Chertsey Road  
Sunbury-on-Thames  
Middlesex  
TW16 7LN  
England

Patents ADP number (If you know it)

6090260001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (If you know it) the or each application number

Country

Priority application number  
(If you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

TRADUCCION OFICIAL No. 2004088  
MILDA AGUILERA DE PIEDRAHITA  
INTERPRETE OFICIAL  
C/ES No. 323 DEL MIN. DE JUSTICIA

Patents Form 1/77

# Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form.  
Do not count copies of the same document

|                                  |   |
|----------------------------------|---|
| Continuation sheets of this form | - |
| Description                      | 9 |
| Claim(s)                         | - |
| Abstract                         | - |
| Drawing(s)                       | - |

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.
- |           |                  |      |         |
|-----------|------------------|------|---------|
| Signature | <u>M. Preece</u> | Date | 5.05.99 |
|           | PREECE, Michael  |      |         |

12. Name and daytime telephone number of person to contact in the United Kingdom

## Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

## Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

RECEIVED OFFICIAL NO. 2000/078  
HILDA  
INSTRUMENTO DE JUSTICIA  
DEB No. 22 DEL MIN. DE JUSTICIA

Patents Form 1/77

**NOVEL COPOLYMERS AND FILMS THEREOF**

The present invention relates to copolymers of ethylene and alpha-olefins in particular to low density copolymers and also to films produced from said copolymers.

In recent years there have been many advances in the production of polyolefin copolymers due to the introduction of metallocene catalysts. Metallocene catalysts offer  
5 the advantage of generally higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single-site in nature. Because of their single-site nature the polyolefin copolymers produced by metallocene catalysts often are quite uniform in their molecular structure. For example, in comparison to traditional Ziegler produced materials, they have relatively narrow molecular weight distributions (MWD)  
10 and narrow Short Chain Branching Distribution (SCBD).

Although certain properties of metallocene products are enhanced by narrow MWD, difficulties are often encountered in the processing of these materials into useful articles and films relative to Ziegler produced materials. In addition, the uniform nature of the SCBD of metallocene produced materials does not readily permit certain  
15 structures to be obtained.

Recently a number of patents have published directed to the preparation of films based on low density polyethylenes prepared using metallocene catalyst compositions.

WO 94/14855 discloses linear low density polyethylene (LLDPE) films prepared using a metallocene, aluminoxane and a carrier. The metallocene component is typically  
20 a bis (cyclopentadienyl) zirconium complex exemplified by bis (n-butylcyclopentadienyl) zirconium dichloride. The LLDPE's disclosed have a narrow Mw/Mn of 2.5-3.0, a melt flow ratio (MFR) of 15-25 and low zirconium residues.

WO 94/26816 also discloses films prepared from ethylene copolymers having a narrow composition distribution. The copolymers are also prepared from traditional metallocenes (eg bis (1-methyl, 3-n-butylcyclopentadienyl) zirconium dichloride and methylalumoxane deposited on silica) and are also characterised as having a narrow  
5 MWD typically in the range 3-4 and in addition by a value of  $M_z/M_w$  of less than 2.0.

However, it is recognised that the polymers produced from these types of catalyst system have deficiencies in processability due to their narrow MWD.

We have now found that it is possible to prepare copolymers of ethylene and alpha-olefins having a narrow MWD and also low or moderate amounts of long chain  
10 branching. The polymers produced have a unique combination of properties and which are suitable for preparing films having an excellent balance of optical and mechanical properties.

Thus, according to the present invention there is provided a copolymer of ethylene and an alpha olefin having 3 to 10 carbon atoms, said polymer having

- 15 (a) a density in the range 0.900 to 0.940  
(b)  $M_w/M_n$  of 2 - 3.4, and  
(c) a  $I_{21}/I_2$  of 18 -24.

The novel copolymers of the present invention preferably have a density in the range 0.900 - 0.925, a  $M_w/M_n$  in the range 2 to 2.8 and a  $I_{21}/I_2$  in the range 19 to 24.

20 The unique copolymers of the present invention may suitably be prepared by use of a metallocene catalyst system comprising a complex having a 'constrained geometry' configuration together with a suitable activator.

Suitable complexes are those disclosed in WO 95/00526 the disclosure of which is incorporated herein by reference.

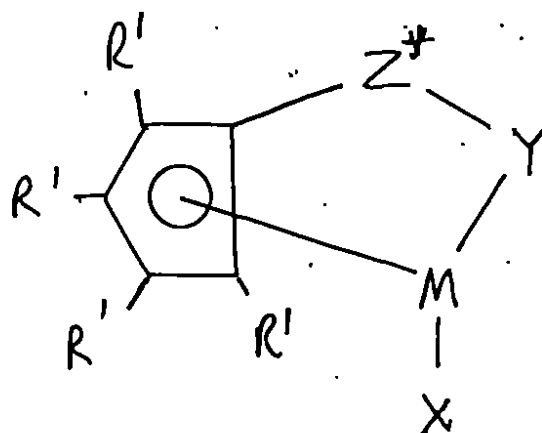
25 Suitable activators may comprise traditional aluminoxane or boron compounds for example borates again disclosed in the aforementioned WO 95/00526.

Preferred metallocene complexes for use in the preparation of the unique copolymers of the present invention may be represented by the general formula:

30

5

10



15

wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germlyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

20

X is a neutral  $\eta^4$  bonded diene group having up to 30 non-hydrogen atoms, which forms a  $\pi$  complex with M;

Y is -O-, -S-, -NR<sup>\*</sup>-, -PR<sup>\*</sup>-,

25

M is titanium or zirconium in the + 2 formal oxidation state;

Z<sup>\*</sup> is SiR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup><sub>2</sub>, SiR<sup>\*</sup><sub>2</sub>, SiR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup><sub>2</sub>, CR<sup>\*</sup><sub>2</sub>, SiR<sup>\*</sup><sub>2</sub>, or GeR<sup>\*</sup><sub>2</sub>, wherein:

30

R<sup>\*</sup> each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R<sup>\*</sup> having up to 10 non-hydrogen atoms, and optionally, two R<sup>\*</sup> groups from Z<sup>\*</sup> (when R<sup>\*</sup> is not hydrogen), or an R<sup>\*</sup> group from Z<sup>\*</sup> and an R<sup>\*</sup> group from Y form a ring system.

Examples of suitable X groups include s-trans- $\eta^4$ -1,4-diphenyl-1,3-butadiene, s-trans- $\eta^4$ -3-methyl-1,3-pentadiene; s-trans- $\eta^4$ -2,4-hexadiene; s-trans- $\eta^4$ -1,3-pentadiene; s-trans- $\eta^4$ -1,4-ditolyl-1,3-butadiene; s-trans- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene; s-cis- $\eta^4$ -3-methyl-1,3-pentadiene; s-cis- $\eta^4$ -1,4-dibenzyl-1,3-butadiene; s-cis- $\eta^4$ -1,3-pentadiene; s-cis- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a  $\eta$ -complex as defined herein with the metal.

Most preferred complexes are amidosilane - or amidoalkanediyl complexes.

A preferred complex for use in the preparation of the copolymers of the present invention is (t-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl) dimethyl silanetitanium - $\eta^4$ -1,3 - pentadiene.

The activator may preferably be a boron compound for example borates such as trialkylammonium salts, in particular.

triethylammonium tetraphenylborate

triethylammonium tetraphenylborate,

tripropylammonium tetraphenylborate,

tri(n-butyl)ammonium tetraphenylborate,

tri(t-butyl)ammonium tetraphenylborate,

N,N-dimethylanilinium tetraphenylborate,

N,N-diethylanilinium tetraphenylborate,

Another type of activator suitable for use with the metallocene complexes of the present invention are the reaction products of (A) ionic compounds comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen and (B) an organometal or metalloid compound wherein the metal or metalloid is from Groups 1-14 of the Periodic Table.

Suitable activators of this type are described in WO 98/27119 the relevant portions of which are incorporated by reference.

A particular preferred activator of this type is the reaction product obtained from alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates and trialkylamines. For example a preferred activator is the reaction product of bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate and triethylamine.

The molar ratio of metallocene complex to activator employed in the process of

the present invention may be in the range 1:10000 to 100:1. A preferred range is from 1:50000 to 10:1 and most preferred from 1:10 to 10:1.

The metallocene catalyst system suitable for use in the present invention is most suitably supported. Typically the support can be an organic or inorganic inert solid.

- 5 However particularly porous supports such as talc, inorganic oxides and resinous support materials such as polyolefins which have well-known advantages in catalysis are preferred. Suitable inorganic oxide materials which may be used include Group 2, 13 14 or 15 metal oxides such as silica, alumina, silica-alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania or zirconia. Other suitable support materials may be employed such as finely divided polyolefins such as polyethylene.

The most preferred support material for use with the supported catalysts according to the process of the present invention is silica. Suitable silicas include Crossfield ES70 and Davidson 948 silicas.

- 15 It is preferable that the silica is dried before use and this is typically carried out by heating at elevated temperatures for example between 200 and 850 °C.

- The copolymers of the present invention are most suitably prepared in the gas phase in particular in a continuous process operating at a temperature >60°C and most preferably at a temperature of 80°C or above. The preferred process is one comprising a fluidised bed reactor. A particularly suitable gas phase process is that disclosed in EP 699213 incorporated herein by reference.

