



(51) International Patent Classification:

C08L 23/16 (2006.01) *C08F 210/18* (2006.01)
C08F 210/16 (2006.01)

(21) International Application Number:

PCT/EP2017/061251

(22) International Filing Date:

11 May 2017 (11.05.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

16170680.9 20 May 2016 (20.05.2016) EP

(71) Applicant: ARLANXEO NETHERLANDS B.V.
[NL/NL]; Urmonderbaan 24, 6167 RD Geleen (NL).(72) Inventors: VAN DUIN, Martin; Rijksweg Zuid 213,
6134 AC SITTARD (NL). QUIROGA NORAMBUE-
NA, Victor, Fidel; Kromme Weg 11, 3620 Lanaken (BE).
VAN ZANDVOORT, Gose; St. Michaellaan 6, 6049 LH
Herlen (NL). ALVAREZ-GRIMA, Maria, Montserrat;
Demerthof 5, 6227 AT Maastricht (NL).(74) Agent: HERBOLD, Matthias; LANXESS Deutschland
GmbH, LEX-IPR, Kennedyplatz 1, 50569 Köln (DE).(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, DJ, 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, KH, KN, KP, KR,
KW, KZ, LA, LC, LK, LR, LS, 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, ST, 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).

Declarations under Rule 4.17:

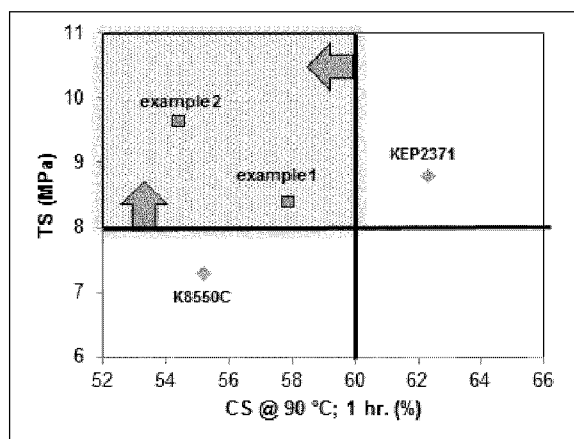
— as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii))

Published:

— with international search report (Art. 21(3))

(54) Title: RUBBER COMPOSITION

Fig. 1:



(57) **Abstract:** A rubber composition, comprising i) an ethylene- α -olefin-non-conjugated-diene copolymer having - a Mooney viscosity ML (1 +8) at 150 °C $\geq$ 85 MU and - an ethylene content $\leq$ 63 wt.% - the diene content is 4 to 8 % by weight of the ethylene- α -olefin-non-conjugated- diene copolymer i), - the non-conjugated diene is a combination of 5-ethylidene-2-norbornene (ENB) and 5-vinylnorbornene (VNB), - the ethylene- α -olefin-non-conjugated-diene copolymer i) has an amount of VNB between 0.05 and 1 wt.%, and has a Mw of at least 400,000 g/mol and, ii) an extender oil of 10 to 40 phr based on the copolymer i) with the sum of the EPDM copolymer i) and the oil ii) amounting to at least 95 wt.% of the composition.

Rubber Composition

The present invention relates to a certain rubber composition having a limited amount of extender oil, a process for its manufacturing, and its use for making highly loaded vulcanizates.

5 For automotive seals, building and construction window gaskets and other applications highly filled vulcanizates are preferred. In particular for automotive applications EPDM rubber compositions are desired that combine good elasticity with good mechanical properties. Highly filled rubber vulcanizates with good elasticity and mechanical properties pose a problem for today's industry.

10 Vulcanized rubber compounds are typically characterized in terms of mechanical performance and elasticity. In the context of this invention, tensile properties, such as tensile strength and elongation at break, and tear strength are critical mechanical properties; compression sets at elevated temperature and at or below room temperature are critical characteristics for elasticity.

15 Ethylene- α -olefin-diene elastomers, particularly ethylene-propylene-diene copolymers (EPDM) are recognized as excellent general-purpose elastomers that are useful in a wide variety of applications. EPDM is consisting of ethylene and propylene repeating units with a smaller amount of non-conjugated diene units to introduce unsaturation and, thus, facilitate crosslinking of the polymer chains. EPDM is a rubber without any unsaturation in
20 the polymer backbone and, thus, has excellent resistance against oxygen, ozone, heat and UV-irradiation compared to polydiene rubbers. Consequently, EPDM rubber is used in outdoor and elevated temperature applications, such as automotive sealing systems, building and construction window gaskets, roof sheeting, coolant hoses and belts. EPDM rubber is typically compounded with fillers, such as reinforcing carbon blacks and inert
25 white fillers, and with plasticizers, especially mineral oil. On the one hand, this results in practical EPDM compounds, which satisfy technical criteria as relevant for mixing, processing and final applications. On the other hand, this enables the production of relatively low-cost compounds with still satisfactory technical performance. However, increasing the total loading of an EPDM compound with very high levels of filler(s) and
30 plasticizer(s) next to the base elastomer results in a deterioration of the mechanical and elastic properties, such as a decrease of the tensile strength, a decrease of the elongation at break and a decrease of the tear strength and an increase of the compression sets at various temperatures. The typical results of this eternal balancing act for EPDM application development are an excellent technical performance at a relatively low
35 compound loading, a relatively poor performance at a very high compound loading or a compromise.

Prior Art

EP2818513 discloses EPDM copolymers with improved elasticity properties, whereby the exemplified rubber has a high amount of extender oil of 50 phr and a very low molecular weight distribution of smaller than 3.0 . In addition, these EPDM polymers are designed for low-damping applications, such as engine mounts. This puts a limit to the total rubber compound loading, because high levels of filler(s) and plasticiser (oil) deteriorate the damping performance and, consequently, low filled compounds (<250 phr) are used.

In Joseph C. Salamone: "Polymeric Materials Encyclopedia Vol. 3 D-E", 23 July 1996 CRC press, XP002761450 one can see that it is possible to measure Mooney at 150 °C, which is needed to achieve reproducible and useful data on viscosity of very high molecular weight rubber polymers.

