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(71) Applicant: **DOW GLOBAL TECHNOLOGIES LLC** [US/US]; 2040 Dow Center, Midland, Michigan 48674 (US).

(72) Inventor; and
(71) Applicant *(for all designated States except US)*: **SUN, Yabin** [CN/CN]; Room 201, Unit 234, No. 399, Nanliu Road, Shanghai 201203 (CN).

(72) Inventors: **CAI, Yu**; Stony Brook, Shanghai 11794 (CN). **ZHANG, Hongliang**; 3F243 No. 936, Zhang Heng Road, Shanghai 201203 (CN). **COGEN, Jeffrey M.**; 6 Braintree Court, Flemington, New Jersey 08822 (US). **SENGUPTA, Saurav S.**; 119 Lincoln Road, Collegeville, Pennsylvania 19426 (US). **PERSON, Timothy J.**; 1521 Finley Circle, Pottstown, Pennsylvania 19464 (US).

(74) Agent: **WU, FENG & ZHANG CO.**; Room 305, Tower B, Beijing Aerospace CPMIEC Building, No.30 Haidian South Road, Haidian District, Beijing 100080 (CN).

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(54) Title: CROSSLINKABLE POLYMERIC COMPOSITIONS WITH N,N,N',N',N",N"-HEXAALLYL-1,3,5-TRIAZINE-2,4,6-TRIAMINE CROSSLINKING COAGENT, METHODS FOR MAKING THE SAME, AND ARTICLES MADE THEREFROM

(57) Abstract: Crosslinkable polymeric compositions comprising a thermoplastic,non-elastomer ethylene-based polymer,an organic peroxide,and a crosslinking coagent comprising N,N,N',N',N",N"-hexaallyl-1,3,5-triazine-2,4,6-triamine. Such crosslinkable polymeric compositions and their crosslinked forms can be employed as polymeric layers in wire and cable applications, such as insulation in power cables.

CROSSLINKABLE POLYMERIC COMPOSITIONS WITH N,N,N',N',N",N"-HEXAALLYL-1,3,5-TRIAZINE-2,4,6-TRIAMINE CROSSLINKING COAGENT, METHODS FOR MAKING THE SAME, AND ARTICLES MADE THEREFROM

FIELD

Various embodiments of the present invention relate to crosslinkable polymeric compositions containinga crosslinking coagent comprising N,N,N',N',N",N"-hexaallyl-1,3,5-triazine-2,4,6-triamine, methods of making the same, and articles made therefrom.

INTRODUCTION

Medium, high, and extra-high voltage ("MV," "HV," and "EHV") cables typically contain a crosslinked polymeric material as an insulation layer, such as a crosslinked polyethylene. Such crosslinked polymeric materials can be prepared from a crosslinkable polymeric composition having a peroxide initiator. The radical reactions between peroxide and polyethylene generate undesirable byproducts which must be removed by elevated temperature in a degassing chamber after crosslinking the polyethylene. Although advances have been achieved in the field of crosslinkable polymeric compositions, improvements are still desired.

SUMMARY

One embodiment is acrosslinkable polymeric composition, comprising:

(a) a thermoplastic, non-elastomer ethylene-based polymer;

(b) an organic peroxide; and

(c) a crosslinking coagent comprising N,N,N',N',N",N"-hexaallyl-1,3,5-triazine-2,4,6-triamine.

DETAILED DESCRIPTION

Various embodiments of the present invention concern crosslinkable polymeric compositions comprising an ethylene-based polymer, an organic peroxide, and acoagent comprising N,N,N',N',N",N"-hexaallyl-1,3,5-triazine-2,4,6-triamine ("HATATA"). Additional embodiments concern crosslinked polymeric compositions prepared from such crosslinkable polymeric compositions. Further embodiments concern coated conductors and processes for producing coated conductors using the crosslinkable polymeric compositions.