- The copolymers according to the present invention may be used to prepare the full range of products normally manufactured from polyethylene copolymer products in the density range 900 to 940 kg/m<sup>3</sup>. They may also be used blended with other polymers such as low density polyethylenes, linear low density polyethylenes, medium density polyethylenes, high density polyethylenes, plastomers and elastomers. Examples of applications include injection moulding, rotomoulding, extrusion into pipes, sheets, films, fibres, non-woven fabrics, cable coverings and other uses which will be known to those skilled in the art. The products are particularly suitable for the production of films and sheets prepared using traditional methods well known in the art. Examples are blowing, orientation of the partially crystallised product. The films exhibit good processability, improved optical and mechanical properties and good heat sealing properties.

The films for example have a dart impact >100g and also a low hexane extractables content of 0.2 - 1.5%.

Thus according to another aspect of the present invention there is provided a film exhibiting a dart impact measured by ASTM D-1709 of >100g, a hexane extractables content of 0.2 - 1.5% said film comprising a copolymer of ethylene and a alpha-olefin having 3-10 carbon atoms and which has

- (a) a density in the range 0.900 to 0.940
- (b)  $M_w/M_n$  of 2 - 3.4 , and
- (c)  $I_{21}/I_2$  of 18 - 24.

The films may be suitable for a number of applications for example industrial, retail, food packaging, non-food packaging and medical applications. Examples include films for bags, garment bags, grocery sacks, merchandise bags, self-serve bags, grocery wet pack, food wrap, pallet stretch wrap, bundling and overwrap, industrial liners, refuse sacks, heavy duty bags, agricultural films, daiper liners, etc.

The films may be utilised as shrink film, cling film, stretch film, sealing film or other suitable type.

#### Methods of test

Melt index was measured by ASTM D1238.  $I_{21}/I_2$  is the ratio of melt indices measured at loads of 21.6 and 2.16kg. Density was measured by ISO 11837, and values for density after annealing are given.

Molecular weight averages were obtained using a Waters 150CV instrument using a calibration for linear polyethylene based upon standards of broad MWD. Hence values given are not corrected for LCB, and somewhat higher values of  $M_w$  and  $M_w/M_n$  would be obtained for corrected data.

Dart impact was measured by ASTM D1709, tear strength by ASTM D1922 and haze by ASTM D1003.

The present invention will now be further illustrated by reference to the accompanying Examples.

#### Example 1

##### (i) Treatment of silica

A suspension of Grace 948 silica (13kg, previously calcined at 250°C for 5

hours) in 110 litres (L) of hexane was made up in a 240L vessel under nitrogen. 1L of a hexane solution containing 2g/L of Stadis 425 was added and stirred at room temperature for 5 minutes. 29.1L of a 892mmolAl/L solution of TEA in hexane was added slowly to the stirred suspension over 30 minutes, while maintaining the temperature of the suspension at 30°C. The suspension was stirred for a further 2 hours. The hexane was filtered, and the silica washed with hexane, so that the aluminium content in the final washing was less than 0.5 mmol Al/litre. Finally the suspension was dried *in vacuo* at 60°C to give a free flowing treated silica powder with residual solvent less than 0.5wt%.

10 (ii) Catalyst fabrication

All steps of the catalyst fabrication were carried out at 20°C. 3L of toluene was added to a 24L vessel equipped with a turbine stirrer, and stirred at 300rpm. 5.01L of a 9.5wt% solution in toluene of bis(hydrogenated tallow alkyl) methyl ammonium tris(pentafluorophenyl)(4-hydroxyphenyl)borate was added during 15 minutes. Then 1.57L of a 250mmolAl/L solution in toluene of TEA was added during 15 minutes and mixture stirred for 30 minutes. The solution obtained was then transferred under nitrogen, with stirring during 2 hours, to an 80L vessel containing 10kg of the TEA treated silica described above. 60L of essence was then rapidly introduced and mixed for 30 minutes. 1.83 kg of a 7.15wt% solution in heptane of (t-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl) dimethylsilanetitanium - $\eta^4$ -1,3-pentadiene was added during 15 minutes. Mixing was continued for 1 hour and 1L of a 2g/L hexane solution of stadis 425 was added. The catalyst slurry was then transferred to a vessel of volume 240L and 70L of hexane added. Excess solvent was removed by decantation, and a further 130L of hexane added. This process was repeated until less than 0.2L of toluene remained in the solvent. 1L of a 2g/L hexane solution of stadis 425 was then added and the catalyst dried under vacuum at 40°C to a residual solvent level of 1wt%.

(iii) Polymerisation using continuous fluidised bed reactor

Ethylene, n-hexene, hydrogen and nitrogen were fed into a continuous fluidised bed reactor of diameter 45cm. Polymer product was continuously removed from the reactor.

30 Operating conditions are given in Table 1.

**Table 1**

|                                        |          |
|----------------------------------------|----------|
| Total pressure (bar)                   | 17.9     |
| Temperature                            | 80 deg.C |
| Ethylene pressure (bar)                | 5.6      |
| 5 H <sub>2</sub> /C <sub>2</sub> ratio | 0.0020   |
| C <sub>6</sub> /C <sub>2</sub> ratio   | 0.0040   |
| production (kg/h)                      | 41       |

The results are given below in Table 2 together with typical values of a LLDPE copolymer from ethylene and hexene exemplified in the literature.

- 10 After degassing, the powder product withdrawn from the reactor was compounded using a ZSK58 twin screw extruder, the additive package being 1250ppm calcium stearate, 500ppm Irganox 1076 and 800ppm Irgafos PEPQ. Blown film was produced at 50kg/hr on a Reifenhauser film line equipped with a die of diameter 150mm and die gap 2.3mm. The film extrusion conditions and properties are given in Table 3.

15

**TABLE 2 Structure properties**

| PROPERTY                                           | EXAMPLE 1    | LLDPE A |
|----------------------------------------------------|--------------|---------|
| Melt Index (dg/min)                                | 1.04         |         |
| MFR (I <sub>21</sub> /I <sub>2</sub> )             | 20.2         | 18      |
| Density (kg/m <sup>3</sup> )                       | 0.9185       | 0.918   |
| M <sub>w</sub>                                     | 92,200       |         |
| M <sub>w</sub> /M <sub>n</sub> uncorrected for LCB | 2.33         | 2.6     |
| Hexene-1 (wt%)                                     | 8.4          |         |
| Peak Melting Temperature (°C)                      | 116.4        | 115     |
| Subsidiary melting peaks(°C)                       | 104.4, 119.5 |         |
| Dart Impact                                        | >1200        | >800    |
| Hexane Extractables                                | 0.3          | 0.6     |

NB. LLDPE A = Example 1 of WO 94/14855

37 48  
40

**TABLE 3 Film properties**

| PROPERTY                  | EXAMPLE 1 | LLDPE A |
|---------------------------|-----------|---------|
| Screw speed (rpm)         | 101.5     |         |
| Melt pressure (bar)       | 237       |         |
| Motor load (A)            | 42        |         |
| Specific energy (kWh/kg)  | 0.192     |         |
| Melt temperature (°C)     | 220.1     |         |
| Blow up ratio             | 2         |         |
| Film thickness (µm)       | 38        |         |
| Dart Impact (g)           | >1200     | >800    |
| MD tear strength (g/25µm) | 188       |         |
| Haze (%)                  | 9.6       |         |
| Gloss (o/oo)              | 58.3      |         |
| Hexane Extractables (%)   | 0.3       | 0.6     |

NB. LLDPE A = Example 1 of WO 94/14855

5

10

15

Traducción en la  
Bolsa P. 331

38 41

TRADUCCION OFICIAL No.2000/088 de un documento escrito en inglés el cual para su identificación se sella con el sello del traductor al tiempo con la presente. Esta traducción ha sido preparada por Hilda Aguilera de Piedrahita, traductora e intérprete oficial debidamente reconocida por el Ministerio de Relaciones Exteriores y autorizada por el Ministerio de Justicia y del Derecho, por Resolución No. 323 de 1980.

(Se traduce el formulario de solicitud de Patente escrita en inglés a favor de BP CHEMICALS LIMITED).

(Sello Pre-impreso) LA OFICINA DE PATENTES Invierte en la Gente

LA OFICINA DE PATENTES, CONCEPT HOUSE

CARDIFF ROAD, NEW PORT, SOUTH WALES, NP10 8QQ

Yo, el suscrito, funcionario debidamente autorizado de acuerdo con la Sección 74(1) y (4) de La Ley de Desregulación y Contratación de 1994, para firmar y expedir certificados a nombre del Contralor General, por el presente certifico que adjunta se encuentra una copia fiel de los documentos originalmente presentados en relación con la solicitud de patente identificada en ellos.

De acuerdo con las Normas de Patentes (Re-registro de Compañías) 1982, si una compañía nombrada en este certificado y en los documentos anexos se ha re-registrado bajo la Ley de Compañías 1980 con el mismo nombre con el que fue registrada inmediatamente antes de el re-registro excepto para la sustitución o inclusión como, la última parte del nombre de las palabras "compañía pública

TRADUCCION OFICIAL No. 2000/088  
HILDA AGUILERA DE PIEDRAHITA  
INTERPRETE OFICIAL  
RES No 323 DEL MIN. DE INTERIO

39 10  
42

limitada" o sus equivalentes en Gálico, las referencias al nombre de la compañía en este certificado y a los documentos anexos se deberán tratar como referencias al nombre con el cual está así re-registrada.

De acuerdo con las reglas, las palabras "compañía pública limitada" se pueden reemplazar por c.p.l., cpl, C.P.L., ó CPL (p.l.c., plc, P.L.C, o PLC).

El Re-registro bajo la Ley de Compañías no constituye un nuevo ente legal pero solamente obliga a la compañía para con ciertas reglas de ley adicionales para compañías.

Firmado (Ilegible)

Fecha: Abril 18 del 2000.

