(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 January 2015 (29.01.2015)

(10) International Publication Number
WO 2015/010857 A1

(51) **International Patent Classification**:
C08F 210/06 (2006.01) ***C08F 210/16*** (2006.01)

(21) **International Application Number**:
PCT/EP2014/063896

(22) **International Filing Date**:
1 July 2014 (01.07.2014)

(25) **Filing Language**: English

(26) **Publication Language**: English

(30) **Priority Data**:
13177342.6 22 July 2013 (22.07.2013) EP

(71) **Applicant**: **BASELL POLIOLEFINE ITALIA S.R.L.** [IT/IT]; Via Soperga 14/A, I-20127 Milano (IT).

(72) **Inventors**: **DESTRO, Mara**; C/O Basell Poliolefine Italia S.r.l., P.le G. Donegani, 12, I-44122 Ferrara (IT). **CIARAFONI, Marco**; C/O Basell Poliolefine Italia S.r.l., P.le G. Donegani, 12, I-44122 Ferrara (IT). **MASSARI, Paola**; C/O Basell Poliolefine Italia S.r.l., P.le G. Donegani, 12, I-44122 Ferrara (IT). **CAPUTO, Tiziana**; C/O Basell Poliolefine Italia S.r.l., P.le G. Donegani, 12, I-44122 Ferrara (IT). **GUIDICINI, Alessandro**; c/o Basell Poliolefine Italia S.r.l., P.le Donegani 12, I-44122 Ferrara (IT).

(74) **Agent**: **COLUCCI, Giuseppe**; c/o Basell Poliolefine Italia S.r.l., Intellectual Property, P.le Donegani 12, I-44122 Ferrara (IT).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(54) **Title**: STERILISABLE ARTICLE MADE OF PROPYLENE COPOLYMER

(57) **Abstract**: Sterilisable articles for use in healthcare or medical applications, such as blow-fill-seal applications, made of a propylene-ethylene random copolymer show good optical properties also after heat sterilization.

STERILISABLE ARTICLE MADE OF PROPYLENE COPOLYMER

[0001] The present invention relates to a sterilisable article comprising a propylene copolymer. Particularly, the invention relates to articles for use in healthcare or medical applications, such as blow-fill-seal applications, that have good optical properties also after heat sterilization. The invention also relates to a process for the production of the propylene copolymer.

[0002] Propylene polymers are having increasing success as materials for the manufacture of articles for use in healthcare and medical applications. Those articles include containers, such as bottles, bags or pouches for biologic liquids, syringes and other items that can be sterilised by autoclaving. Its success is due to a good balance of mechanical properties and resistance to sterilization treatment. It is important that the properties of the material used for this kind of application do not deteriorate after a heat treatment for sterilization. Particularly, medical/healthcare containers should maintain as much as possible their transparency after sterilization to enable inspection of their content.

[0003] Several attempts have been made to improve the sterilization resistance of propylene polymers. Typically improvements entail a higher complexity of the base material.

[0004] EP 1849826 B1, for example, describes articles for sterilization comprising a polyolefin composition containing an heterophasic propylene copolymer and an ethylene homopolymer.

[0005] EP 2176340 B1 relates to sterilisable polypropylene compositions comprising a matrix resin and an elastomeric resin as the disperses phase, wherein the matrix resin comprises a propylene homopolymer and a propylene copolymer.

[0006] WO 2012/084768 describes a propylene polymer composition having a good balance of elasticity and transparency for use in the preparation if infusion bottles. The composition comprises 60-90% of a crystalline copolymer of propylene with 1.0-5.0% of ethylene-derived units and 10-40% of a copolymer of propylene with 18-32% of ethylene-derived units, the composition having a melt flow rate value of 1.0-2.0 g/10 min.

[0007] It has now been found that, by using specific propylene random copolymers, manufactured articles can be obtained exhibiting surprisingly good optical properties (transparency) also after heat sterilisation. That result is based on the unexpected finding that the transparency, particularly after heat sterilization, as a function of the comonomer amount shows a deviation from linear behavior.

[0008] Therefore, an object of the present invention is a healthcare or medical article comprising a propylene-ethylene copolymer having a content of ethylene units comprised between 4.0 and 5.4 % by weight, preferably between 4.3 and 5.3 % by weight, more preferably between 4.6 and 5.2 % by weight, and having a value of melt flow rate "L" (230°C, 2.16Kg) of from 1.0 to 3.0 g/10 min, preferably of from 1.5 to 2.5 g/10 min.

[0009] The present invention relates to all kind of healthcare or medical articles. Examples of those articles include:

- rigid containers, such as bottles, vials, ampoules, blisters;
- flexible containers, such as bags, pouches, collapsible bottles, lidstocks;
- other packaging items, such as films;
- devices, such as syringes, tubing, needle hubs and protectors, inhalers, filters and filter housings, blood collection systems;
- hospital disposables.

[0010] Particularly interesting articles according to the invention are those produced by the Blow-Fill-Seal (BFS) technology. That technology refers to a manufacturing process used to aseptically manufacture liquid-filled containers. The basic concept of BFS is that a container is formed, filled, and sealed in a continuous process in a sterile enclosed area inside a machine. That technology can thus be used to produce sterile pharmaceutical liquid dosage forms, for the filling of vials for parenteral preparations and infusions, ophthalmic products and inhalation products.

[0011] The articles of the invention show good optical properties, particularly, good transparency, both before and after heat sterilisation.

[0012] The propylene-ethylene copolymers for use in the preparation of the healthcare or medical article of the invention, generally referred to as random copolymer, have good optical properties. They generally show haze values, measured on a 1 mm plaque, lower than 40 %, preferably lower than 35 %, even more preferably lower than 30 % without addition of any clarifying or nucleating agents. After being subjected to heat sterilisation their optical properties get worse, but haze values, measured on a 1 mm plaque, remain acceptable, generally lower than 45 %.