Crosslinkable Polymeric Composition

As noted above, one component of the crosslinkable polymeric compositions described herein is an ethylene-based polymer. As used herein, "ethylene-based" polymers are polymers

prepared from ethylene monomers as the primary (i.e., greater than 50 weight percent ("wt%")) monomer component, though other co-monomers may also be employed. "Polymer" means a macromolecular compound prepared by reacting (i.e., polymerizing) monomers of the same or different type, and includes homopolymers and interpolymers. "Interpolymer" means a polymer prepared by the polymerization of at least two different monomer types. This generic term includes copolymers (usually employed to refer to polymers prepared from two different monomer types), and polymers prepared from more than two different monomer types (e.g., terpolymers (three different monomer types) and quaterpolymers (four different monomer types)).

The starting ethylene-based polymers suitable for use herein are thermoplastic. As known to those skilled in the art, the term "thermoplastic" denotes a polymer that becomes pliable or moldable above a specific temperature and returns to a solid state upon cooling. Additionally, the ethylene-based polymer is not an elastomer. As known to those skilled in the art, "elastomers" are defined as materials which experience large reversible deformations under relatively low stress. Some examples of commercially available elastomers include natural rubber, ethylene/propylene (EPM) copolymers, ethylene/vinyl acetate copolymers, ethylene/propylene/diene (EPDM) copolymers, styrene/butadiene copolymers, chlorinated polyethylene, and silicone rubber. Such polymers are expressly excluded from use as the ethylene-based polymer herein.

In addition, in various embodiments, the ethylene-based polymer can be non-polar. As used with respect to polymers, the term "non-polar" denotes a polymer containing no polar bonds between carbon atoms and other atoms having a higher electronegativity relative to carbon(such as O, N, F, Cl) or, if such polar bonds are present, a polymer in which there is no net dipole because of the symmetrical arrangement of such polar bonds. In various embodiments, the ethylene-based polymer can contain no polar bonds between carbon atoms and other atoms having higher electronegativity relative to carbon.

In various embodiments, the ethylene-based polymer has no halide-containing monomers incorporated therein. Specifically, in various embodiments, the ethylene-based polymer has no fluoromonomers or chloromonomers incorporated therein. As such, in various embodiments, the ethylene-based polymer is neither a fluoropolymer nor a chloropolymer.

In various embodiments, the ethylene-based polymer can be an ethylene homopolymer. As used herein, "homopolymer" denotes a polymer consisting of repeating units derived from a single monomer type, but does not exclude residual amounts of other components used in preparing the homopolymer, such as chain transfer agents.

In an embodiment, the ethylene-based polymer can be an ethylene/alpha-olefin ("α-olefin") interpolymer having an α-olefin content of at least 1 wt%, at least 5 wt%, at least 10 wt%, at least 15 wt%, at least 20 wt%, or at least 25 wt% based on the entire interpolymer weight. These interpolymers can have an α-olefin content of less than 50 wt%, less than 45 wt%, less than 40 wt%, or less than 35 wt% based on the entire interpolymer weight. When an α-olefin is employed, the α-olefin can be a C_{3-20} (i.e., having 3 to 20 carbon atoms) linear, branched or cyclic α-olefin. Examples of C_{3-20} α-olefins include propene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. The α-olefins can also have a cyclic structure such as cyclohexane or cyclopentane, resulting in an α-olefin such as 3-cyclohexyl-1-propene (allyl cyclohexane) and vinyl cyclohexane. Illustrative ethylene/α-olefin interpolymers include ethylene/propylene, ethylene/1-butene, ethylene/1-hexene, ethylene/1-octene, ethylene/propylene/1-octene, ethylene/propylene/1-butene, and ethylene/1-butene/1-octene.

In various embodiments, the ethylene-based polymer can be used alone or in combination with one or more other types of ethylene-based polymers (e.g., a blend of two or more ethylene-based polymers that differ from one another by monomer composition and content, catalytic method of preparation, etc). If a blend of ethylene-based polymers is employed, the polymers can be blended by any in-reactor or post-reactor process.

In various embodiments, the ethylene-based polymer can be selected from the group consisting of low-density polyethylene ("LDPE"), linear-low-density polyethylene ("LLDPE"), very-low-density polyethylene ("VLDPE"), and combinations of two or more thereof.