(SELLO DE OBLEA DE LA OFICINA DE PATENTES)

Una Agencia Ejecutiva del Departamento de Comercio e Industria

---

### LA OFICINA DE PATENTES

(Sello a Tinta: 5 de Mayo, 1999)

F r mato de Patentes 1/77

05May99 E444952-1 D00173

Ley de Patentes de 1977 (Regla 16)

P01/7700 0.00 - 9910370.7

(Sello a Tinta de la Oficina de Patentes, 5 Mayo 1999)

Solicitud de otorgamiento de una patente

La Oficina de Patentes

*(Véanse las notas al respaldo de este formulario.*

Cardiff Road, New Port

*También puede obtener un folleto explicativo de la*

Gwent NP9 1RH

*Oficina de Patentes como ayuda para llenar el presente*

40 43

Group Patents & Agreements  
Chertsey Road  
Sunbury\_on \_Thames  
Middlesex  
TW16 7LN  
Inglaterra

Número ADP de las Patentes (*si lo sabe*): 6090260001

6. Si está declarando la prioridad de una o de más solicitudes de patente anteriores, diga el país y la fecha de presentación de la o de cada una de las solicitudes anteriores y (*si lo sabe*) el o cada uno de los números de solicitud.

País:

Número de Solicitud de la Prioridad (*si lo sabe*):

Fecha de Presentación (*Día/Mes/Año*)

7. Si esta solicitud se divide o de lo contrario se deriva de una solicitud anterior en el Reino Unido, diga el número y la fecha de presentación de la solicitud anterior.

Número de Solicitud Anterior:

Fecha de Presentación (*Día/Mes/Año*):

8. Se requiere de una declaración de invención y de derecho para otorgar una patente como soporte de la presente solicitud? Si

(Responda afirmativamente si:

- a) cualquier solicitante nombrado en 3. no es inventor, o
- b) existe un inventor quien no está nombrado como solicitante, o
- c) cualquiera de los aplicantes nombrados es una sociedad:)

Vea nota (d)

Formulario de Patentes 1/77

2005/088  
TRANSDUCCION OFICIAL DEL  
MILDA AGUILERA DE PIEDRABITA  
INTERPRETE OFICIAL  
RES No 323 DEL MIN. DE JUSTICIA

41 44 10

formulario).

1. Su Referencia: BPCL 9158

2. Número de Solicitud de la Patente: **9910370.7**

*(La Oficina de Patentes llenará esta parte)*

3. Nombre Completo, dirección y código postal de o de cada uno de los solicitantes *(Subrayar todos los apellidos)*:

BP CHEMICALS LIMITED

BRITANNIC HOUSE

1 Finsbury Circus

LONDRES

EC2M 7BA

Número ADP de las Patentes *(si lo sabe)*: 4141891002

Si el solicitante es una sociedad, dar el país/estado de su constitución:

INGLATERRA, REINO UNIDO

4. Nombre de la Invención: COPOLÍMEROS NOVEDOSOS Y PELÍCULAS  
PRODUCIDAS A PARTIR DE ELLOS

5. Nombre de su Agente *(si lo tiene)*

PREECE, Michael

"Dirección para Notificación" en el Reino Unido, donde se debe enviar toda la correspondencia *(incluyendo el código postal)*

BP INTERNATIONAL LIMITED

2000/088  
PRODUCCION ORIGINAL NO.  
MILDA 4  
IN  
RES NO. 273 011 414 DE JUSTICIA

42 13  
45

**F rmulario de Patentes 1/77**

9. Llene el número de páginas de cualquiera de los siguientes ítems que está presentando con este formulario. No cuente las copias del mismo documento.

Hojas a continuación de este formulario:-

Descripción: 9

Reivindicaciones:-

Resmen:-

Dibujo(s): -

10. Si está también presentando cualquiera de los siguientes, declare cuántos al frente de cada ítem.

- Documentos de prioridad:
- Traducciones de documentos de prioridad:
- Declaración de Invención y derecho de otorgar una patente (*Formulario de Patentes 7/77*):
- Solicitud para examen preliminar y búsqueda (*Formulario de Patentes 9/77*):
- Solicitud de Examen Sustantivo (*Formulario de Patentes 10/77*):
- Cualesquiera otros documentos (*Favor especificar*):

11. Yo/nosotros solicito (amos) el otorgamiento de la patente con base en esta solicitud.

Firma (Firmado) PREECE Michael, Fecha 5.05.99

93 44  
46

12. Nombre y número telefónico durante el día de la persona a contactar en el Reino Unido

#### **Advertencia**

*Después de que se ha presentado la solicitud para una patente, el Contralor de la Oficina de Patentes decidirá si la publicación o la comunicación de la invención debería prohibirse o restringirse bajo la Sección 22 de la Ley de Patentes 1977. Usted será informado si es necesario prohibir o restringir su invención de esta manera. Adicionalmente, si usted vive en el Reino Unido, la Sección 23 de la Ley de Patentes 1977 no le permite solicitar una patente en el extranjero sin antes obtener permiso escrito de la Oficina de Patentes a menos de que una solicitud haya sido presentada con por lo menos 6 semanas de anterioridad en el Reino Unido para una patente para el mismo invento y no ha habido aviso prohibiendo su publicación o su comunicación, o dicho aviso ha sido revocado.*

#### **Notas**

- a) *Si necesita ayuda para llenar este formulario o tiene alguna pregunta, favor contactar la Oficina de Patentes en 0645 500505.*
- b) *Escriba sus respuestas en mayúsculas usando tinta negra o máquina de escribir.*
- c) *Si no hay suficiente espacio para todos los detalles en cualquier parte de este formulario, por favor continúe en una hoja de papel aparte y escriba "véase hoja de continuación" en la(s) parte(s) relevante(s). Cualquier hoja de continuación se debe anexar a este formulario.*
- d) *Si ha respondido afirmativamente, se deberá presentar el formulario de*

889722  
PRODUCCION OFICIAL  
CUBA  
INVENTO OFICIAL  
DEL MIN. DE INTERIO

44 45 47

**Patentes 7/77.**

- e) Una vez completado el formulario, tiene que acordarse de firmarlo y fecharlo.
- f) Para detalles de la tarifa y formas de pago, favor dirigirse a la Oficina de Patentes.

**Forma de Patentes 1/77**

ES TRADUCCION FIEL Y COMPLETA de la cual se deja copia en los archivos de esta oficina para su confrontación y a la cual me remito.

Santafé de Bogotá, Mayo 21, 2000.

*Hilda Aguilera de Piedrahíta*  
2000688  
TRADUCCION OFICIAL POR  
NILDA AGUILERA DE PIEDRAHITA  
INTERPRETE OFICIAL  
CALLE NO. 223 DEL MUN. DE JUSTICIA



The  
Patent  
Office



INVESTOR IN PEOPLE

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

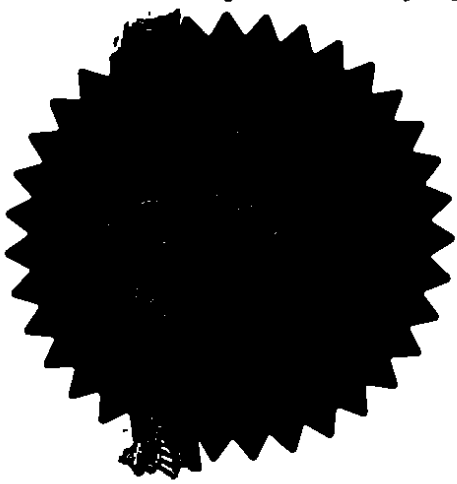
Columbia  
12.33.1  
48  
45

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

*L. Mahoney*

Dated 17 April 2000

TRADUCCION OFICIAL No. 2000/027  
MILDA AGUILERA DE PIFORAMITA  
INTERPRETE OFICIAL  
RES No. 323 DEL MIN. DE JUSTICIA

An Executive Agency of the Department of Trade and Industry

The  
Patent  
Office



18NOV99 E492656-1 003022  
P01/7700 0.00-9927205.6

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

# Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

17 NOV 1999

|                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                                                                                                        |                                        |                                                 |                                        |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------|-------------------------------------------------|----------------------------------------|
| 1. Your reference                                                                                                                                                                                                                                                                                                     | 9196                                                                                                                                                                                                                                                   |                                        |                                                 |                                        |
| 2. Patent application number<br>(The Patent Office will fill in this part)                                                                                                                                                                                                                                            | <b>9927205.6</b>                                                                                                                                                                                                                                       |                                        |                                                 |                                        |
| 3. Full name, address and postcode of the or of each applicant ( <u>underline all surnames</u> )                                                                                                                                                                                                                      | BP CHEMICALS LIMITED<br>BRITANNIC HOUSE<br>1 FINSBURY CIRCUS<br>LONDON<br>EC2M 7BA<br><br>Patents ADP number (If you know it)<br><br>If the applicant is a corporate body, give the country/state of its incorporation                                 |                                        |                                                 |                                        |
|                                                                                                                                                                                                                                                                                                                       | ENGLAND , UNITED KINGDOM                                                                                                                                                                                                                               |                                        |                                                 |                                        |
| 4. Title of the invention                                                                                                                                                                                                                                                                                             | NOVEL COPOLYMERS AND FILMS THEREOF                                                                                                                                                                                                                     |                                        |                                                 |                                        |
| 5. Name of your agent (if you have one)                                                                                                                                                                                                                                                                               | WILSON, Michael John                                                                                                                                                                                                                                   |                                        |                                                 |                                        |
| "Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)                                                                                                                                                                                                       | BP INTERNATIONAL LIMITED<br>PATENTS & AGREEMENTS<br>CHERTSEY ROAD<br>SUNBURY-ON-THAMES<br>MIDDLESEX<br>TW16 7LN                                                                                                                                        |                                        |                                                 |                                        |
|                                                                                                                                                                                                                                                                                                                       | Patents ADP number (If you know it)                                                                                                                                                                                                                    |                                        |                                                 |                                        |
| 6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number                                                                                            | <table border="0"> <tr> <td style="text-align: center;">Country</td> <td style="text-align: center;">Priority application number<br/>(if you know it)</td> <td style="text-align: center;">Date of filing<br/>(day / month / year)</td> </tr> </table> | Country                                | Priority application number<br>(if you know it) | Date of filing<br>(day / month / year) |
| Country                                                                                                                                                                                                                                                                                                               | Priority application number<br>(if you know it)                                                                                                                                                                                                        | Date of filing<br>(day / month / year) |                                                 |                                        |
| 7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application                                                                                                                                                                 | <table border="0"> <tr> <td style="text-align: center;">Number of earlier application</td> <td style="text-align: center;">Date of filing<br/>(day / month / year)</td> </tr> </table>                                                                 | Number of earlier application          | Date of filing<br>(day / month / year)          |                                        |
| Number of earlier application                                                                                                                                                                                                                                                                                         | Date of filing<br>(day / month / year)                                                                                                                                                                                                                 |                                        |                                                 |                                        |
| 8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:<br>a) any applicant named in part 3 is not an inventor, or<br>b) there is an inventor who is not named as an applicant, or<br>c) any named applicant is a corporate body.<br>See note (d)) | YES                                                                                                                                                                                                                                                    |                                        |                                                 |                                        |