In EP2902412 also terpolymers are disclosed for elasticity purposes. The exemplified polymers do not contain any oil, which in case of high-molecular weight EPDM rubbers will prohibit efficient mixing of compounds, thus resulting in unacceptable long mixing times or two subsequent mixing cycles. In addition, only terpolymers with ENB are described, which will have insufficient levels of controlled long chain branching and, thus, will have high compound Mooney viscosities, resulting in low extrusion and moulding productivity.

In US9139727 rubber compositions for anti-vibration applications are disclosed. However, such rubber compositions consist of blends of two EPDMs, which requires multiple reactor technology. In addition, the need for low damping performance of such rubber applications requires low filled compounds (<250 phr).

In US5229478 high molecular weight EPDM elastomers based on hexadiene or ENB produced with a metallocene catalyst are exemplified. The drawback of such high molecular weight terpolymers is that they do not contain oil, which will prohibit efficient mixing of compounds of EPDM rubber. In addition, only terpolymers with hexadiene or ENB are described, which will have insufficient levels of long chain branching and, thus, will have high compound Mooney viscosities.

In JP2002-047363A oil-free terpolymers and quaterpolymers are mentioned having quite

high ethylene contents. The drawback of such EPDMs is that the absence of extender oil puts a limit to the maximum molecular weight in view of efficient mixing and that high ethylene contents result in EPDMs with high crystallinity, which result in inferior elasticity at room-temperature and below.

5

Oil-free terpolymers are also mentioned in JP2002-047382, which again in case of very high molecular weight EPDMs will suffer from mixing limitations.

10

In US3884993 EPM and EPDM rubbers having improved processability are exemplified. However, these EP(D)M products are bimodal of composition, requiring multiple reactor technology for their production. These polymers are also oil-free, which severely limits mixing efficiency, and contain low levels of diene, which results in slow vulcanisation.

15

Other terpolymers are disclosed in JP371161 B2 having low Mooney viscosity and quite high oil contents. As far as the EPDM polymers are concerned, the very high oil levels makes them rather highly priced products.

20

An EPDM vulcanizate to be used in an automotive solid seal should typically have a compression set (22 hr compression at 90 °C; cooling for 3 hr in compressed state at room temperature and measurement after 1 hr relaxation at room temperature according to DVR VW 3307), below 60%. Furthermore, the tensile strength according to DIN ISO 37 shall be preferably higher than 8 MPa for test plaques prepared from the automotive solid seal compound.

25

Numerous commercial EPDM grades as mentioned in Table 1 are known for this purpose, but still can be improved in order to fulfill these stringent requirements in particular for automotive applications in particular for high loaded rubber vulcanizates.

Table 1: Characteristic of commercial EPDM products

EPDM product	brochure data						
	Mooney viscosity				chemical composition		
	ML (1+4) @ 125 °C (MU)	ML (1+8) @ 125 °C (MU)	ML (1+4) @ 150 °C (MU)	ML (1+8) @ 150 °C (MU)	ethylene content (wt.%)	ENB content (wt.%)	oil content (phr)
Esprene® 5277F ¹⁾			81		54	8,5	
Royalene® 515 ²⁾			82		56	9,5	
KEP2371 ³⁾		115			70	7,0	
Keltan® 8550C ⁴⁾	80				48	5,5	
Keltan® 9950C ⁴⁾				60	44	9,0	
Keltan® 3973 ⁴⁾	34				66	9,0	30
Keltan® 9565Q ⁴⁾				67	62	5,5	50
Keltan® 5469 ⁴⁾	52				63	4,5	100

¹⁾ Sumitomo Chemical; see http://www.sumitomo-chem.co.jp/polyolefin/03product/pdf/22esprene_epdm.pdf

²⁾ Lion Elastomers; see http://lionelastomers.com/main/royalene_royaledge

³⁾ Kumho Polychem; see <http://www.kumhopolychem.co.kr/eng/product/epdm?seq=1>

⁴⁾ Arlanxeo; see <http://keltan.com/en/the-power-of-keltan/premium-quality/brochures/>

Hence, the object of the present invention is to provide a rubber composition that shows improved properties, in particular good elasticity and good mechanical properties when used to make vulcanizates, in particular with a high total loading.

This object is achieved with a rubber composition, comprising

- i) an ethylene- α -olefin- non-conjugated-diene copolymer having
 - a Mooney viscosity ML (1+8) at 150 °C $\geq$ 85 MU and
 - an ethylene content $\leq$ 63 wt.%, preferably $\leq$ 60 wt.%,
 - the non-conjugated-diene content is 4 to 8 % by weight of the ethylene- α -olefin-non-conjugated-diene copolymer i),
 - the non-conjugated diene is a combination of 5-ethylidene-2-norbornene (ENB) and 5-vinylnorbornene (VNB),
 - the ethylene- α -olefin-non-conjugated-diene copolymer i) has an amount of VNB between 0.05 and 1 wt.%, and has a Mw of at least 400,000 g/mol and,

- ii) an extender oil of 10 to 40 phr based on the copolymer i),

with the sum of i) the EPDM copolymer and ii) the oil amounting to at least 95 wt.% of the composition.

Ethylene- α -olefin-non-conjugated-diene copolymer (i)

5 The preferred ethylene content, more precisely spoken the structural unit in the copolymer derived from the ethylene monomer is 63% by weight of the polymer or lower, preferably $\leq$ 60 wt.%. A more preferred ethylene content is from 35 to 63 wt.%, preferably from 55 to 60 wt.%.

Examples of the α -olefin of the ethylene- α -olefin-non-conjugated diene copolymer of the present invention are propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene and 1-decene. Of these, propylene and 1-butene are preferred. Propylene is the most preferred.

10 Preferably, the diene content is 4 to 6% by weight of the ethylene- α -olefin-non-conjugated-diene copolymer.

Preferably the sum of ethylene, non-conjugated diene(s) and α -olefin is higher than 99 wt.%, in particular 100 wt.% of the monomers.

15 In a preferred embodiment the Mooney viscosity of the ethylene- α -olefin-non-conjugated-diene copolymer i) ML (1+8) at 150 °C is $\geq$ 95 MU, preferred $\geq$ 100 MU, in particular 100 to 200 MU.