[0013] The propylene-ethylene copolymers for use in the article of the invention generally have:

- a melting temperature (T_m) of from 135°C to 140°C;
- a fraction soluble in xylene at room temperature of between 10.0 % by weight and 15.0 % by weight;
- a flexural modulus of lower than 700 MPa, both before and after heat sterilisation;
- a molecular weight distribution M_w/M_n of higher than 4.0, preferably higher than 5.0.

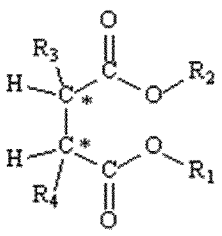
[0014] The propylene-ethylene copolymer for use in the article of the invention having a content of ethylene units comprised between 4.0 and 5.4 % by weight can be obtained by a process, that represents another object of the invention, carried out in the presence of a catalyst system comprising the product obtained by contacting the following components:

(a) a solid catalyst component comprising a magnesium halide, a titanium compound having at least a Ti-halogen bond and at least two electron donor compounds one of which being present in an amount from 40 to 90% by mole with respect to the total amount of donors and being selected from succinates and the other being selected from 1,3 diethers,

(b) an aluminum hydrocarbyl compound, and

(c) optionally an external electron donor compound.

[0015] The succinate is preferably selected from succinates of formula (I):

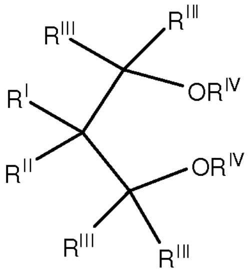


(I)

wherein the radicals R1 and R2, equal to or different from each other, are a C1-C20 linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms; and the radicals R3 and R4 equal to or different from each other, are C1-C20 alkyl, C3-C20 cycloalkyl, C5-C20 aryl, arylalkyl or alkylaryl group with the proviso that at least one of them is a branched alkyl; said compounds being, with respect to the two asymmetric carbon atoms identified in the structure of formula (I), stereoisomers of the type (S,R) or (R,S). R1 and R2 are preferably C1-C8 alkyl, cycloalkyl, aryl, arylalkyl and alkylaryl groups. Particularly preferred are the compounds in which R1 and R2 are selected from primary alkyls and in particular branched primary alkyls. Examples of suitable R1 and R2 groups are methyl, ethyl, n-propyl, n-butyl, isobutyl, neopentyl, 2-ethylhexyl. Particularly preferred are ethyl, isobutyl, and neopentyl. Particularly preferred are the compounds in which the R3 and/or R4 radicals are secondary alkyls like isopropyl, sec-butyl, 2-pentyl, 3-pentyl or cycloakyls like cyclohexyl, cyclopentyl, cyclohexylmethyl.

[0016] Examples of the above-mentioned compounds are the (S,R) (S,R) forms pure or in mixture, optionally in racemic form, of diethyl 2,3-bis(trimethylsilyl)succinate, diethyl 2,3-bis(2-ethylbutyl)succinate, diethyl 2,3-dibenzylsuccinate, diethyl 2,3-diisopropylsuccinate, diisobutyl 2,3-diisopropylsuccinate, diethyl 2,3-bis(cyclohexylmethyl)succinate, diethyl 2,3-diisobutylsuccinate, diethyl 2,3-dineopentylsuccinate, diethyl 2,3-dicyclopentylsuccinate, diethyl 2,3-dicyclohexylsuccinate.

[0017] Among the 1,3-diethers mentioned above, particularly preferred are the compounds of formula (II):



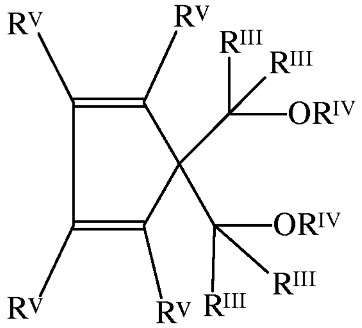
(II)

where RI and RII are the same or different and are hydrogen or linear or branched C1-C18 hydrocarbon groups which can also form one or more cyclic structures; RIII groups, equal or different from each other, are hydrogen or C1-C18 hydrocarbon groups; RIV groups equal or different from each other, have the same meaning of RIII except that they cannot be hydrogen; each of RI to RIV groups can contain heteroatoms selected from halogens, N, O, S and Si. Preferably, RIV is a 1-6 carbon atom alkyl radical and more particularly a methyl while the RIII radicals are preferably hydrogen. Moreover, when RI is methyl, ethyl, propyl, or isopropyl, RII can be ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, isopentyl, 2-ethylhexyl, cyclopentyl, cyclohexyl, methylcyclohexyl, phenyl or benzyl; when RI is hydrogen, RII can be ethyl, butyl, sec-butyl, tert-butyl, 2-ethylhexyl, cyclohexylethyl, diphenylmethyl, p-chlorophenyl, 1-naphthyl, 1-decahydronaphthyl; RI and RII can also be the same and can be ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, neopentyl, phenyl, benzyl, cyclohexyl, cyclopentyl.