TRADUCCION OFICIAL NO. 200/007  
HILDA AGUILERA DE PIEDRANITA  
INTERPRETE OFICIAL  
PER No 023 DEL MIN DE JUSTICIA

# Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description 18

Claim(s) -

Abstract -

Drawing(s) -

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. I/We request the grant of a patent on the basis of this application.  
Signature *Michael John Wilson* Date 17.11.99  
WILSON, Michael John

12. Name and daytime telephone number of person to contact in the United Kingdom 01932 763207

## Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

## Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

REGISTRATION, OFICIAL No. 2000/087  
WICDA  
INSTRUMENTO DE REGISTRO  
DES No. 323 DEL MIN. DE JUSTICIA

Patents Form 1/77

47 50

# **NOVEL COPOLYMERS AND FILMS THEREOF**

The present invention relates to copolymers of ethylene and alpha-olefins in particular to low density copolymers and also to films produced from said copolymers.

In recent years there have been many advances in the production of polyolefin copolymers due to the introduction of metallocene catalysts. Metallocene catalysts offer the advantage of generally higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single-site in nature. Because of their single-site nature the polyolefin copolymers produced by metallocene catalysts often are quite uniform in their molecular structure. For example, in comparison to traditional Ziegler produced materials, they have relatively narrow molecular weight distributions (MWD) and narrow Short Chain Branching Distribution (SCBD).

Although certain properties of metallocene products are enhanced by narrow MWD, difficulties are often encountered in the processing of these materials into useful articles and films relative to Ziegler produced materials. In addition, the uniform nature of the SCBD of metallocene produced materials does not readily permit certain structures to be obtained.

Recently a number of patents have published directed to the preparation of films based on low density polyethylenes prepared using metallocene catalyst compositions.

WO 94/14855 discloses linear low density polyethylene (LLDPE) films prepared using a metallocene, aluminoxane and a carrier. The metallocene component is typically a bis (cyclopentadienyl) zirconium complex exemplified by bis (n-butylcyclopentadienyl) zirconium dichloride. The LLDPE's disclosed have a narrow Mw/Mn of 2.5-3.0, a melt flow ratio (MFR) of 15-25 and low zirconium residues.

WO 94/26816 also discloses films prepared from ethylene copolymers having a narrow composition distribution. The copolymers are also prepared from traditional metallocenes (eg bis (1-methyl, 3-n-butylcyclopentadienyl) zirconium dichloride and methylalumoxane deposited on silica) and are also characterised as having a narrow  
5 MWD typically in the range 3-4 and in addition by a value of  $M_z/M_w$  of less than 2.0.

However, it is recognised that the polymers produced from these types of catalyst system have deficiencies in processability due to their narrow MWD. Various approaches have been proposed in order to overcome this deficiency. An effective method to regain processability in polymers of narrow  $M_w/M_n$  is by the use of certain catalysts which  
10 have the ability to incorporate long chain branching (LCB) into the polymer molecular structure. Such catalysts have been well described in the literature, illustrative examples being given in WO 93/08221 and EP-A-676421.

Furthermore, WO 97/44371 discloses polymers and films where long chain branching is present, and the products have a particularly advantageous placement of the comonomer within the polymer structure. Polymers are exemplified having both narrow  
15 and broad  $M_w/M_n$ , for example from 2.19 up to 6.0, and activation energy of flow, which is an indicator of LCB, from 7.39 to 19.2 kcal/mol (31.1 to 80.8 kJ/mol). However, there are no examples of polymers of narrow  $M_w/M_n$ , for example less than 3.4, which also have a low or moderate amount of LCB, as indicated by an activation  
20 energy of flow less than 11.1 kcal/mol (46.7 kJ/mol).

We have now found that it is possible to prepare copolymers of ethylene and alpha-olefins having narrow  $M_w/M_n$  and low or moderate amounts of LCB. These polymers are suitable for many applications which will be known to those skilled in the art, but in particular are advantageous for preparing films with an excellent balance of  
25 processing, optical and mechanical properties.

Thus, according to the present invention there is provided a copolymer of ethylene and an alpha olefin having 3 to 10 carbon atoms, said polymer having

- (a) a density in the range 0.900 to 0.940
- (b)  $M_w/M_n$  of 2 - 3.4
- (c)  $I_{21}/I_2$  from 16 to 24
- (d) activation energy of flow from 28 to 45 kJ/mol
- (e) a ratio  $E_a(\text{HMW})/E_a(\text{LMW}) > 1.1$ , and

(f) a ratio  $g'(\text{HMW})/g'(\text{LMW})$  from 0.85 to 0.95

Preferred copolymers are those having

- (a) a density in the range 0.900 to 0.925
- (b)  $M_w/M_n$  in the range 2 to 3
- (c)  $I_{21}/I_2$  from 18 - 24
- (d) activation energy of flow from 28 to 45 kJ/mol
- (e) a ratio  $E_a(\text{HMW})/E_a(\text{LMW}) > 1.1$ , and
- (f) a ratio  $g'(\text{HMW})/g'(\text{LMW})$  from 0.85 to 0.95

Most preferred copolymers are those having

- (a) a density in the range 0.900 to 0.925
- (b)  $M_w/M_n$  in the range 2.5 to 3
- (c)  $I_{21}/I_2$  from 18 - 24
- (d) activation energy of flow from 28 to 45 kJ/mol
- (e) a ratio  $E_a(\text{HMW})/E_a(\text{LMW}) > 1.1$ , and
- (f) a ratio  $g'(\text{HMW})/g'(\text{LMW})$  from 0.85 to 0.95

The significance of the parameters  $E_a(\text{HMW})/E_a(\text{LMW})$  and  $g'(\text{HMW})/g'(\text{LMW})$  is described below. The experimental procedures for their measurements are described later in the text.

The polymers contain an amount of LCB which is clearly visible by techniques such as GPC/viscometry and flow activation energy. The content of LCB is lower than reported in many earlier publications, but is still sufficient, when coupled with broadened  $M_w/M_n$ , to give improved processability compared to linear polymers of narrow MWD ( $M_w/M_n$  less than about 3), which do not contain LCB.

For the measurement of LCB, we have found that the most useful techniques are those which have a particular sensitivity to the presence of LCB in the high molecular weight chains. For these high molecular weight molecules, the physical effects of LCB on the solution and melt properties of the polymer are maximised. Hence detection of LCB using methods based upon solution and melt properties is facilitated.

Activation energy of flow is commonly used as an indicator of the presence of LCB in polyethylenes as summarised in WO 97/44371. For lower amounts of LCB, for which the global activation energy is of the order of 28 to 45 kJ/mol, it is found that the LCB has a strong effect upon the activation energy as measured at low test rates ie the

region in which the rheology is dominated by the high molecular weight (HMW) species. Therefore, the ratio of activation energy derived from the low rate data  $E_a(\text{HMW})$  tends to exceed that derived from the high rate data,  $E_a(\text{LMW})$ . Hence polymers containing LCB predominantly in the high molecular weight chains tend to show the ratio

5  $E_a(\text{HMW})/E_a(\text{LMW})$  greater than unity.

A further well established method indicating the presence of LCB is gel permeation chromatography with on-line detection of viscosity (GPC/OLV). By combining the data from 2 detectors, the ratio  $g'$  can be derived as a function of molecular weight;  $g'$  is the ratio of the measured intrinsic viscosity  $[\eta]$  divided by the  
10 intrinsic viscosity  $[\eta]_{\text{linear}}$  of a linear polymer having the same molecular weight. In polymers containing LCB, the  $g'$  measured at high molecular weights tends to be less than that measured at low molecular weights. To quantify this effect, we have used a simple ratio  $g'(\text{HMW})/g'(\text{LMW})$ .  $g'(\text{HMW})$  is the weighted mean value of  $g'$  calculated for the 30% of the polymer having the highest molecular weight, while  $g'(\text{LMW})$  is the  
15 weighted mean value of  $g'$  calculated for the 30% of the polymer having lowest molecular weight. For linear polymers,  $g'$  is equal to 1 at all molecular weights, and so  $g'(\text{HMW})/g'(\text{LMW})$  is also equal to 1 when there is no LCB present. For polymers containing LCB,  $g'(\text{HMW})/g'(\text{LMW})$  is less than 1. It should be noted that for the  $g'$  data can be corrected for the effect of short chain branching (SCB). This would normally  
20 be done using a mean value of SCB content, the correction being applied uniformly at all molecular weights. Such a correction has not been apply here because in measuring the ratio  $g'(\text{HMW})/g'(\text{LMW})$  the same correction would apply to both  $g'$  values and there would be no net effect on the results reported here.