20 The ethylene- α -olefin-non-conjugated-diene copolymer (i) preferably does have a weight average molecular weight (M_w) (measured by high-temperature gel permeation chromatography (GPC), using a calibration curve prepared using a standard ethylene-propylene copolymer) of from 400,000 to 700,000 g/mol.

Also preferred is the rubber composition of the present invention wherein the ethylene- α -olefin-non-conjugated diene copolymer i) has a molecular weight distribution, namely, weight average molecular weight / number average molecular weight (M_w/M_n), measured
25 by high-temperature GPC in the range of 3.5 to 6.0 .

Furthermore, the copolymer i) is preferably branched with a $\Delta\delta$ between 0 and 30, more preferred is a $\Delta\delta$ between 5 and 20, even more preferred is a $\Delta\delta$ between 5 and 15.

30 $\Delta\delta$ (expressed in degrees) is the difference between the phase angle δ at a frequency of 0.1 rad/s and the phase angle δ at a frequency of 100 rad/s, as determined by Dynamic Mechanical Spectroscopy (DMS) at 125 °C. This quantity $\Delta\delta$ is a measure for the amount of long chain branched structures present in the polymer and has been introduced in H.C.

Booij, Kautschuk + Gummi Kunststoffe, Vol. 44, No. 2, pages 128-130, which is incorporated herein by reference.

Such a $\Delta\delta$ value can in particular be achieved with the use of small amounts of VNB as diene between 0.1 and 0.75 wt.%.

5 **Extender oil (ii)**

The optional "extender oil" ii) used in the present invention preferably means a petroleum softening agent conventionally used in the production of oil-extended rubber. Examples of the extender oil are paraffinic, naphthenic and aromatic extender oils obtained by purifying, and if necessary further processing, of high boiling fractions of petroleum.

10 Wherein "phr" means parts in weight per hundred parts in rubber copolymer. These extender oils generally show a dynamic viscosity of from 5 to 35 mm²/s at 100 °C. Preferred processing oils are paraffinic ones. A suitable paraffinic oil is e.g. Sunpar[®] 2280, available from Sunoco, clear paraffinic oil like Conopure[®] 12P, available from ConocoPhillips, or white oil like ParaLux[®] 6001 available from Chevron Texaco. Oils made
15 via a gas to liquid (GTL) process, like e.g. Risella[®] X 430 from Shell, are also preferred.

The rubber composition of the present invention consisting of at least 95 wt.% of the components i) and ii), preferably at least 98 wt.%, allows the balance to be used by auxiliary agents iii) as defined hereinafter.

20 **Auxiliary agents (iii)**

Auxiliary agents are further ingredients in addition to the components i) and ii) of the present rubber composition, like antioxidants such as Irganox[®] 1076 from BASF, UV stabilizers, partitioning agents or processing aids like talc or metal salts, such as e.g. zinc stearate, magnesium stearate or calcium stearate, that will remain in the rubber after
25 manufacturing.

Process

The present invention also refers to a process for manufacturing the rubber composition according to the present invention. The rubber composition can be manufactured by mixing the components i), optionally ii) and further auxiliary agents iii).

30 Furthermore, a process for producing the ethylene- α -olefin-non-conjugated-diene copolymer (i) without or with the extender oil ii) of the present invention is not particularly limited. The product can be produced by a solution, slurry or gas phase polymerization process, using e.g. a conventional vanadium-based catalyst, a metallocene catalyst or a

post-metallocene catalyst. Suitable processes and catalysts are known in the literature.

The rubber composition of the present invention can be produced by a process wherein the extender oil (ii) is blended with the ethylene- α -olefin-non-conjugated-diene copolymer (i) during the production step thereof. The addition preferably takes place after the polymerization reactor, but before the removal of volatiles, for instance before a steam stripper or a dry finishing extruder. More specifically, it is produced by a process wherein the extender oil (ii) is blended with the ethylene- α -olefin-non-conjugated-diene copolymer (i) which is dissolved or suspended in the reaction media coming from the polymerization reactor.

The present invention also relates to a process for forming a vulcanized rubber article, comprising the steps of:

- mixing:
 - a) the rubber composition according to the present invention,
 - b) a vulcanization package,
 - c) one or more fillers,
 - d) one or more plasticizers and
 - e) optionally, other rubber additives to form a vulcanizable rubber composition, wherein said mixture having a total compound loading of at least 250 phr, in particular at least 350 phr, preferably at least 450 phr and even more preferably of at least 550 phr and
- processing such a mixture to form the final shape of an extruded or moulded article and
- vulcanizing said vulcanizable rubber composition.

The total compound loading is defined as the sum of all ingredients in the vulcanizable rubber composition or its vulcanizate, i.e. the ingredients of the copolymer rubber composition of the present invention a), the vulcanization package b), the filler(s) c), the plasticizer(s) d) and other additive(s) e) in parts in weight per hundred parts in weight of rubber (phr).

Such a process preferably comprises, for example, the steps of (i) kneading the rubber composition of the present invention with fillers, plasticizers, a vulcanizing package, and, if necessary, the above-mentioned other ingredients, in a conventional kneading machine, such as an open roll mill, an internal mixer, a kneader or an extruder to obtain a mixed compound, and (ii) vulcanizing (cross-linking, curing) the resulting kneaded compound under heating. Such a mixing process can be done in one or more steps, as known to a

man skilled in the art.

Vulcanised compounds of such an rubber composition according to the present invention enable vulcanizates with high compound loadings, which still combine good mechanical properties with good elasticity.

Vulcanization package b)

Examples of the vulcanizing agent are sulfur; sulfur chloride; sulfur dichloride; 4,4'-dithiodimorpholine; morpholine disulfide; alkylphenol disulfide; tetramethylthiuram disulfide (TMTD); tertaethylthiuram disulfide (TETD); selenium dimethyldithiocarbamate; and organic peroxides, such as dicumyl peroxide (DCP), 2,5-di(t-butylperoxy)-2,5-dimethylhexane (DTBPH), di(t-butylperoxyisopropyl)benzene (DTBPIB), 2,5-di(benzoylperoxy)-2,5-dimethylhexane, 2,5-(t-butylperoxy)-2,5-dimethyl-3-hexyne (DTBPHY), di-t-butylperoxide and di-t-butylperoxide-3,3,5-trimethylcyclohexane (DTBTCH) or mixtures of these peroxides. Of these, preferred are sulfur, TMTD, TETD, DCP, DTBPH, DTBPIB, DTBPHY and DTBTCH.