[0018] Specific examples of 1,3-diethers that can be advantageously used include: 2-(2-ethylhexyl)1,3-dimethoxypropane, 2-isopropyl-1,3-dimethoxypropane, 2-butyl-1,3-dimethoxypropane, 2-sec-butyl-1,3-dimethoxypropane, 2-cyclohexyl-1,3-dimethoxypropane, 2-phenyl-1,3-dimethoxypropane, 2-tert-butyl-1,3-dimethoxypropane, 2-cumyl-1,3-dimethoxypropane, 2-(2-phenylethyl)-1,3-dimethoxypropane, 2-(2-cyclohexylethyl)-1,3-dimethoxypropane, 2-(p-chlorophenyl)-1,3-dimethoxypropane, 2-(diphenylmethyl)-1,3-dimethoxypropane, 2(1-naphthyl)-1,3-dimethoxypropane, 2(p-fluorophenyl)-1,3-dimethoxypropane, 2(1-decahydronaphthyl)-1,3-dimethoxypropane, 2(p-tert-butylphenyl)-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2,2-diethyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane, 2,2-dibutyl-1,3-dimethoxypropane, 2,2-diethyl-1,3-diethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-diethoxypropane, 2,2-dibutyl-1,3-diethoxypropane, 2-methyl-2-ethyl-1,3-dimethoxypropane, 2-methyl-2-propyl-1,3-dimethoxypropane, 2-methyl-2-benzyl-1,3-dimethoxypropane, 2-methyl-2-phenyl-1,3-dimethoxypropane, 2-methyl-2-cyclohexyl-1,3-dimethoxypropane, 2-methyl-2-methylcyclohexyl-1,3-dimethoxypropane, 2,2-bis(p-chlorophenyl)-1,3-dimethoxypropane, 2,2-bis(2-phenylethyl)-1,3-

dimethoxypropane, 2,2-bis(2-cyclohexylethyl)-1,3-dimethoxypropane, 2-methyl-2-isobutyl-1,3-dimethoxypropane, 2-methyl-2-(2-ethylhexyl)-1,3-dimethoxypropane, 2,2-bis(2-ethylhexyl)-1,3-dimethoxypropane,2,2-bis(p-methylphenyl)-1,3-dimethoxypropane, 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-diphenyl-1,3-dimethoxypropane, 2,2-dibenzyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-diethoxypropane, 2,2-diisobutyl-1,3-dibutoxypropane, 2-isobutyl-2-isopropyl-1,3-dimetoxypropane, 2,2-di-sec-butyl-1,3-dimetoxypropane, 2,2-di-tert-butyl-1,3-dimethoxypropane, 2,2-dineopentyl-1,3-dimethoxypropane, 2-iso-propyl-2-isopentyl-1,3-dimethoxypropane, 2-phenyl-2-benzyl-1,3-dimetoxypropane, 2-cyclohexyl-2-cyclohexylmethyl-1,3-dimethoxypropane.

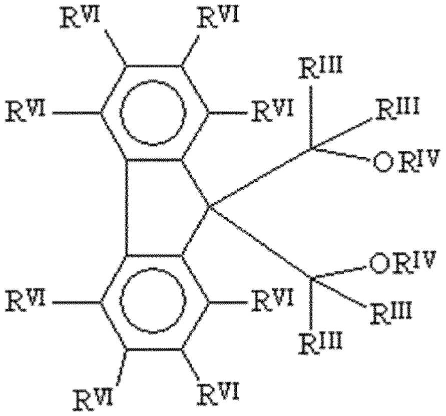
[0019] Furthermore, particularly preferred are the 1,3-diethers of formula (III):



(III)

wherein the radicals RIV have the same meaning explained above and the radicals RIII and RV radicals, equal or different to each other, are selected from the group consisting of hydrogen; halogens, preferably Cl and F; C1-C20 alkyl radicals, linear or branched; C3-C20 cycloalkyl, C6-C20 aryl, C7-C20 alkaryl and C7-C20 aralkyl radicals and two or more of the RV radicals can be bonded to each other to form condensed cyclic structures, saturated or unsaturated, optionally substituted with RVI radicals selected from the group consisting of halogens, preferably Cl and F; Cl-C20 alkyl radicals, linear or branched; C3-C20 cycloalkyl, C6-C20 aryl, C7-C20 alkaryl and C7-C20 aralkyl radicals; said radicals RV and RVI optionally containing one or more heteroatoms as substitutes for carbon or hydrogen atoms, or both.

[0020] Preferably, in the 1,3-diethers of formulae (I) and (II) all the RIII radicals are hydrogen, and all the RIV radicals are methyl. Moreover, are particularly preferred the 1,3-diethers of formula (II) in which two or more of the RV radicals are bonded to each other to form one or more condensed cyclic structures, preferably benzenic, optionally substituted by RVI radicals. Specially preferred are the compounds of formula (IV):



(IV)

wherein the RVI radicals equal or different are hydrogen; halogens, preferably Cl and F; Cl-C20 alkyl radicals, linear or branched; C3-C20 cycloalkyl, C6-C20 aryl, C7-C20 alkylaryl and C7-C20 aralkyl radicals, optionally containing one or more heteroatoms selected from the group consisting of N, 0, S, P, Si and halogens, in particular Cl and F, as substitutes for carbon or hydrogen atoms, or both; the radicals RIII and RIV are as defined above for formula (II).