Another method to quantify LCB content in polyethylenes is by carbon-13  
25 Nuclear Magnetic Resonance ( $^{13}\text{C}$ -NMR). For the low amounts of LCB observed for polymers of the invention it is generally accepted that this technique can give a reliable quantification of the number of LCB points present in the polymer when the polymer is a homopolymer or a copolymer of ethylene and propylene or butene-1. For the purposes of this specification, a measurement of LCB by  $^{13}\text{C}$ - NMR is achieved in such polymers by  
30 quantification of the isolated peak at about 38.3ppm corresponding to the CH carbon of a tri-functional long chain branch. A tri-functional long chain branch is taken to mean a structure for which at least the first four carbon atoms of each of the 3 chains radiating

from the CH branch carbon are all present as CH<sub>2</sub> groups. Care must be exercised in making such measures to ensure that sufficient signal:noise is obtained to quantify the resonance and that spurious LCB structures are not generated during the sample heating by oxidation induced free-radical reactions.

5           The above described analysis of LCB by <sup>13</sup>C-NMR is much more difficult when the copolymer contains hexene-1. This is because the resonance corresponding to an LCB is very close to or overlapping that for the CH carbon at the branch site of the n-butyl branch obtained from this comonomer. Unless the two CH resonances can be resolved, which is unlikely using NMR equipment currently available, LCB could only be  
10       determined for an ethylene/hexene-1 copolymer using the above described technique if the amount of n-butyl branches was so low, in comparison to the amount of LCB present, that it could either be ignored or a reliable subtraction carried out on the CH resonance at about 38.3ppm.

          We have prepared an ethylene/butene-1 copolymer containing 6.5wt% butene-1  
15       using a preferred catalyst system for preparing copolymers of this invention. This polymer contained 0.12 LCB/10,000 total carbons using the <sup>13</sup>C-NMR technique described above. The spectrum was obtained from a 600MHz NMR spectrometer after 912,000 scans. The polymer also contained 0.25 n-butyl branches/10,000 total carbons. No detectable oxidation was observed during this analysis with a limit of detection of  
20       approximately 0.05/10,000 total carbons.

          Despite a relatively low average LCB content, it would be expected that such polymers would show distinctly modified rheological behaviour in comparison with truly linear polymers. If the LCB is concentrated in the molecules of higher molecular weight, as is known to be the case, then an average value of 0.12 LCB/10,000 total carbons in  
25       the whole polymer could correspond to about 0.3 or more LCB/10,000 for molecules of molecular weight about one million. Hence these molecules would be expected to contain at least 2 LCB points per molecule, equivalent to a branched structure with 5 arms. Such molecules are known to display very different rheological properties to linear molecules.

30       The polymers of the invention also show quite low amounts of vinyl unsaturation as determined by either infra-red spectroscopy or preferably proton NMR. For a polymer of melt index(2.16kg) about 1, values are less than 0.05 vinyl groups per 1000 carbon

atoms or even as low as less than 0.02 vinyl groups per 1000 carbon atoms. Again, for melt index(2.16kg) about 1, total unsaturations are also low compared to some other metallocene polymers containing LCB, the total unsaturations as measured by proton NMR to be the sum of vinyl, vinylidene, tri-substituted and cis+trans di-substituted  
5 internal unsaturation being less than 0.2 per 1000 carbon atoms. Products with higher or lower melt index, and hence lower or higher number average molecular weights, may show respectively higher or lower terminal unsaturations, in proportion to the total number of chain ends present.

The comonomer present in the polymers of the invention is not randomly placed  
10 within the polymer structure. If the comonomer was randomly placed, it would be expected that the elution trace derived from temperature rising elution fractionation (TREF) would show a single narrow peak, the melting endotherm as measured by differential scanning calorimetry would also show a substantially singular and narrow peak. It would also be expected that little variation would be expected in either the  
15 amount of comonomer measured as a function of molecular weight by techniques such as GPC/FTIR, or the molecular weight of fractions measured as a function of comonomer content by techniques such as TREF/DV. These techniques for structure determination are described in the aforementioned WO 97/44371.

However, the comonomer is placed in a way as to give a distinct broadening of  
20 the TREF elution data, often with the appearance of one or two or even three peaks. At a polymer density of about 918kg/m<sup>3</sup> the TREF data typically show two main peaks, one at about 87°C and another distinct but smaller peak at about 72°C, the latter being about 2/3 of the height of the former. These peaks represent a heterogeneity in the amount of comonomer incorporated in the polymer chains. A third peak is often visible at about  
25 100°C; this peak is considered to be nothing other than a consequence of the fact that the polymer molecules of low comonomer content tend to crystallise into large chain folded crystals which melt and dissolve in the TREF experiment in a narrow range of temperatures at about 100°C. The same peak is very clearly visible in certain types of LLDPE polymers produced by ziegler catalysts and it is present in TREF analysis of  
30 MDPE and HDPE type polyethylenes. Thus the third peak at about 100°C is more a result of the crystallisation of linear or near-linear molecules, than a feature which can be simply interpreted as representing a particular and separate polymer species.

The behaviour seen in melting endotherms by DSC reflects the behaviour in TREF in that one, two or three peaks are typically seen. Three peaks are often seen for polymers of density about  $918 \text{ kg/m}^3$ , when heated at  $10^\circ\text{C/min.}$  after crystallisation at the same rate. As is usual, it would be expected that the peaks seen in TREF and DSC would move to lower temperatures for polymers of lower density and to higher temperatures for polymer of higher density.

The amount of comonomer measured as a function of molecular weight by GPC/FTIR shows an increase as molecular weight increases. The associated parameter  $C_{pf}$  is greater than 1.1. The measurement of  $C_{pf}$  is described in WO 97/44371.

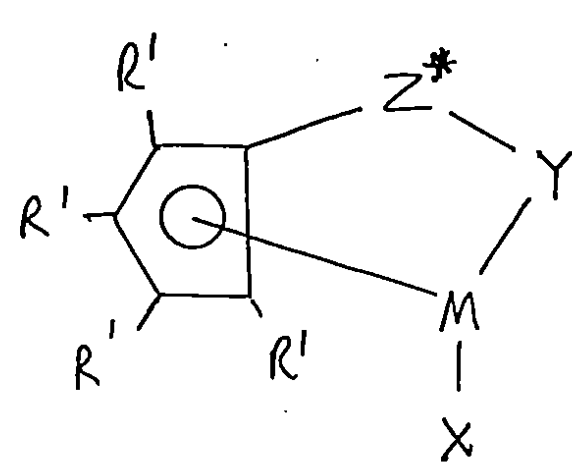
The copolymers of the present invention exhibit extensional rheological behaviour, in particular strain-hardening properties, consistent with the presence of long chain branching.

The unique copolymers of the present invention may suitably be prepared by use of a metallocene catalyst system comprising a complex having a 'constrained geometry' configuration together with a suitable activator.

Suitable complexes are those disclosed in WO 95/00526 the disclosure of which is incorporated herein by reference.

Suitable activators may comprise traditional aluminoxane or boron compounds for example borates again disclosed in the aforementioned WO 95/00526.

Preferred metallocene complexes for use in the preparation of the unique copolymers of the present invention may be represented by the general formula:



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral  $\eta^4$  bonded diene group having up to 30 non-hydrogen atoms, which forms a  $\pi$  complex with M;

Y is -O-, -S-, -NR\*, -PR\*,

10 M is titanium or zirconium in the + 2 formal oxidation state;

Z\* is SiR\*<sub>2</sub>, CR\*<sub>2</sub>, SiR\*<sub>2</sub>, SiR\*<sub>2</sub>, CR\*<sub>2</sub>, CR\*<sub>2</sub>, CR\*<sub>2</sub>, SiR\*<sub>2</sub>, or GeR\*<sub>2</sub>, wherein:

15 R\* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R\* having up to 10 non-hydrogen atoms, and optionally, two R\* groups from Z\* (when R\* is not hydrogen), or an R\* group from Z\* and an R\* group from Y form a ring system.

20 Examples of suitable X groups include s-trans- $\eta^4$ -1,4-diphenyl-1,3-butadiene, s-trans- $\eta^4$ -3-methyl-1,3-pentadiene; s-trans- $\eta^4$ -2,4-hexadiene; s-trans- $\eta^4$ -1,3-pentadiene; s-trans- $\eta^4$ -1,4-ditolyl-1,3-butadiene; s-trans- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene; s-cis- $\eta^4$ -3-methyl-1,3-pentadiene; s-cis- $\eta^4$ -1,4-dibenzyl-1,3-butadiene; s-cis- $\eta^4$ -1,3-pentadiene; s-cis- $\eta^4$ -1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a  $\eta$ -complex as defined herein with the metal.

Most preferred complexes are those wherein M is titanium.

25 Most preferred complexes are amidosilane - or amidoalkanediyl complexes.

A preferred complex for use in the preparation of the copolymers of the present invention is (t-butylamido) (tetramethyl- $\eta^5$ -cyclopentadienyl) dimethyl silanetitanium - $\eta^4$ -1,3 - pentadiene.