In case of sulfur vulcanization, sulfur is preferably used in an amount of 0.1 to 10 phr, preferably from 0.5 to 5 phr or even more preferably 0.5 to 2 phr.

In case of peroxide cure, the organic peroxide is used in an amount of usually from 0.1 to 15 phr and preferably from 0.5 to 5 phr.

Sulfur as vulcanizing agent may be used, if necessary, in combination with one or more vulcanization accelerators and one or more vulcanization activators. Examples of the vulcanization accelerators are N-cyclohexyl-2-benzothiazole-sufenamide, N-oxydiethylene-2-benzothiazole-sulfen-amide, N,N-diisopropyl-2-benzothiazole-sulfenamide, 2-mercaptobenzothiazole, 2-(2,4-dinitrophenyl)mercaptobenzothiazole, 2-(2,6-diethyl-4-morpholinothio)benzothiazole, dibenzothiazyl-disulfide, diphenylguanidine, triphenylguanidine, di-o-tolylguanidine, o-tolyl-bi-guanide, diphenylguanidine-phthalate, an acetaldehyde-aniline reaction product, a butylaldehyde-aniline condensate, hexamethylenetetramine, acetaldehyde ammonia, 2-mercaptoimidazoline, thiocarbaniride, diethylthiourea, dibutylthiourea, trimethylthiourea, di-o-tolylthiourea, tetramethylthiuram monosulfide, TMTD, TETD, terabutylthiuram disulfide, dipentamethylenethiuram tetrasulfide, zinc dimethyldithiocarbamate, zinc diethyl-thiocarbamate, zinc di-n-butylthiocarbamate, zinc ethylphenyldithiocarbamate, zinc butylphenyldithiocarbamate, sodium dimethyldithiocarbamate, selenium dimethyldithiocarbamate, tellurium

diethyldithiocarbamate, zinc dibutylxanthate and ethylenethiourea. The vulcanization accelerators, if used, are used preferably in an amount of from 0.1 to 10 parts by weight, and even more preferred from 0.2 to 5 parts by weight and in particular between 0.25 and 2 phr, per 100 parts by weight of the ethylene- α -olefin-non-conjugated-diene (i).

- 5 Examples of the vulcanization activator are metal oxides, such as magnesium oxide and zinc oxide, and stearic acid or the reaction product like zinc stearate. Of these, preferred is zinc oxide combined with stearic acid. The vulcanization activators are used usually in amounts from 0.5 to 10 phr based on the EPDM copolymer (i), preferably in amounts from 0.5 to 5 phr.
- 10 When peroxide or a mixture of peroxides is used as the vulcanizing agent, peroxide coagents may be used. Examples of such peroxide coagent are cyanurate compounds, such as triallyl cyanurate and triallylisocyanurate, (meth)acrylate compounds, such as trimethylolpropane trimethacrylate and ethyleneglycol dimethacrylate, zinc dimethacrylate and zinc diacrylate, divinylbenzene, p-quinonedioxime, m-phenylene dimaleimide, (high
- 15 vinyl) polybutadiene, and combinations thereof. Preferably, 0.1 to 5 phr of the peroxide coagents may be used. Even more preferred, 0.25 to 2.5 phr of the peroxide coagent may be used. When peroxides are used as the vulcanizing agent in addition, sulphur (elementary or as part of sulphur accelerators or sulphur donors) can be used to obtain so-called hybrid curing systems. These curing systems combine high heat resistant
- 20 properties, typical for peroxide cure, with very good ultimate properties, such as tensile and tear, as well as excellent dynamic and fatigue properties typically associated with sulfur vulcanization systems. Applied dosing levels of sulfur are preferably from 0.05 to 1.0 phr, preferably from 0.2 to 0.5 phr.

Fillers c)

- 25 Preferably the filler is used in an amount of 20 to 500 phr in the process of the present invention. Preferred fillers are carbon black and/or inorganic fillers such as silica, calcium carbonate, talc and clay, which are conventionally used for rubber. The type of carbon black is classified according ASTM D-1765 for its particle size (BET in m^2/g) and structure (DBP adsorption in $\text{cm}^3/100 \text{ g}$). Preferably carbon black fillers are used with a BET
- 30 number in from 5 to 150, and DBP numbers in from 30 to 140. In the industry these type of carbon blacks are often designated to by abbreviations, such as MT, SRF, GPF, FEF, HAF, ISAF, SAF. The inorganic fillers may be surface treated with e.g. suitable silanes. Combinations of two or more of such fillers may be used. Most preferably used are carbon black and/or silanized silica.

Plasticizers d)

As plasticizer the same as the extender oil ii) of the present invention can be used. Furthermore as plasticizer lubricating oil, paraffin, liquid paraffin, petroleum asphalt, vaseline, low molecular weight polyisobutylene or polybutylene, liquid EPDM or EPM, coal
5 tar pitch, castor oil, linseed oil, bee's wax, atactic polypropylene and cumarone indene resin can be mentioned. Preferred is the addition of 20 to 250 phr of a paraffinic process oil. This paraffinic oil may be made according to a GTL process.

Other rubber additives e)

As other rubber additives e) the same as the auxiliary agents iii) mentioned above can be
10 used. The vulcanizable rubber composition may in addition also contain other additives, such as dessicants (e.g. calcium oxide), tackifiers (e.g., resin), bonding agents, pigments, process aids (e.g. factice, fatty acids, stearates, poly- or diethylene glycol), antioxidants, heat stabilisers (e.g. poly-2,2,4-trimethyl-1,2-dihydroquinoline or zinc 2-mercaptobenzimidazole), UV stabilisers, anti-ozonants, blowing agents, as well as mould
15 release additives.

The present invention also relates to a vulcanized rubber article made from the vulcanizable rubber composition of the present invention. Examples of such vulcanized rubber articles are an automotive solid seal, a building and construction window gasket, a
20 thermoplastic vulcanizate, an engine mount, and highly filled compounds for low hardness applications and injection moulding applications.

Examples

Preparation of EPDM copolymers examples 1 and 2.