[0021] Specific examples of compounds comprised in formulae (II) and (III) are:
1,1-bis(methoxymethyl)-cyclopentadiene;
1,1-bis(methoxymethyl)-2,3,4,5-tetramethylcyclopentadiene;
1,1-bis(methoxymethyl)-2,3,4,5-tetraphenylcyclopentadiene;
1,1-bis(methoxymethyl)-2,3,4,5-tetrafluorocyclopentadiene;
1,1-bis(methoxymethyl)-3,4-dicyclopentylcyclopentadiene;
1,1--bis(methoxymethyl)indene; 1,1-bis(methoxymethyl)-2,3-dimethylindene;
1,1-bis(methoxymethyl)-4,5,6,7-tetrahydroindene;
1,1-bis(methoxymethyl)-2,3,6,7-tetrafluoroindene;
1,1-bis(methoxymethyl)-4,7-dimethylindene;
1,1-bis(methoxymethyl)-3,6-dimethylindene;

1,1-bis(methoxymethyl)-4-phenylindene;
1,1-bis(methoxymethyl)-4-phenyl-2-methylindene;
1,1-bis(methoxymethyl)-4-cyclohexylindene;
1,1-bis(methoxymethyl)-7-(3,3,3-trifluoropropyl)indene;
1,1-bis(methoxymethyl)-7-trimethyisilylindene;
1,1-bis(methoxymethyl)-7-trifluoromethylindene;
1,1-bis(methoxymethyl)-4,7-dimethyl-4,5,6,7-tetrahydroindene;
1,1-bis(methoxymethyl)-7-methylindene;
1,1-bis(methoxymethyl)-7-cyclopenthylindene;
1,1-bis(methoxymethyl)-7-isopropylindene;
1,1-bis(methoxymethyl)-7-cyclohexylindene;
1,1-bis(methoxymethyl)-7-tert-butylindene;
1,1-bis(methoxymethyl)-7-tert-butyl-2-methylindene;
1,1-bis(methoxymethyl)-7-phenylindene;
1,1-bis(methoxymethyl)-2-phenylindene;
1,1-bis(methoxymethyl)-1H-benz[e]indene;
1,1-bis(methoxymethyl)-1H-2-methylbenz[e]indene;
9,9-bis(methoxymethyl)fluorene;
9,9-bis(methoxymethyl)-2,3,6,7-tetramethylfluorene;
9,9-bis(methoxymethyl)-2,3,4,5,6,7-hexafluorofluorene;
9,9-bis(methoxymethyl)-2,3-benzofluorene;
9,9-bis(methoxymethyl)-2,3,6,7-dibenzofluorene;
9,9-bis(methoxymethyl)-2,7-diisopropylfluorene;
9,9-bis(methoxymethyl)-1,8-dichlorofluorene;
9,9-bis(methoxymethyl)-2,7-dicyclopentylfluorene;
9,9-bis(methoxymethyl)-1,8-difluorofluorene;
9,9-bis(methoxymethyl)-1,2,3,4-tetrahydrofluorene;
9,9-bis(methoxymethyl)-1,2,3,4,5,6,7,8-octahydrofluorene;
9,9-bis(methoxymethyl)-4-tert-butylfluorene.

[0022] As explained above, the catalyst component (a) comprises, in addition to the above electron donors, a titanium compound having at least a Ti-halogen bond and a Mg halide. The magnesium halide is preferably MgCl2 in active form which is widely known from the patent literature as a support for

Ziegler-Natta catalysts. Patents USP 4,298,718 and USP 4,495,338 were the first to describe the use of these compounds in Ziegler-Natta catalysis. It is known from these patents that the magnesium dihalides in active form used as support or co-support in components of catalysts for the polymerization of olefins are characterized by X-ray spectra in which the most intense diffraction line that appears in the spectrum of the non-active halide is diminished in intensity and is replaced by a halo whose maximum intensity is displaced towards lower angles relative to that of the more intense line.

[0023] The preferred titanium compounds used in the catalyst component of the present invention are $TiCl_4$ and $TiCl_3$; furthermore, also Ti-haloalcoholates of formula $Ti(OR)_{n-y}X_y$ can be used, where n is the valence of titanium, y is a number between 1 and n-1 X is halogen and R is a hydrocarbon radical having from 1 to 10 carbon atoms.

[0024] Preferably, the catalyst component (a) has an average particle size ranging from 15 to 80 μm, more preferably from 20 to 70 μm and even more preferably from 25 to 65 μm. As explained the succinate is present in an amount ranging from 40 to 90% by weight with respect to the total amount of donors. Preferably it ranges from 50 to 85% by weight and more preferably from 65 to 80% by weight. The 1,3-diether preferably constitutes the remaining amount.

[0025] The alkyl-Al compound (b) is preferably chosen among the trialkyl aluminum compounds such as for example triethylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum. It is also possible to use mixtures of trialkylaluminum's with alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides such as $AlEt_2Cl$ and $Al_2Et_3Cl_3$.

[0026] Preferred external electron-donor compounds include silicon compounds, ethers, esters such as ethyl 4-ethoxybenzoate, amines, heterocyclic compounds and particularly 2,2,6,6-tetramethyl piperidine, ketones and the 1,3-diethers. Another class of preferred external donor compounds is that of silicon compounds of formula $R_a^5R_b^6Si(OR^7)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^5, R^6, and R^7, are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms. Particularly preferred are methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, dicyclopentyldimethoxysilane, 2-ethylpiperidinyl-2-t-butyldimethoxysilane and 1,1,1,trifluoropropyl-2-ethylpiperidinyl-dimethoxysilane and 1,1,1,trifluoropropyl-metil-dimethoxysilane. The external electron donor compound is used in such an amount to give a molar ratio between the organo-aluminum compound and said electron donor compound of from 5 to 500, preferably from 5 to 400 and more preferably from 10 to 200.

[0027] The catalyst-forming components can be contacted with a liquid inert hydrocarbon solvent such as, e.g., propane, n-hexane or n-heptane, at a temperature below about 60°C and preferably from about 0 to 30°C for a time period of from about 6 seconds to 60 minutes.

[0028] The above catalyst components (a), (b) and optionally (c) can be fed to a pre-contacting vessel, in amounts such that the weight ratio (b)/(a) is in the range of 0.1-10 and, if the compound (c) is present, the weight ratio (b)/(c) is weight ratio corresponding to the molar ratio as defined above. Preferably, the said components are pre-contacted at a temperature of from 10 to 20°C for 1-30 minutes. The precontact vessel is generally a stirred tank reactor.