30 The activator may preferably be a boron compound for example borates such as trialkylammonium salts, in particular.

triethylammonium tetraphenylborate

triethylammonium tetraphenylborate,

tripropylammonium tetraphenylborate,  
tri(n-butyl)ammonium tetraphenylborate,  
tri(t-butyl)ammonium tetraphenylborate,  
N,N-dimethylanilinium tetraphenylborate,  
N,N-diethylanilinium tetraphenylborate,

Another type of activator suitable for use with the metallocene complexes of the present invention are the reaction products of (A) ionic compounds comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen and (B) an organometal or metalloid compound wherein the metal or metalloid is from Groups 1-14 of the Periodic Table.

Suitable activators of this type are described in WO 98/27119 the relevant portions of which are incorporated by reference.

A particular preferred activator of this type is the reaction product obtained from alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates and trialkylaluminium. For example a preferred activator is the reaction product of bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate and triethylaluminium.

The molar ratio of metallocene complex to activator employed in the process of the present invention may be in the range 1:10000 to 100:1. A preferred range is from 1:50000 to 10:1 and most preferred from 1:10 to 10:1.

The metallocene catalyst system suitable for use in the present invention is most suitably supported. Typically the support can be an organic or inorganic inert solid. However particularly porous supports such as talc, inorganic oxides and resinous support materials such as polyolefins which have well-known advantages in catalysis are preferred. Suitable inorganic oxide materials which may be used include Group 2, 13 14 or 15 metal oxides such as silica, alumina, silica-alumina and mixtures thereof.

Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania or zirconia. Other suitable support materials may be employed such as finely divided polyolefins such as polyethylene.

The most preferred support material for use with the supported catalysts according to the process of the present invention is silica. Suitable silicas include

Crossfield ES70 and Davidson 948 silicas:

It is preferable that the silica is dried before use and this is typically carried out by heating at elevated temperatures for example between 200 and 850 °C.

When prepared by use of the preferred catalyst systems described above the  
5 unique copolymers of the present invention have a titanium content in the range 0.1 to 2.0 ppm.

According to another aspect of the present invention there are provided copolymers of ethylene and alpha olefins having 3 to 10 carbon atoms having

- (a) a density in the range 0.900 to 0.940
- 10 (b) Mw/Mn of 2.5-3.0
- (c)  $I_{21}/I_2$  of 15 to 25, and
- (d) melting point of 95°C to 135°C

The copolymers of the present invention comprise copolymers of ethylene and alpha-olefins having 3 to 10 carbon atoms. Preferred alpha olefins comprise 1-butene, 1-  
15 hexene and 4-methyl-1-pentene.

The copolymers of the present invention are most suitably prepared in the gas phase in particular in a continuous process operating at a temperature >60°C and most preferably at a temperature of 80°C or above. The preferred process is one comprising a fluidised bed reactor. A particularly suitable gas phase process is that disclosed in EP  
20 699213 incorporated herein by reference.

The copolymers according to the present invention may be used to prepare the full range of products normally manufactured from polyethylene copolymer products in the density range 900 to 940 kg/m<sup>3</sup>. They may also be used blended with other polymers such as low density polyethylenes, linear low density polyethylenes, medium density  
25 polyethylenes, high density polyethylenes, plastomers and elastomers. Examples of applications include injection moulding, rotomoulding, extrusion into pipes, sheets, films, fibres, non-woven fabrics, cable coverings and other uses which will be known to those skilled in the art. The products are particularly suitable for the production of films and sheets prepared using traditional methods well known in the art. Examples are blowing,  
30 orientation of the partially crystallised product. The films exhibit good processability, improved optical and mechanical properties and good heat sealing properties.

The films exhibit a haze ranging from 3 to 20, a dart impact >100g and also

exhibit a low hexane extractable content of 0.2 - 1.5%.

Thus according to another aspect of the present invention there is provided a film exhibiting a haze determined by ASTM D-1003 ranging from 3 to 20, a dart impact measured by ASTM D-1709 of >100g, a hexane extractables content of 0.2 - 1.5% said film comprising a copolymer of ethylene and an alpha-olefin having 3-10 carbon atoms and which has

- (a) a density in the range 0.900 to 0.940
- (b) Mw/Mn of 2 - 3.4
- (c)  $I_{21}/I_2$  from 16 to 24
- (d) activation energy of flow from 28 to 45 kJ/mol
- (e) a ratio  $E_a(\text{HMW})/E_a(\text{LMW}) > 1.1$ , and
- (f) a ratio  $g'(\text{HMW})/g'(\text{LMW})$  from 0.85 to 0.95

Preferred films are those exhibiting a haze determined by ASTM D-1003 ranging from 3 to 20, a dart impact measured by ASTM D-1709 of >100g, a hexane extractables content of 0.2 - 1.5% said film comprising a copolymer of ethylene and an alpha-olefin having 3-10 carbon atoms and which has

- (a) a density in the range 0.900 to 0.925
- (b) Mw/Mn in the range 2.5 to 3
- (c)  $I_{21}/I_2$  from 18 - 24
- (d) activation energy of flow from 28 to 45 kJ/mol
- (e) a ratio  $E_a(\text{HMW})/E_a(\text{LMW}) > 1.1$ , and
- (f) a ratio  $g'(\text{HMW})/g'(\text{LMW})$  from 0.85 to 0.95

In another aspect of the present invention there is provided a film exhibiting a haze determined by ASTM D-1003 ranging from 3 to 20, a dart impact measured by ASTM D-1709 of >100g, a hexane extractables content of 0.2 - 1.5% said film comprising a copolymer of ethylene and an alpha-olefin having 3-10 carbon atoms and which has

- (a) a density in the range 0.900 to 0.940
- (b) Mw/Mn of 2.5-3.0
- (c)  $I_{21}/I_2$  of 15 to 25, and
- (d) melting point of 95°C to 135°C

The films may be suitable for a number of applications for example industrial,

retail, food packaging, non-food packaging and medical applications. Examples include films for bags, garment bags, grocery sacks, merchandise bags, self-serve bags, grocery wet pack, food wrap, pallet stretch wrap, bundling and overwrap, industrial liners, refuse sacks, heavy duty bags, agricultural films, daiper liners, etc.

- 5           The films may be utilised as shrink film, cling film, stretch film, sealing film or other suitable type.

**Methods of test**

**Melt index** (190/2.16) was measured according to ISO 1133.

- 10           **Melt flow ratio** (MFR) was calculated from the ratio of flow rates determined according to ISO 1133 under condition (190/21.6) and condition (190/2.16).

**Density** was measured using a density column according to ISO 1872/1-1986, except that the melt index extrudates were not annealed but were left to cool on a sheet of polymeric material for 30 minutes.

- 15           **Apparent molecular weight distribution** and associated averages, uncorrected for long chain branching, were determined by Gel Permeation Chromatography using a Waters 150CV. The solvent used was 1,2,4 Trichlorobenzene at 145°C, stabilised with 0.05% BHT. The nominal flow rate was 1 ml/min. Solutions of concentration 0.05 to 0.1%w/w were prepared at 155°C for 1.5 to 2 hours with stirring, and the nominal injection volume was set at 250ml. 3 Shodex AT80M/S columns were used with a plate  
20           count (at half height) of typically 23,000. The differential refractometer detector alone was used for these studies. Calibration was achieved using broad molecular weight linear polyethylene standards as described previously (Analysis, 1976, Vol 4 no 10, p450). A correction for dispersion broadening was applied as described by Hamielec (J.Appl. Polymer Sci., 14, 1519 (1970). This calibration has been checked against the NIST  
25           certified polyethylene SRM1475, the values obtained being 52,000 for Mw and 19,800 for Mn.

- 30           **Molecular weight distribution** and associated averages, corrected for LCB, together with g' values as a function of MW were determined by GPC/OLV using a Waters 150CV fitted with a Viscotek 150R differential viscometer. The Trisec version 3 software supplied by Viscotek was used for data treatment. SRM1475 was used as a linear reference polymer. The solvent used was 1,2,4 Trichlorobenzene at 142°C, stabilised with 0.2g/l Santonox R. The flow rate was nominally 1ml/min, the injection

53 24  
56

volume 400µl and the concentration injected 0.7 to 0.8 mg/ml. The system was operated with 3 Shodex columns AT806MS, UT607S and AT804S, plus a Waters HR2 column.

A Universal Calibration was constructed using narrow polystyrene standards and the Mark Houwink constants thus obtained experimentally for polystyrene were  $\log K = -$

5 3.8283,  $\alpha = 0.687$ . Polyethylene Mark Houwink constants obtained from analysis of SRM1475 were  $\log K = -3.335$ ,  $\alpha = 0.705$ , and these were used in the calculations of  $g'$ .

The values for  $g'(\text{HMW})/g'(\text{LMW})$  were obtained from measurements of  $g'$  vs molecular weight obtained using the GPC/OLV system as described above. The values

10 were calculated as the weighted mean value over the range of interest, as follows:

$$g'(\text{HMW}) / g'(\text{LMW}) = \sum_{i=70}^{i=100} w_i \cdot g'_i / \sum_{i=0}^{i=30} w_i \cdot g'_i$$

where for each molecular weight slice of the MWD,  $w_i$  is the relative weight of polymer present,  $g'_i$  is the measured  $g'$  parameter at that molecular weight, and  $i_x$  defines the slice

15 in the MWD at which  $x\%$  of the polymer has lower molecular weight.

Melting behaviour was determined by differential scanning calorimetry using a Perkin Elmer DSC-7 instrument, following the methodology outlined in ASTM D3417 except that the first heating was carried out at 20°C/min. The peak melting temperature was taken as the temperature corresponding to the maximum heat flow observed during

20 the second heating of the polymer at 10°C/min.

The titanium content of the copolymers was measured indirectly from an analysis by X-ray fluorescence (XFR) of silicon content in the polymer and the known composition of the catalyst in terms of silica and reactive species supported thereon. The quantity of titanium in the catalyst was determined by either inductively coupled plasma

25 atomic emission spectroscopy (ICP-AES) or stomic absorption (AA).