The polymerization was carried out in a solution polymerization reactor with a volume of 3L. The hexanes, ethylene, propylene, dienes and hydrogen feed streams were purified by contacting with various absorption media to remove catalyst-killing impurities, such as water, oxygen and polar compounds, as is known to those skilled in the art. The process is continuous in all feed streams. Pre-mixed hexanes, propylene, ethylene, dienes, hydrogen, tri-octyl aluminium and butylated hydroxytoluene were pre-cooled before being fed to the reactor. A solution, containing the catalyst compound 19 as disclosed in WO2005/090418 and triphenylcarbenium tetrakis(perfluorophenyl)borate, was fed separately to the reactor. The hydrogen content was adjusted to achieve the desired polymer Mooney as given in Table 2. The polymer solution was continuously removed through a discharge line, where a solution of Irganox[®] 1076 in iso-propanol was added, optionally a paraffinic extender oil was added to the polymer solution, and, finally, the solution of polymer (and oil) is worked up by continuously steam stripping. The final EPDM sample was obtained after batch-wise drying of the polymer on a 2-roll mill.

The EPDM polymers examples 1 and 2 were analyzed using FT-IR for chemical composition, according to ASTM D 3900 and D 6047, oil content via extraction with acetone, Mooney viscosity ML(1+8) @ 150 °C according to ISO 289, the degree of branching as indicated by the parameter as explained in H.C. Booij, Kautsch. Gummi Kunstst. 44 (1991) 128 and GPC for the molecular weights Mw and Mn and molecular weight distribution MWD. Table 2 compares the polymer characteristics of EPDM examples 1 and 2 with those of the commercial references KEP2371 and K8550C.

The propylene wt.% content is not given in Table 2, but can be calculated for the given grades to be 100% minus the sum of ethylene, ENB and VNB contents. For the commercial grades in Table 2 the ethylene and ENB data are taken from the brochures and the VNB content was measured according to ASTM D 6047.

Table 2 compares the polymer characteristics of EPDM examples 1 and 2 with those of the commercial grades KEP2371 and K8550C.

Table 2: EPDM compositions

EPDM		K8550C	KEP2371	example 1	example 2
ethylene	(wt.%)	48 ¹⁾	70 ²⁾	56,5	60,4
ENB	(wt.%)	5.5 ¹⁾	7 ²⁾	4,9	4,8
VNB	(wt.%)	0,26	0,0	0,23	0,22
oil	(phr)	0 ¹⁾	0 ²⁾	0	12,6
ML (1+8) @ 150 °C	(MU)	52,4	88,2	86,7	104 ³⁾
Δδ	(°)	18,2	14	11,0	14,8
Mn	kg/mol	89	89	95	139
Mw	kg/mol	310	370	390	510
Mw/Mn		3,5	4,2	4,1	3,7

¹⁾ data from Arlanxeo Performance Elastomers; see <http://keltan.com/en/the-power-of-keltan/premium-quality/brochures/>

²⁾ Kumho Polychem; see <http://www.kumhopolychem.co.kr/eng/product/epdm?seq=1>

³⁾ ML (1+8) @ 150 °C of product composed of EPDM with ML (1+8) @ 150 ° of 104 and 12.6 phr of oil isC 87.8 MU

Table 1a: Overview of various commercial EPDM products and inventive grades

EPDM product	Mooney viscosity					chemical composition		
	brochure data				calculated ⁶⁾	brochure data		
	ML (1+4) @ 125 °C	ML (1+8) @ 125 °C	ML (1+4) @ 150 °C	ML (1+8) @ 150 °C	ML (1+8) @ 150 °C polymer	ethylene content	ENB content	oil content
	(MU)	(MU)	(MU)	(MU)	(MU)	(wt.%)	(wt.%)	(phr)
Esprene® 5277F ¹⁾			81		74	54	8,5	
Royalene® 515 ²⁾			82		75	56	9,5	
KEP2371 ³⁾		115			88	70	7,0	
Keltan® 8550C ⁴⁾	80				52	48	5,5	
Keltan® 9950C ⁴⁾				60	60	44	9,0	
Keltan® 3973 ⁴⁾	34				52	66	9,0	30
Keltan® 9565Q ⁴⁾				67	124	62	5,5	50
Keltan® 5469 ⁴⁾	52				144	63	4,5	100
example 1 ⁵⁾				88	88	58	5,0	
example 2 ⁵⁾				88	105	56	5,5	15

¹⁾ Sumitomo Chemical; see http://www.sumitomo-chem.co.jp/polyolefin/03product/pdf/22esprene_epdm.pdf

²⁾ Lion Elastomers; see http://lionelastomers.com/main/royalene_royaledge

³⁾ Kumho Polychem; see <http://www.kumhopolychem.co.kr/eng/product/epdm?seq=1>

⁴⁾ Arlanxeo; see <http://keltan.com/en/the-power-of-keltan/premium-quality/brochures/>

- 5) this invention
- 6) to allow a comparison, the Mooney data to the extent data at 150 °C were not available or not measured have been converted to ML (1+8) @ 150 °C by using correlations based on experimental data for ML (1+4) @ 125 °C, ML (1+8) @ 125 °C, ML (1+4) @ 150 °C and ML (1+8) @ 150 °C for a variety of EPDM polymers; a correction for the presence of oil was made for ML (1+4) @ 125 °C with 1.5 MU/phr oil which was based on ML (1+4) @ 125 °C data for oil-extended EPDM polymers before and after acetone extraction of the oil.

Preparation of a vulcanizable rubber composition

Ingredients:

Various vulcanizable rubber compositions based on four different EPDM products without or with 15 phr extender oil (cf. Table 2) and in roughly 400, 500 and 600 phr compounds were prepared (Table 3). The ingredients used for the various compound evaluations are listed in Table 4.