[0029] Preferably, the precontacted catalyst is then fed to a prepolymerization reactor where a prepolymerization step takes place. The prepolymerization step can be carried out in a first reactor selected from a loop reactor or a continuously stirred tank reactor, and is generally carried out in liquid-phase. The liquid medium comprises liquid alpha-olefin monomer(s), optionally with the addition of an inert hydrocarbon solvent. Said hydrocarbon solvent can be either aromatic, such as toluene, or aliphatic, such as propane, hexane, heptane, isobutane, cyclohexane and 2,2,4-trimethylpentane. The amount of hydrocarbon solvent, if any, is lower than 40% by weight with respect to the total amount of alpha-olefins, preferably lower than 20% by weight. Preferably, step (i)a is carried out in the absence of inert hydrocarbon solvents.

[0030] The average residence time in this reactor generally ranges from 2 to 40 minutes, preferably from 5 to 25 minutes. The temperature ranges between

10°C and 50°C, preferably between 15°C and 35°C. Adopting these conditions allows to obtain a pre-polymerization degree in the preferred range from 60 to 800g per gram of solid catalyst component, preferably from 150 to 500 g per gram of solid catalyst component. Step (i)a is further characterized by a low concentration of solid in the slurry, typically in the range from 50 g to 300 g of solid per liter of slurry.

[0031] The slurry containing the catalyst, preferably in pre-polymerized form, is fed to a gas-phase or liquid-phase polymerization reactor where the copolymer for use in the healthcare or medical article of the invention is prepared. In case of a gas-phase reactor, it generally consists of a fluidized or stirred, fixed bed reactor or a reactor comprising two interconnected polymerization zones one of which, working under fast fluidization conditions and the other in which the polymer flows under the action of gravity. The liquid phase process can be either in slurry, solution or bulk (liquid monomer). This latter technology is the most preferred and can be carried out in various types of reactors such as continuous stirred tank reactors, loop reactors or plug-flow ones. The polymerization is generally carried out at temperature of from 20 to 120°C, preferably of from 40 to 85°C. When the polymerization is carried out in gas-phase the operating pressure is generally between 0.5 and 10 MPa, preferably between 1 and 5 MPa. In the bulk polymerization the operating pressure is generally between 1 and 6 MPa preferably between 1.5 and 4 MPa. Preferably, the copolymer for use in the healthcare or medical article of the invention is prepared by polymerizing propylene in mixture with ethylene in liquid monomer, more preferably in a loop reactor.

[0032] Hydrogen can be used as a molecular weight regulator.

[0033] Conventional additives, fillers and pigments, commonly used in olefin polymers, may be added, such as nucleating agents, extension oils, mineral fillers, and other organic and inorganic pigments. The addition of inorganic fillers, such as talc, calcium carbonate and mineral fillers, also brings about an improvement to some mechanical properties, such as flexural modulus and HDT. Talc can also have a nucleating effect.

EXAMPLES

[0034] The following examples are given to illustrate the present invention without any limiting purpose.

Test methods

Molar ratio of feed gases

[0035] Determined by gas-chromatography.

Average Particle Size of the adduct and catalysts

[0036] Determined by a method based on the principle of the optical diffraction of monochromatic laser light with the "Malvern Instr. 2600" apparatus. The average size is given as P50.

Comonomer content

[0037] The content of ethylene comonomer was determined by infrared spectroscopy by collecting the IR spectrum of the sample vs. an air background with a Fourier Transform Infrared spectrometer (FTIR). The instrument data acquisition parameters are:

- purge time: 30 seconds minimum
- collect time: 3 minutes minimum
- apodization: Happ-Genzel
- resolution: 2 cm^{-1}.

[0038] Sample Preparation - Using a hydraulic press, a thick sheet is obtained by pressing about g 1 of sample between two aluminum foils. A small portion is cut from this sheet to mold a film. Recommended film thickness ranges between 0.02 and 0.05 cm (8 – 20 mils). Pressing temperature is 180±10°C (356°F) and about 10 kg/cm2 (142.2 PSI) pressure for about one minute. The pressure is released, the sample removed from the press and cooled to room temperature.

[0039] The spectrum of pressed film sample is recorded in absorbance vs. wavenumbers (cm^{-1}). The following measurements are used to calculate ethylene content:

- Area (At) of the combination absorption bands between 4482 and 3950 cm^{-1} which is used for spectrometric normalization of film thickness;
- Area (AC2) of the absorption band between 750-700 cm^{-1} after two proper consecutive spectroscopic subtractions of an isotactic non-additivated

polypropylene spectrum and then of a reference spectrum of an ethylene-propylene random copolymer in the range 800-690 cm^{-1};

- Height (DC4) of the absorption band at 769 cm^{-1} (maximum value), after two proper consecutive spectroscopic subtractions of an isotactic non-additivated polypropylene spectrum and then of a reference spectrum of an ethylene-propylene random copolymer in the range 800-690 cm^{-1}.

[0040] In order to calculate the ethylene content, a calibration straight line for ethylene obtained by using samples of known amount of ethylene is needed and is obtained by plotting AC2/At versus ethylene molar percent (%C2m). The slope GC2 is calculated from a linear regression.

[0041] The spectra of the unknown samples are recorded and then (At), (AC2) and (DC4) of the unknown sample are calculated. The ethylene content by weight is obtained from the ethylene content (% molar fraction C2m) of the sample is calculated as follows:

$$\%C2m = \frac{1}{G_{C2}} \cdot \frac{A_{C2}}{A_t}$$

Melt flow rate (MFR “L”)

[0042] Determined according to ISO 1133 (230°C, 2.16 Kg)

Melting temperature (T_m) and crystallization temperature (T_c)

[0043] Both determined by differential scanning calorimetry (DSC) according to the ASTM D 3417 method, which is equivalent to the ISO 11357/1 and 3 method.