Hexane extractable content, after extraction for 2 hours, was determined on film samples according to ASTM D-5227 except that the volume of solvent used was 300 ml.

Dart impact was measured by ASTM D1709, tear strength by ASTM D1922, and haze by ASTM D1003.

30 Flow Activation Energy (Ea) Measurement

Rheological measurements were carried out on a Rheometrics RDS-2 with 25 mm diameter parallel plates in the dynamic mode. Two strain sweep (SS) experiments were initially carried out to determine the linear viscoelastic strain that would generate a torque signal which is greater than 10% of the full scale (2000 g-cm) of the transducer over the full frequency (eg 0.01 to 100 rad/s) and temperature (eg 170° to 210°C) ranges. The first SS experiment was carried out at the highest test temperature (eg 210°C) with a low applied frequency of 0.1 rad/s. This test is used to determine the sensitivity of the torque at low frequency. The second experiment was carried out at the lowest test temperature (eg 170°C) with a high applied frequency of 100 rad/s. This is to ensure that the selected applied strain is well within the linear viscoelastic region of the polymer so that the oscillatory rheological measurements do not induce structural changes to the polymer during testing. This procedure was carried out for all the samples.

The bulk dynamic rheological properties (eg  $G'$ ,  $G''$  and  $\eta^*$ ) of all the polymers were then measured at 170°, 190° and 210°C. At each temperature, scans were performed as a function of angular shear frequency (from 100 to 0.01 rad/s) at a constant shear strain appropriately determined by the above procedure.

The dynamic rheological data was then analysed using the Rheometrics RHIOS V4.4 Software. The following conditions were selected for the time-temperature (t-T) superposition and the determination of the flow activation energies ( $E_a$ ) according to an Arrhenius equation,  $a_T = \exp(E_a/kT)$ , which relates the shift factor ( $a_T$ ) to  $E_a$ :

|                         |                                      |
|-------------------------|--------------------------------------|
| Rheological Parameters: | $G'(w)$ , $G''(w)$ & $h^*(w)$        |
| Reference Temperature:  | 190°C                                |
| Shift Mode:             | 2D (ie horizontal & vertical shifts) |
| Shift Accuracy:         | High                                 |
| Interpolation Mode:     | Spline                               |

The flow activation energy as obtained by the above t-T superposition procedure over the four decades of test frequency (ie 0.01 to 100 rad/s) is defined as an average flow activation energy,  $E_a(\text{average})$ , while that over the two decades angular frequency of 0.01 to 1 rad/s as the Higher Molecular Weight flow activation energy,  $E_a(\text{HMW})$  and

59 28  
54

that over the two decades angular frequency of 1 to 100 rad/s as the Lower Molecular Weight flow activation energy,  $E_a$ (LMW).

The present invention will now be further illustrated by reference to the accompanying Examples.

5 Example 1

(i) Treatment of silica

A suspension of Grace 948 silica (13kg, previously calcined at 250°C for 5 hours) in 110 litres (L) of hexane was made up in a 240L vessel under nitrogen. 1L of a hexane solution containing 2g/L of Stadis 425 was added and stirred at room  
10 temperature for 5 minutes. 29.1L of a 892mmolAl/L solution of triethylaluminium (TEA) in hexane was added slowly to the stirred suspension over 30 minutes, while maintaining the temperature of the suspension at 30°C. The suspension was stirred for a further 2 hours. The hexane was filtered, and the silica washed with hexane, so that the aluminium content in the final washing was less than 0.5 mmol Al/litre. Finally the  
15 suspension was dried *in vacuo* at 60°C to give a free flowing treated silica powder with residual solvent less than 0.5wt%.

(ii) Catalyst fabrication

All steps of the catalyst fabrication were carried out at 20°C. 3L of toluene was added to a 24L vessel equipped with a turbine stirrer, and stirred at 300rpm. 5.01L of a  
20 9.5wt% solution in toluene of bis(hydrogenated tallow alkyl) methyl ammonium tris(pentafluorophenyl)(4-hydroxyphenyl)borate was added during 15 minutes. Then 1.57L of a 250mmolAl/L solution in toluene of triethylaluminium was added during 15 minutes and mixture stirred for 30 minutes. The solution obtained was then transferred under nitrogen, with stirring during 2 hours, to an 80L vessel containing 10kg of the  
25 TEA treated silica described above. 60L of essence was then rapidly introduced and mixed for 30 minutes. 1.83 kg of a 7.15wt% solution in heptane of (t-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl) dimethylsilanetitanium - $\eta^4$ -1,3-pentadiene was added during 15 minutes. Mixing was continued for 1 hour and 1L of a 2g/L hexane solution of stadis 425 was added. The catalyst slurry was then transferred to a vessel of  
30 volume 240L and 70L of hexane added. Excess solvent was removed by decantation, and a further 130L of hexane added. This process was repeated until less than 0.2L of toluene remained in the solvent. 1L of a 2g/L hexane solution of stadis 425 was then

added and the catalyst dried under vacuum at 40°C to a residual solvent level of 1wt%.

(iii) Polymerisation using continuous fluidised bed reactor

Ethylene, 1-hexene, hydrogen and nitrogen were fed into a continuous fluidised bed reactor of diameter 45cm. Polymer product was continuously removed from the reactor.

5 Operating conditions are given in Table 1.

The results are given below in Table 2 together with typical values of a LLDPE copolymer from ethylene and 1-hexene exemplified in the literature from WO 94/14855.

10 After degassing, the powder product withdrawn from the reactor was compounded using a ZSK58 twin screw extruder (the additive package being 1250ppm calcium stearate, 500ppm Irganox 1076 and 800ppm Irgafos PEPQ). Blown film was produced at 50kg/hr on a Reifenhäuser film line equipped with a die of diameter 150mm and die gap 2.3mm. The film extrusion conditions and properties of the resultant films are also shown in Table 2.

Examples 2 and 3

15 The catalyst of example 1 was used to produce the ethylene/1-hexene copolymers of examples 2 and 3 using the polymerisation conditions shown in Table 1. Structural properties of these copolymers and films thereof are shown in Table 2.

Examples 4 and 5

20 The procedure used in example 1 was scaled up to produce a catalyst of batch size approx. 75 kg. This catalyst was used to prepare copolymers in a commercial gas phase scale reactor of diameter 5 metres again using the polymerisation conditions shown in Table 1. Copolymers of ethylene and 1-hexene were prepared of melt index about 1 g/10min. and density 0.918 g/cc. The structural properties of the copolymers and films thereof are shown in Table 2.

25

30

55 76  
58

**TABLE 1**

| Example                              | 1      | 2      | 3      | 4      | 5      |
|--------------------------------------|--------|--------|--------|--------|--------|
|                                      |        |        |        |        |        |
| total pressure (bar)                 | 17.9   | 18.9   | 19.0   | 19.8   | 20     |
| temperature (°C)                     | 80     | 75     | 70     | 75     | 75     |
| ethylene pressure (bar)              | 5.6    | 5.7    | 4.0    | 8.1    | 8.2    |
| H <sub>2</sub> /C <sub>2</sub> ratio | 0.0020 | 0.0025 | 0.0024 | 0.0023 | 0.0023 |
| C <sub>6</sub> /C <sub>2</sub> ratio | 0.0040 | 0.0044 | 0.0036 | 0.0050 | 0.0049 |
| production (kg/hr)                   | 41     | 45     | 38     | 8.7    | 10     |

5

10

15

20

**TABLE 2 Structure Properties**

| Property/Condition                     | Example 1 | 2      | 3      | 4      | 5      | LLDPE* |
|----------------------------------------|-----------|--------|--------|--------|--------|--------|
| Melt Index (dg/min)                    | 1.04      | 1.57   | 1.2    | 1.3    | 1.07   | 1.0    |
| MFR ( $I_{21}/I_2$ )                   | 20.2      | 21.5   | 22.9   | 19.8   | 21.3   | 18     |
| Density (g/cc)                         | 0.9185    | 0.9173 | 0.9198 | 0.9189 | 0.9184 | 0.918  |
| $M_w$                                  | 92,200    | 85,500 | 93,800 |        |        |        |
| $M_w/M_n$<br>(uncorrected for LCB)     | 2.33      | 2.5    | 3.2    | 2.7    | 2.6    | 2.6    |
| $g'(\text{HMW})/g'(\text{LMW})$        | 0.912     | 0.915  | 0/912  |        |        |        |
| Activation energy of flow<br>(kJ/mol)  | 32        |        |        | 32     | 33     |        |
| $E_a(\text{HMW})/E_a(\text{LMW})$      | 1.55      |        |        |        |        |        |
| Peak melting temperature<br>(°C)       | 116.4     | 117.3  | 118.4  | 117.9  | 118.0  | 115    |
| Silicon analysis by XRF (ppm<br>w/w)   |           |        |        | 168    | 180    |        |
| titanium content (ppm)                 |           |        |        | 0.32   | 0.35   |        |
| dart impact (g)                        | >1200     | >1200  | >1200  | >1300  | >1300  | >800   |
| hexane extractables (wt %)             | 0.3       |        |        |        |        | 0.6    |
| haze (%)                               | 9.6       | 13.5   | 19.6   |        |        | 5 - 7  |
| gloss                                  | 58.3      | 44.6   | 34.1   |        |        |        |
| MD tear strength (g/25 $\mu\text{m}$ ) | 188       | 210    | 210    |        |        | 370    |

NB. \* represents data from WO 94/14855

56 28  
60

TRADUCCION OFICIAL No.2000/087 de un documento escrito en inglés el cual para su identificación se sella con el sello del traductor al tiempo con la presente. Esta traducción ha sido preparada por Hilda Aguilera de Piedrahita, traductora e intérprete oficial debidamente reconocida por el Ministerio de Relaciones Exteriores y autorizada por el Ministerio de Justicia y del Derecho, por Resolución No. 323 de 1980.