Table 3: EPDM compound compositions used for evaluating different EPDM products without oil or with 15 phr of oil in 400, 500 and 600 phr compounds.

ingredient	composition based on A), B) or C)			composition based on D)		
	400 phr	500 phr	600 phr	400 phr	500 phr	600 phr
non-oil EPDM A), B) or C)	100	100	100	0	0	0
EPDM D)	0	0	0	115	115	115
Corax® N-550	120	160	200	120	160	200
Whiting BSH	80	100	120	80	100	120
Sunpar® 2280	80	115	150	65	100	135
ZnO aktiv®	5	5	5	5	5	5
Edenor® C 18 98-100	1	1	1	1	1	1
PEG (4000)	2	2	2	2	2	2
milled sulfur 90/95	0.3	0.3	0.3	0.3	0.3	0.3
Rhenogran® CaO-80	6.9	6.9	6.9	6.9	6.9	6.9
Rhenogran® TBBS-80	0.5	0.5	0.5	0.5	0.5	0.5
Rhenogran® MBTS-80	1.3	1.3	1.3	1.3	1.3	1.3
Rhenogran® ZBEC-70	2	2	2	2	2	2
Rhenogran® ZDBP-50	2	2	2	2	2	2
Rhenogran® ZAT-70	0.6	0.6	0.6	0.6	0.6	0.6
Rhenogran® S-80	0.75	0.75	0.75	0.75	0.75	0.75
Rhenogran® DTDC-80	1	1	1	1	1	1
Vulkalent® E/C	0.5	0.5	0.5	0.5	0.5	0.5
total	403.85	498.85	593.85	403.85	498.85	593.85

A) Kumho KEP2371; B) Arlanxeo Keltan® 8550C; C) Example 1; D) Example 2

Table 4: Overview of compound ingredients used

ingredient	chemical composition	supplier
Corax [®] N-550	carbon black	Evonik
Whiting BSH	calcium carbonate	Omya
Sunpar [®] 2280	paraphinic oil	Sunoco
ZnO aktiv [®]	zinc oxide	Rhein Chemie Additives
Edenor [®] C 18 98-100	stearic acid	Emery Oleochemicals
PEG 4000	polyethylene glycol	Merck
milled sulfur 90/95	sulfur	VWR International
Rhenogran [®] CaO-80	80% calcium oxide on carrier	Rhein Chemie Additives
Rhenogran [®] TBBS-80	80% N-tert.-butyl-2-benzothiazyl sulfenamide on carrier	Rhein Chemie Additives
Rhenogran [®] MBTS-80	80% dibenzothiazole disulfide on carrier	Rhein Chemie Additives
Rhenogran [®] ZBEC-70	70% zinc-dibenzyl-dithiocarbamate on carrier	Rhein Chemie Additives
Rhenogran [®] ZDBP-50	50% zinc dialkyldithiophosphate on carrier	Rhein Chemie Additives
Rhenogran [®] ZAT-70	70% zinc amine dithiophosphate on carrier	Rhein Chemie Additives
Rhenogran [®] S-80	80% sulfur on carrier	Rhein Chemie Additives
Rhenogran [®] DTDC-80	80% caprolactam disulfide	Rhein Chemie Additives
Vulkalent [®] E/C	N-phenyl-N-(trichloromethylsulfonyl)-benzene sulphonamide	Rhein Chemie Additives

5 Experimental part and test methods

All compounds were prepared on a laboratory internal mixer (GK1,5 E1 from Harburg-Freudenberger Maschinenbau GmbH; ram pressure 7 bar, 45 rpm, 70 % degree of filling and total mixing time 4 min). Chemicals of the vulcanization system were added on an open mill (200 mm diameter of the rolls; 20 rpm, 40 °C roll temperature and friction 1, 22).

10 Test specimens have been prepared for all compounds by curing test plates of 2 mm and 6 mm thickness at 180 °C to a time equivalent to 1.1 and 1.25 times t₉₀ (t₉₀ is the time to reach 90 % of maximum torque during the rheometer measurement).

Various mechanical and elastic properties were measured in accordance with the test methods listed in Table 5.

Table 5: Test methods.

method	standard	characteristic	abbreviation	unit
compound				
Mooney viscosity	DIN 53523 - 3	Mooney viscosity (1+4) @ 100 °C	compound ML	(MU)
Mooney scorch	DIN 53523 - 4	scorch time for 5% rise of torque versus minimum torque @ 125 °C	t5s	(sec.)
rheometry	DIN 53529	torque difference MH-ML @ 180 °C	DS	(dNm)
		time to 1 dNm rise above minimum torque @ 180 °C	ts2	(sec.)
		time to 90% of maximum torque @ 180 °C	t90	(sec.)
vulcanisate				
hardness	DIN ISO 7619-1	hardness	Hh	(Sh A)
tensile test	DIN ISO 37	modulus at 100% elongation	M100%	(MPa)
		modulus at 300% elongation	M300%	(MPa)
		elongation at break	eab	(%)
		tensile strength	TS	(MPa)
Delft tear test	ISO 34 - 2	tear resistance	tear	(N/mm)
compression set test	DIN ISO 815	compression set for 24 hr @ -25 °C	CS @ -25 °C	(%)
		compression set for 24 hr @ 100 °C	CS @ 100 °C	(%)
		compression set for 24 hr @ 70 °C	CS @ 70 °C	(%)
		compression set for 24 hr @ 23 °C	CS @ 23 °C	(%)
compression set test	DVR VW - 3307	compression set for 22 hr @ 90 °C; storage in clamps 3 hr. @ 23 °C; 5 sec. relaxation	CS @ 90 °C; 5 sec.	(%)
		compression set for 22 hr @ 90 °C; storage in clamps 3 hr. @ 23 °C; 1 hr. relaxation	CS @ 90 °C; 1 hr.	(%)
		compression set for 72 hr @ 23 °C; 5 sec. relaxation	CS @ 23 °C; 5 sec.	(%)
		compression set for 72 hr @ 23 °C; 1 hr. relaxation	CS @ 23 °C; 1 hr	(%)

Tables 6, 7 and 8 show the compound properties and the mechanical and elastic properties of the corresponding vulcanizates, based on compound formulations with about 600, 500 and 400 phr, respectively, with the four EPDMs investigated (cf. Tables 2 and 3). The data from Table 6 are next compared with typical requirements for automotive, solid seals of i) tensile strength > 8 MPa for test plaques combined with ii) the compression set according to DVR VW 3307 (22 hr. compression at 90 °C, cooling for 3 hrs. in compressed state at room temperature and measurement after 1 hr. relaxation at room temperature) below 60%. K8550C does fulfill the compression set requirement CS 90 °C; 1 hr, but not the tensile strength requirement. KEP2731 does fulfill the tensile strength requirement, but not the compression set CS 90 °C; 1 hr requirement. The two EPDM examples according to the present invention fulfill both the tensile strength and compression set CS 90 °C; 1 hr requirements in this 600 phr compound. In Figure 1 the tensile strength in MPa is plotted vs the compression set CS 90 °C; 1 hr in %, and the typical DVR VW 3307 specifications (top left quadrant) are given. For the vulcanizates based on examples 1 and 2 as of the present invention it can be seen that they fulfill the strong requirements of both a very high tensile strength of larger than 8 MPa and a compression set CS 90 °C; 1 hr below 60% for a total loading of about 600 phr. These properties are not achievable by the vulcanizates based on the respective commercial EPDM grades available for such purpose.