Xylene solubles

[0044] Determined as follows: 2.5 g of polymer and 250 ml of xylene are introduced in a glass flask equipped with a refrigerator and a magnetic stirrer. The temperature is raised in 30 minutes up to the boiling point of the solvent. The so obtained clear solution is then kept under reflux and stirring for further 30 minutes. The closed flask is then kept in thermostatic water bath at 25° C for 30 minutes. The so formed solid is filtered on quick filtering paper. 100 ml of the filtered liquid is poured in a previously weighed aluminum container, which is heated on a heating plate under nitrogen flow, to remove the solvent by evaporation. The container is then kept on an oven at 80° C under vacuum until constant weight is obtained. The weight percentage of polymer soluble in xylene at room temperature is then calculated.

Flexural modulus (MEF)

[0045] Determined according to ISO 178.

Izod impact strength

[0046] Determined according to ISO 180/1A.

Ductile brittle transition temperature (DB/TT)

[0047] The bi-axial impact resistance is determined through impact with an automatic, computerized striking hammer. The circular test specimens are obtained by cutting with circular hand punch (38 mm diameter) plaques obtained as described below. The circular test specimens are conditioned for at least 12 hours at 23°C and 50 RH and then placed in a thermostatic bath at testing temperature for 1 hour. The force-time curve is detected during impact of a striking hammer (5.3 kg, hemispheric punch with a ½” diameter) on a circular specimen resting on a ring support. The machine used is a CEAST 6758/000 type model no. 2. The DB/TT is the temperature at which 50% of the samples undergoes fragile break when submitted to the above-mentioned impact test. The plaques for DB/TT measurements, having dimensions of 127x127x1.5 mm are prepared according to the following method. The injection press is a Negri Bossi™ type (NB 90) with a clamping force of 90 tons. The mold is a rectangular plaque (127x127x1.5mm). Main process parameters are reported below:

- Back pressure: 20 bar
- Injection time: 3 sec
- Maximum Injection pressure: 14 MPa
- Hydraulic injection pressure: 6-3 Mpa
- First holding hydraulic pressure: 4±2 Mpa
- First holding time: 3 sec
- Second holding hydraulic pressure: 3±2 Mpa
- Second holding time: 7 sec
- Cooling time: 20 sec
- Mold temperature: 60 °C
- Melt temperature 220 to 280 °C

Stress at yield and elongation at break

[0048] Determined according to ISO 527.

Haze on plaque

[0049] The plaques are prepared by using a Battenfeld™ type BA 500CD injection press with a clamping force of 50 tons. The insert mould leads to the moulding of two plaques (55x60x1 mm each). The plaques are conditioned for 12 to 48 hours at relative humidity of 50±5% and temperature of 23±1° C. The instrument used for the test is a Gardner photometer with Haze-meter UX-10 equipped with a G.E. 1209 lamp and filter C. The instrument calibration is made by carrying out a measurement in the absence of the sample (0% Haze) and a measurement with intercepted light beam (100% Haze). The measurement and computation principle are given in the norm ASTM-D1003. The haze measurement is carried out on five plaques.

Haze on film

[0050] Cast film specimens with a thickness of 50 μm are prepared by extruding each polymer composition in a single screw Collin extruder (length/diameter ratio of screw: 30) at a film drawing speed of 7 m/min. and a melt temperature of 210-250 °C. Haze on film is determined on 50 μm thick films of the test composition, prepared as described above. The measurement is carried out on a 50 x 50 mm portion cut from the central zone of the film. The instrument used for the test is a Gardner photometer with Haze-meter UX-10 equipped with a G.E. 1209 lamp and filter C. The instrument calibration is made by carrying out a measurement in the absence of the sample (0% Haze) and a measurement with intercepted light beam (100% Haze).

Haze on bottles

[0051] The same method and instrument described for haze measurement on plaque is used. Samples of 1.4 mm thickness are cut from bottles' bottom in order to obtain a flat sample that the specimen holder could grasp:

Top load on bottles

[0052] An Instron dynamometer equipped with a balance of 0.2gr accuracy and with a micrometer of 0.01mm accuracy is used. After at least 10-hours conditioning at 23°±1°C and 50% relative humidity, the bottle is settled between the two plates of the dynamometer and compressed with a stress velocity of the plate of 5cm/min. The stress at collapse of the bottle is recorded and the value reported in N. The Top Load value is the mean value obtained from measurements repeated on 10 bottles.

Sterilization procedure

[0053] The sample is placed in a steam sterilization autoclave Systec DX-65 set at 121 degree Celsius and 2.1 bar of nitrogen internal pressure. After 20 minutes of treatment in the autoclave, the item is let cool down to room temperature and conditioned at room temperature for 48 hours before testing.

Example 1C (comparative)

Preparation of the solid catalyst component

[0054] Into a 500 mL four-necked round flask, purged with nitrogen, 250 mL of $TiCl_4$ were introduced at 0°C. While stirring, 10.0 g of microspheroidal $MgCl_2 \bullet 2.1C_2H_5OH$ having average particle size of 47μm (prepared in accordance with the method described in example 1 of EP728769) and an amount of diethyl 2,3-diisopropylsuccinate such as to have a Mg/succinate molar ratio of 15 were added. The temperature was raised to 100°C and kept at this value for 60 minutes. After that the stirring was stopped and the liquid was siphoned off. After siphoning, fresh $TiCl_4$ and an amount of 9,9-bis(methoxymethyl) fluorene such as to have a Mg/diether molar ratio of 30 were added. Then the temperature was raised to 110°C and kept for 30 minutes under stirring. After sedimentation and siphoning at 85°C, fresh $TiCl_4$ was added. Then the temperature was raised to 90°C for 15min. After sedimentation and siphoning at 90°C the solid was washed three times with anhydrous hexane (3 x 100 ml) at 60 °C and additional three times with anhydrous hexane (3 x 100 ml) at 25 °C. The obtained solid catalyst component had a total amount of internal electron donor compounds of 12.0% by weight with respect to the weight of the solid catalyst component.