(Se traduce el formulario de solicitud de Patente escrita en inglés a favor de BP CHEMICALS LIMITED).

(Sello Pre-impreso) LA OFICINA DE PATENTES Invierte en la Gente

LA OFICINA DE PATENTES, CONCEPT HOUSE

CARDIFF ROAD, NEW PORT, SOUTH WALES, NP10 8QQ

Yo, el suscrito, funcionario debidamente autorizado de acuerdo con la Sección 74(1) y (4) de La Ley de Desregulación y Contratación de 1994, para firmar y expedir certificados a nombre del Contralor General, por el presente certifico que adjunta se encuentra una copia fiel de los documentos originalmente presentados en relación con la solicitud de patente identificada en ellos.

De acuerdo con las Normas de Patentes (Re-registro de Compañías) 1982, si una compañía nombrada en este certificado y en los documentos anexos se ha re-registrado bajo la Ley de Compañías 1980 con el mismo nombre con el que fue registrada inmediatamente antes de el re-registro excepto para la sustitución o inclusión como, la última parte del nombre de las palabras "compañía pública

TRADUCCION OFICIAL No. 2000/087  
HILDA AGUILERA DE PIEDRAHITA  
INTERPRETE OFICIAL  
RES No. 323 DEL MIN. OF JUSTICE

57 29  
61

limitada" o sus equivalentes en Gálico, las referencias al nombre de la compañía en este certificado y a los documentos anexos se deberán tratar como referencias al nombre con el cual está así re-registrada.

De acuerdo con las reglas, las palabras "compañía pública limitada" se pueden reemplazar por c.p.l., cpl, C.P.L., ó CPL (p.l.c., plc, P.L.C, o PLC).

El Re-registro bajo la Ley de Compañías no constituye un nuevo ente legal pero solamente obliga a la compañía para con ciertas reglas de ley adicionales para compañías.

Firmado (R. Mahoney)

Fecha: Abril 17 del 2000.

(SELLO DE OBLEA DE LA OFICINA DE PATENTES)

Una Agencia Ejecutiva del Departamento de Comercio e Industria

**LA OFICINA DE PATENTES**

F rmatato de Patentes 1/77 18Nov99 E492656-1 C03022

Ley de Patentes de 1977 (Regla 16) P01/7700 0.00 - 9927205.6

(Sello a Tinta de la Oficina de Patentes, 17 Nov 1999)

|                                                               |                               |
|---------------------------------------------------------------|-------------------------------|
| <b>Solicitud de otorgamiento de una patente</b>               | <b>La Oficina de Patentes</b> |
| <i>(Véanse las notas al respaldo de este formulario.</i>      | <b>Cardiff Road, New Port</b> |
| <i>También puede obtener un folleto explicativo de la</i>     | <b>Gwent NP9 1RH</b>          |
| <i>Oficina de Patentes como ayuda para llenar el presente</i> |                               |
| <i>formulario).</i>                                           |                               |

TRADUCCION OFICIAL NO. 2000687  
HILDA AGUILERA DE MIERANITA  
INTERPRETE OFICIAL  
RES. NO. 223 DEL MIN. DE JUSTICIA

58 30  
62

1. Su Referencia: 9196 17 Noviembre 1999

2. Número de Solicitud de la Patente: **9927205.6**

*(La Oficina de Patentes llenará esta parte)*

3. Nombre Completo, dirección y código postal de o de cada uno de los solicitantes *(Subrayar todos los apellidos)*:

BP CHEMICALS LIMITED

BRITANNIC HOUSE

1 FINSBURY CIRCUS

LONDRES

EC2M 7BA

Número ADP de las Patentes *(si lo sabe)*: 4141891002

Si el solicitante es una sociedad, dar el país/estado de su constitución:

INGLATERRA, REINO UNIDO

4. Nombre de la Invención: COPOLÍMEROS NOVEDOSOS Y PELÍCULAS  
PRODUCIDAS A PARTIR DE ELLOS

5. Nombre de su Agente *(si lo tiene)*

WILSON, Michael John

"Dirección para Notificación" en el Reino Unido, donde se debe enviar toda la correspondencia *(incluyendo el código postal)*

BP INTERNATIONAL LIMITED

PATENTS & AGREEMENTS

PRODUCCIÓN ORIGINAL DE  
MILCA S. R. L.  
INFORMACIÓN  
893 No. 223 DEL NIV. DE HOSTEDAD

59 25 63

CHERTSEY ROAD

SUNBURY\_ON\_THAMES

MIDDLESEX

TW16 7LN

Número ADP de las Patentes (*si lo sabe*): 18556001

6. Si está declarando la prioridad de una o de más solicitudes de patente anteriores, diga el país y la fecha de presentación de la o de cada una de las solicitudes anteriores y (*si lo sabe*) el o cada uno de los números de solicitud.

País:

Número de Solicitud de la Prioridad (*si lo sabe*):

Fecha de Presentación (*Día/Mes/Año*)

7. Si esta solicitud se divide o de lo contrario se deriva de una solicitud anterior en el Reino Unido, diga el número y la fecha de presentación de la solicitud anterior.

Número de Solicitud Anterior:

Fecha de Presentación (*Día/Mes/Año*):

8. Se requiere de una declaración de invención y de derecho para otorgar una patente como soporte de la presente solicitud? SI

(Responda afirmativamente si:

a) cualquier solicitante nombrado en 3. no es inventor, o

b) existe un inventor quien no está nombrado como solicitante, o

c) cualquiera de los aplicantes nombrados es una sociedad:)

Vea nota (d)

Formulario de Patentes 1/77

60 32  
64

## Formulario de Patentes 1/77

9. Llene el número de páginas de cualquiera de los siguientes ítems que está presentando con este formulario. No cuente las copias del mismo documento.

Hojas a continuación de este formulario:

Descripción: 18

Reivindicaciones:

Resumen:

Dibujo(s):

10. Si está también presentando cualquiera de los siguientes, declare cuántos al frente de cada ítem.

- Documentos de prioridad:
- Traducciones de documentos de prioridad:
- Declaración de Invención y derecho de otorgar una patente (*Formulario de Patentes 7/77*):
- Solicitud para examen preliminar y búsqueda (*Formulario de Patentes 9/77*):
- Solicitud de Examen Sustantivo (*Formulario de Patentes 10/77*):
- Cualesquiera otros documentos (*Favor especificar*):

11. Yo/nosotros solicito (amos) el otorgamiento de la patente con base en esta solicitud. Firma (Firmado) Michael John Wilson, Fecha 17.11.99

12. Nombre y número telefónico durante el día de la persona a contactar en el

61 37  
65

Reino Unido

01932 763207

### **Advertencia**

*Después de que se ha presentado la solicitud para una patente, el Contralor de la Oficina de Patentes decidirá si la publicación o la comunicación de la invención debería prohibirse o restringirse bajo la Sección 22 de la Ley de Patentes 1977. Usted será informado si es necesario prohibir o restringir su invención de esta manera. Adicionalmente, si usted vive en el Reino Unido, la Sección 23 de la Ley de Patentes 1977 no le permite solicitar una patente en el extranjero sin antes obtener permiso escrito de la Oficina de Patentes a menos de que una solicitud haya sido presentada con por lo menos 6 semanas de anterioridad en el Reino Unido para una patente para el mismo invento y no ha habido aviso prohibiendo su publicación o su comunicación, o dicho aviso ha sido revocado.*

### **Notas**

- a) Si necesita ayuda para llenar este formulario o tiene alguna pregunta, favor contactar la Oficina de Patentes en 0645 500505.*
- b) Escriba sus respuestas en mayúsculas usando tinta negra o máquina de escribir.*
- c) Si no hay suficiente espacio para todos los detalles en cualquier parte de este formulario, por favor continúe en una hoja de papel aparte y escriba "véase hoja de continuación" en la(s) parte(s) relevante(s). Cualquier hoja de continuación se debe anexar a este formulario.*
- d) Si ha respondido afirmativamente, se deberá presentar el formulario de*

PRODUCCION OFICIAL No. 2000/087  
UNION EUROPEA DE PROTECCION DE PATENTES  
UNION EUROPEA DE PROTECCION DE PATENTES  
UNION EUROPEA DE PROTECCION DE PATENTES

62 34  
66

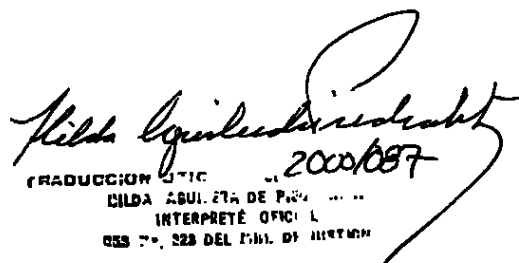
Patentes 7/77.

- e) Una vez completado el formulario, tiene que acordarse de firmarlo y fecharlo.
- f) Para detalles de la tarifa y formas de pago, favor dirigirse a la Oficina de Patentes.

Forma de Patentes 1/77

-----  
ES TRADUCCION FIEL Y COMPLETA de la cual se deja copia en los archivos de esta oficina para su confrontación y a la cual me remito.

Santafé de Bogotá, Mayo 21, 2000.

  
TRADUCCION FIEL  
HILDA GONZALEZ DE PARRA  
INTERPRETE OFICIAL  
CALLE 100, 323 DEL PISO DE INTERCOM