Table 6: Properties of compounds and vulcanizate for 593.85 phr compound formulation

EPDM		K8550C	KEP2371	example 1	example 2
compound					
compound ML	(MU)	49,0	54,9	50,6	67,0
t5s	(sec.)	654	527	682	616
ΔS	(dNm)	11,9	11,9	10,99	12,0
ts2	(sec.)	53	47	53	50
t90	(sec.)	165	140	156	159
vulcanisate					
Hh	(Sh A)	67,9	69,3	65,0	66,0
M100%	(MPa)	3,2	3,7	3,2	3,3
M300%	(MPa)	-	-	8,1	9,3
eab	(%)	282	279	312	313
TS	(MPa)	7,3	8,8	8,4	9,6
tear	(N/mm)	27,5	32,3	32,2	32,5
CS @ -25 °C	(%)	64,9	91,6	86,9	91,4
CS @ 100 °C	(%)	30,2	29,1	34,5	31,1
CS @ 70 °C	(%)	9,4	11,6	10,7	12,7
CS @ 23 °C	(%)	4,6	11,5	6,2	7,8
CS @ 90 °C; 5 sec.	(%)	63,5	70,2	61,8	59,9
CS @ 90 °C; 1 hr.	(%)	55,2	62,3	57,9	54,4
CS @ 23 °C; 5 sec.	(%)	20,9	28,6	22,0	20,1
CS @ 23 °C; 1 hr	(%)	12,2	15,9	12,8	10,1

5

In a similar way, the two examples of the present invention combine a tensile strength larger than 8 MPa with a compression set at 23 °C according to DIN ISO 815 below 10% in the 600 phr compounds, whereas the commercial EPDM products do not.

10

For the 500 phr compound formulations (Table 7) only the two examples of the present invention combine a tensile strength larger than 10 MPa with a compression set CS 90 °C; 1 hr below 53% and a compression set at 23 °C according to DIN ISO 815 below 8%, whereas the commercial EPDM products do not. Finally, for the 400 phr compound formulations (Table 8) only the two examples of the present invention combine a tensile strength larger than 11 MPa with a compression set at 23 °C according to DIN ISO 815 below 8%.

15

Table 7: Properties of compounds and vulcanisate for 498.85 phr compound formulation.

EPDM		K8550C	KEP2371	example 1	example 2
compound					
compound ML	(MU)	53,4	63,0	60,0	75,7
t5s	(sec.)	638	495	623	548
ΔS	(dNm)	13,9	13,8	13,63	14,4
ts2	(sec.)	50	44	49	46
t90	(sec.)	159	133	148	149
vulcanisate					
Hh	(Sh A)	65,6	68,5	66,0	65,9
M100%	(MPa)	3,4	4	3,4	3,4
M300%	(MPa)	8,7	10,4	9,7	10,4
eab	(%)	332	325	339	349
TS	(MPa)	9,3	10,8	10,6	11,6
tear	(N/mm)	37,7	35,3	36	38,9
CS @ -25 °C	(%)	55,7	93,5	82,5	92,4
CS @ 100 °C	(%)	28,5	26,1	30,0	27,4
CS @ 70 °C	(%)	8,6	11,7	10,0	11,2
CS @ 23 °C	(%)	4,7	10,3	6,3	6,6
CS @ 90 °C; 5 sec.	(%)	54,4	62,9	52,9	54,0
CS @ 90 °C; 1 hr.	(%)	49,5	53,7	49,7	46,4
CS @ 23 °C; 5 sec.	(%)	18,9	23,0	19,5	20,4
CS @ 23 °C; 1 hr	(%)	11,4	12,7	10,4	12,2

Table 8: Properties of compounds and vulcanisate for 403.85 phr compound formulation.

EPDM		K8550C	KEP2371	example 1	example 2
compound					
compound ML	(MU)	61,7	72,7	68,3	89,6
t5s	(sec.)	622	490	627	530
ΔS	(dNm)	16,7	16,2	16,31	17,8
ts2	(sec.)	47	42	46	43
t90	(sec.)	153	124	153	144
vulcanisate					
Hh	(Sh A)	66,8	68,4	65,2	65,5
M100%	(MPa)	3,2	3,6	3,3	3,4
M300%	(MPa)	9	10,8	10,4	11,6
eab	(%)	367	370	368	383
TS	(MPa)	10,5	12,4	12,3	14,2
tear	(N/mm)	35,4	40,3	37,9	40,4
CS @ -25 °C	(%)	49,7	92,6	80,9	89,8
CS @ 100 °C	(%)	25,8	24,4	27,0	23,8
CS @ 70 °C	(%)	8,1	11,4	9,5	8,9
CS @ 23 °C	(%)	5,1	10,3	5,8	6,4

Patent claims

1. A rubber composition, comprising

i) an ethylene- α -olefin-non-conjugated-diene copolymer having

- a Mooney viscosity ML (1+8) at 150 °C $\geq$ 85 MU and
- an ethylene content $\leq$ 63 wt. %
- the diene content is 4 to 8 % by weight of the ethylene- α -olefin-non-conjugated-diene copolymer i),
- the non-conjugated diene is a combination of 5-ethylidene-2-norbornene (ENB) and 5-vinylnorbornene (VNB),
- the ethylene- α -olefin-non-conjugated-diene copolymer i) has an amount of VNB between 0.05 and 1 wt. %, and has a Mw of at least 400,000 g/mol and,

ii) an extender oil of 10 to 40 phr based on the copolymer i)

with the sum of the EPDM copolymer i) and the oil ii) amounting to at least 95 wt. % of the composition.