Preparation of the catalyst system – Precontact

[0055] Before introducing it into the polymerization reactors, the solid catalyst component described above is contacted with aluminum-triethyl (TEAL) and with the dicyclopentyldimethoxysilane (D donor) under the conditions reported in Table 1.

Prepolymerization

[0056] The catalyst system is then subject to prepolymerization treatment at 20°C by maintaining it in suspension in liquid propylene for a residence time of 9 minutes before introducing it into the polymerization reactor.

Polymerization

[0057] The polymerization was carried out in continuous mode in a liquid phase loop reactor. Hydrogen was used as molecular weight regulator. The polymer particles exiting from the polymerization step were subjected to a steam treatment to remove the unreacted monomers and dried under a nitrogen flow.

[0058] The main precontact, prepolymerization and polymerization conditions and the quantities of monomers and hydrogen fed to the polymerization reactor are reported in Table 1. Characterization data for the obtained polymers are reported in Table 2.

[0059] Then the polymer particles were introduced in an extruder, wherein they were mixed with 1500 ppm of Irganox 1010, 900 ppm of Irgafos 168 and 150 ppm of DHT-4A. The previously said Irganox 1010 is pentaerytrityl tetrakis 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propanoate, while Irgafos 168 is tris (2,4-di-tert-butylphenyl) phosphite, both marketed by Ciba Geigy. The polymer particles were extruded under nitrogen atmosphere in a twin screw extruder, at a rotation speed of 250 rpm and a melt temperature of 200-250° C.

Preparation of bottle specimens

[0060] Cylindrical 1L bottles (35g) were prepared from the compositions of the examples, with a blow molding machine AUTOMA SPEED 3M - Extrusion continuous Incline Shuttle. The main process parameters are reported below:

- screw diameter: 70 mm
- length /diameter (L/D) ratio: 24
- melt temperature: 250 °C
- mould temperature: 25 °C

The bottles were tested for Haze and top load properties. Characterization results are reported in Table 2.

Examples 2 and 3C (comparative)

[0061] It was worked according to Example 1C, except that the polymerization run was conducted in continuous mode in a reactor being a gas-phase polymerization reactor comprising two interconnected polymerization zones, a riser and a downcomer, as described in European Patent EP782587 and that in the granulation step 20 ppm of Luperox 101 were added.

[0062] The main precontact, prepolymerization and polymerization conditions and the quantities of monomers and hydrogen fed to the polymerization reactor are reported in Table 1. Characterization data for the obtained polymers and bottles are reported in Table 2.

Table 1 – Process conditions

Example		1C	2	3C
TEAL/external donor	wt/wt	5.1	3	3
TEAL/catalyst	wt/wt	28	6	8
TEAL/C_3^-	Kg/t	0.17	N/A	N/A
Temperature	°C	70	70	70
Pressure	bar-g	38.9	25	25
Split holdup riser	wt%	N/A	39	42
Split holdup downcomer	wt%	N/A	61	58
C_2^- riser	mole%	N/A	2.7	2.4
C_2^- feed	Kg/h	2.1	N/A	N/A
H_2/C_3^- riser	mol/mol	N/A	0.007	0.01
H_2 feed concentration	ppm	750	N/A	N/A

Notes: C_2^- = ethylene; C_3^- = propylene; H_2 = hydrogen; N/A = not applicable

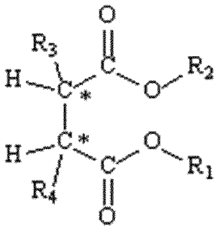
Table 2 – Polymers and bottles characterization

Example		1C	2	3C
MFR	g/10’	1.7	0.70	0.82
MFR after visbreaking	g/10’	N/A	2.22	1.93
Ethylene units	%wt	3.0	4.9	5.5
M_w/M_n		n/a	6.9	6.1
XS	%	5.2	12.2	14.1
Tm	°C	146.6	137.0	134.2
Tc	°C	100.6	92.2	88.6
MEF	MPa	1031	570	530
MEF after sterilization	MPa	1131	650	590
Izod Impact 23°C	kJ/m^2	11.0	14.1	27.7
Izod Impact 0°C	kJ/m^2	n/a	4.4	6.9
Izod Impact -20°C	kJ/m^2	n/a	2.5	2.7
D/B TT	°C	>10	-3.0	-7.0
Stress at yield	MPa	23.8	20.3	19.0
Elongation at break	%	608	460	460
Haze on 1mm plaque	%	45.7	27.4	24.1
Haze/plaque after steriliz.	%	n/a	42.6	46.0
Haze on 50 μ cast film	%	n/a	0.1	0.3
Haze/film after steriliz.	%	n/a	11.8	15.2
Haze on 1-litre bottle (35gr)	%	46.3	24.5	28.5
Haze/bottle after steriliz.	%	48.4	29.2	33.8
Top load on bottle	N	318	185	165

Notes: N/A = not applicable; n/a = not available

CLAIMS

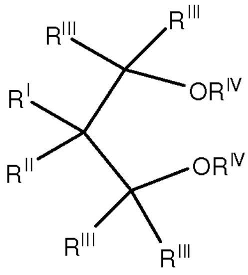
1. A healthcare or medical article comprising a propylene-ethylene copolymer having a content of ethylene units comprised between 4.0 and 5.4 % by weight, preferably between 4.3 and 5.3 % by weight, more preferably between 4.6 and 5.2 % by weight, and having a value of melt flow rate “L” (230°C, 2.16Kg) of from 1.0 to 3.0 g/10 min, preferably of from 1.5 to 2.5 g/10 min.
2. The article according to claim 1, wherein the propylene-ethylene copolymer has a fraction soluble in xylene at room temperature of between 10.0 % by weight and 15.0 % by weight.
3. The article according to claim 1 or 2, which is a container.
4. The article according to claim 3, which is selected among bottles, bags and pouches.
5. The article according to any of claims 1 to 4, which is produced by the Blow-Fill-Seal (BFS) technology.
6. A process for the preparation of a propylene-ethylene copolymer having a content of ethylene units comprised between 4.0 and 5.4 % by weight comprising the step of copolymerizing propylene and ethylene in the presence of a catalyst system comprising the product obtained by contacting the following components:
   (a) a solid catalyst component comprising a magnesium halide, a titanium compound having at least a Ti-halogen bond and at least two electron donor compounds one of which being present in an amount from 40 to 90% by mole with respect to the total amount of donors and being selected from succinates and the other being selected from 1,3 diethers,
   (b) an aluminum hydrocarbyl compound, and
   (c) optionally an external electron donor compound.
7. The process according to claim 6, wherein the succinate is of formula (I):



(I)

wherein the radicals R1 and R2, equal to, or different from, each other are a C1-C20 linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms; and the radicals R3 and R4 equal to, or different from, each other, are C1-C20 alkyl, C3-C20 cycloalkyl, C5-C20 aryl, arylalkyl or alkylaryl group with the proviso that at least one of them is a branched alkyl; said compounds being, with respect to the two asymmetric carbon atoms identified in the structure of formula (I), stereoisomers of the type (S,R) or (R,S).

8. The process according to claim 6 or 7, wherein the 1,3-diether is of formula (II):



(II)

wherein RI and RII are the same or different and are hydrogen or linear or branched C1-C18 hydrocarbon groups which can also form one or more cyclic structures; RIII groups, equal or different from each other, are hydrogen or C1-C18 hydrocarbon groups; RIV groups equal or different from each other, have the same meaning of RIII except that they cannot be hydrogen; each of RI to RIV groups can contain heteroatoms selected from halogens, N, O, S and Si.

9. The process according to any of claims 6 to 8, wherein the catalyst component (a) has an average particle size ranging from 15 to 80 µm.

10. The process according to any of claims 6 to 9, wherein the succinate is present in amount ranging from 40 to 90% by moles with respect to the total amount of internal donors.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2014/063896

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/063896

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F210/06 C08F210/16
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 2 030 996 A1 (BOREALIS TECH OY [FI]) 4 March 2009 (2009-03-04) examples 5,6 claims 1,10 page 1, paragraph 1; examples 5,6; table 1 paragraph [0044] - paragraph [0045] -----	1-5
Y	WO 2008/012144 A1 (BASELL POLIOLEFINE SRL [IT]; CAVALIERI CLAUDIO [IT]; BECCARINI ENRICO) 31 January 2008 (2008-01-31) examples 1,2; table 1 -----	1-5
X,P	EP 2 722 348 A1 (BASELL POLIOLEFINE SRL [IT]) 23 April 2014 (2014-04-23) claims 1,2,3,4 examples 1-3 table 2 ----- -/--	6-10

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 18 November 2014	Date of mailing of the international search report 24/11/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Fischer, Brigitte

3

International application No
PCT/EP2014/063896

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2009/067337 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; HUGHES MORGAN M [US]; ANSEMS PATRICI) 28 May 2009 (2009-05-28) example 5; table 2 -----	1
A	WO 2009/054833 A2 (NOVOLEN TECH HOLDINGS CV [NL]; DIMESKA ANITA [US]; MAIER RALPH-DIETER) 30 April 2009 (2009-04-30) examples 35,43,59 -----	1

3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2014/063896

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2030996 A1	04-03-2009	AT 519790 T	15-08-2011
		CN 102131838 A	20-07-2011
		EP 2030996 A1	04-03-2009
		EP 2195355 A1	16-06-2010
		PL 2195355 T3	31-01-2012
		US 2010247375 A1	30-09-2010
		WO 2009027389 A1	05-03-2009
WO 2008012144 A1	31-01-2008	EP 2046845 A1	15-04-2009
		US 2009192271 A1	30-07-2009
		WO 2008012144 A1	31-01-2008
EP 2722348 A1	23-04-2014	EP 2722348 A1	23-04-2014
		WO 2014060217 A1	24-04-2014
WO 2009067337 A1	28-05-2009	CN 101918463 A	15-12-2010
		EP 2212359 A1	04-08-2010
		ES 2435568 T3	20-12-2013
		US 2010285253 A1	11-11-2010
		WO 2009067337 A1	28-05-2009
WO 2009054833 A2	30-04-2009	EP 2235071 A2	06-10-2010
		WO 2009054833 A2	30-04-2009

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-5

   Healthcare or medical article comprising a propylene-ethylene copolymer having a content of ethylene units comprised between 4.0 and 5.4 % by weight, preferably between 4.3 and 5.3 % by weight, more preferably between 4.6 and 5.2 % by weight, and having a value of melt flow rate "L" (230°C, 2.16Kg) of from 1.0 to 3.0 g/10 min, preferably of from 1.5 to 2.5 g/10 min.

   ---

2. claims: 6-10

   Process for the preparation of a propylene-ethylene copolymer having a content of ethylene units comprised between 4.0 and 5.4 % by weight

   ---