2. The rubber composition according to claim 1 wherein the Mooney viscosity ML (1+8) at 150 °C of the ethylene- α -olefin-non-conjugated-diene copolymer i) is between 85 and 150 MU.

3. The rubber composition according to at least one of the claims 1 to 2, wherein the ethylene content of the ethylene- α -olefin-non-conjugated-diene copolymer i) is between 55 and 63 wt. %.

4. The rubber composition according to at least one of the claims 1 to 3, wherein the ethylene content of the ethylene- α -olefin-non-conjugated-diene copolymer i) is $\leq$ 60 wt. %.

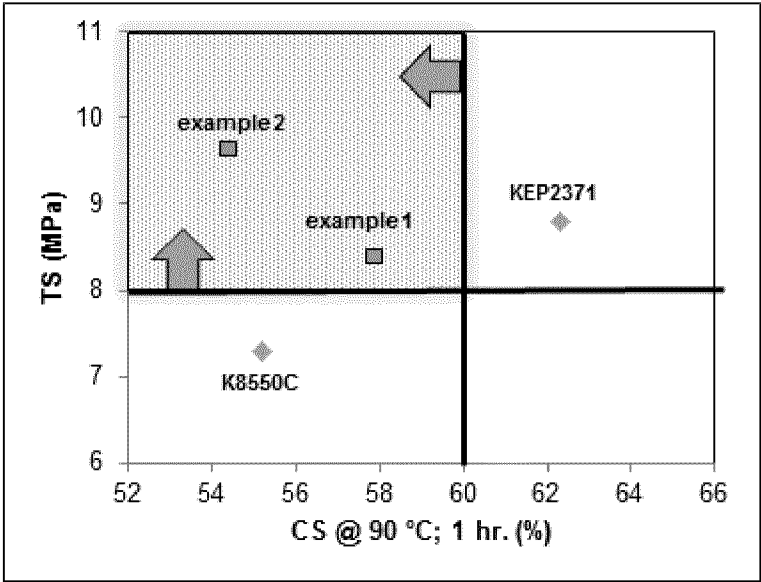
5. The rubber composition according to at least one of the claims 1 to 4, wherein the ethylene content of the ethylene- α -olefin-non-conjugated-diene copolymer i) is between 55 and 60 wt. %.

6. The rubber composition according to at least one of the claims 1 to 5 wherein the ethylene- α -olefin-non-conjugated-diene copolymer i) has a molecular weight distribution (MWD = Mw/Mn) of 3.5 to 6.0.

7. The rubber composition according to at least one of the claims 1 to 6 wherein the ethylene- α -olefin-non-conjugated-diene copolymer i) has a $\Delta\delta$ between 0 and 30, more preferred between 5 and 20, preferably between 5 and 15.
- 5 8. The rubber composition according to at least one of the claims 1 to 7 wherein the diene content is 4 to 6 % by weight of the ethylene- α -olefin-non-conjugated-diene copolymer i).
- 10 9. The rubber composition according to at least one of the claims 1 to 8 wherein the ethylene- α -olefin-non-conjugated-diene copolymer i) has an amount of VNB between 0.1 and 0.75 wt.%.
- 15 10. The rubber composition according to at least one of the claims 1 to 9, wherein the α -olefin of the ethylene- α -olefin-non-conjugated-diene copolymer i) is selected from the group consisting of propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene and 1-decene, preferably propylene.
- 20 11. The rubber composition according to at least one of the claims 1 to 10, wherein the extender oil ii) is selected from the group consisting of paraffinic, naphthenic and aromatic extender oils obtained by purifying high boiling fractions of petroleum, preferably paraffinic oil.
- 25 12. A process for forming a vulcanized rubber article comprising the steps of:
- mixing:

25 a) the rubber composition according to at least one of the claims 1 to 11,
b) a vulcanization package,
c) one or more filler(s),
d) one or more plasticizer(s) and
e) optionally, other rubber additives to form a vulcanizable rubber composition, wherein said mixture having a total compound loading of at least 250
30 phr, in particular at least 350 phr, preferably at least 450 phr and even more preferably of at least 550 phr and
 - processing such a mixture to form the final shape of an extruded or moulded article and vulcanizing said vulcanizable rubber composition.

Fig. 1:



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/061251

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L23/16 C08F210/16 C08F210/18
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)
C08L 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.
A	US 2009/209672 A1 (EBATA HIROKI [JP] ET AL) 20 August 2009 (2009-08-20) the whole document -----	1-12
A	EP 2 818 513 A1 (LANXESS ELASTOMERS BV [NL]) 31 December 2014 (2014-12-31) example 1 -----	1-12
A	Joseph C. Salamone: "Polymeric Materials Encyclopedia Volume 3 D-E", 23 July 1996 (1996-07-23), CRC press, XP002761450, the whole document -----	1-12
A	EP 2 902 421 A1 (LG CHEMICAL LTD [KR]) 5 August 2015 (2015-08-05) the whole document -----	1-12



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

23 May 2017

Date of mailing of the international search report

02/06/2017

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

Ritter, Nicola

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/061251

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009209672	A1	20-08-2009	AT 556097 T 15-05-2012
		CN 101883798 A	10-11-2010
		CN 104262520 A	07-01-2015
		EP 2221323 A1	25-08-2010
		JP 5717342 B2	13-05-2015
		KR 20100090714 A	16-08-2010
		US 2009209672 A1	20-08-2009
		WO 2009072503 A1	11-06-2009

EP 2818513	A1	31-12-2014	CA 2914191 A1 31-12-2014
		CN 105339426 A	17-02-2016
		EP 2818513 A1	31-12-2014
		JP 2016523304 A	08-08-2016
		KR 20160023697 A	03-03-2016
		US 2016152796 A1	02-06-2016
		WO 2014206952 A1	31-12-2014

EP 2902421	A1	05-08-2015	EP 2902421 A1 05-08-2015
		JP 6109953 B2	05-04-2017
		JP 2015533913 A	26-11-2015
		KR 101391692 B1	07-05-2014
		US 2015299361 A1	22-10-2015
		WO 2014077428 A1	22-05-2014