In an embodiment, the ethylene-based polymer can be an LDPE. LDPEs are generally highly branched ethylene homopolymers, and can be prepared via high pressure processes (i.e., HP-LDPE). LDPEs suitable for use herein can have a density ranging from 0.91 to 0.94 g/cm^3. In various embodiments, the ethylene-based polymer is a high-pressure LDPE having a density of at least 0.915 g/cm^3, but less than 0.94 g/cm^3, or less than 0.93 g/cm^3. Polymer densities provided herein are determined according to ASTM International ("ASTM") method D792.

LDPEs suitable for use herein can have a melt index (I_2) of less than 20 g / 10 min., or ranging from 0.1 to 10 g / 10 min., from 0.5 to 5 g/10min., from 1 to 3 g / 10 min., or an I_2 of 2 g / 10 min. Melt indices provided herein are determined according to ASTM method D1238. Unless otherwise noted, melt indices are determined at 190 °C and 2.16 Kg (i.e., I_2). Generally, LDPEs have a broad molecular weight distribution ("MWD") resulting in a relatively high polydispersity index ("PDI;" ratio of weight-average molecular weight to number-average molecular weight).

In an embodiment, the ethylene-based polymer can be an LLDPE. LLDPEs are generally ethylene-based polymers having a heterogeneous distribution of comonomer (e.g., α-olefin monomer), and are characterized by short-chain branching. For example, LLDPEs can be copolymers of ethylene and α-olefin monomers, such as those described above. LLDPEs suitable for use herein can have a density ranging from 0.916 to 0.925 g/cm^3. LLDPEs suitable for use herein can have a melt index (I_2) ranging from 1 to 20 g/10 min., or from 3 to 8 g/10 min.

In an embodiment, the ethylene-based polymer can be a VLDPE. VLDPEs may also be known in the art as ultra-low-density polyethylenes, or ULDPEs. VLDPEs are generally ethylene-based polymers having a heterogeneous distribution of comonomer (e.g., α-olefin monomer), and are characterized by short-chain branching. For example, VLDPEs can be copolymers of ethylene and α-olefin monomers, such as one or more of those α-olefin monomers described above. VLDPEs suitable for use herein can have a density ranging from 0.87 to 0.915 g/cm^3. VLDPEs suitable for use herein can have a melt index (I_2) ranging from 0.1 to 20 g/10 min., or from 0.3 to 5 g/10 min.

In an embodiment, the ethylene-based polymer can comprise a combination of any two or more of the above-described ethylene-based polymers.

Production processes used for preparing ethylene-based polymers are wide, varied, and known in the art. Any conventional or hereafter discovered production process for producing ethylene-based polymers having the properties described above may be employed for preparing the ethylene-based polymers described herein. In general, polymerization can be accomplished at conditions known in the art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, at temperatures from 0 to 250 °C, or 30 or 200 °C, and pressures from atmospheric to 10,000 atmospheres (1,013 megaPascal ("MPa")). In most polymerization reactions, the molar ratio of catalyst to polymerizable compounds employed is from 10^{-12}:1 to 10^{-1}:1, or from 10^{-9}:1 to 10^{-5}:1.

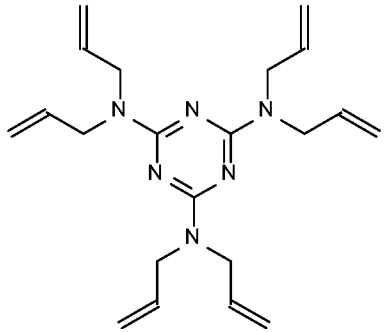
An example of an ethylene-based polymer suitable for use herein is low-density polyethylene produced in a high pressure process and having a density of 0.92 g/cm^3 and a melt index (I_2) of 2 g/10 min.

As noted above, the above-described ethylene-based polymer is combined with an organic peroxide. As used herein, "organic peroxide" denotes a peroxide having the structure: R^1-O-O-R^2, or R^1-O-O-R-O-O-R^2, where each of R^1 and R^2 is a hydrocarbyl moiety, and R is a hydrocarbylene moiety. As used herein, "hydrocarbyl" denotes a univalent group formed by removing a hydrogen atom from a hydrocarbon (e.g. ethyl, phenyl) optionally having one or more heteroatoms. As used herein, "hydrocarbylene" denotes a bivalent group formed by removing two hydrogen atoms from a hydrocarbon optionally having one or more heteroatoms. The organic peroxide can be any dialkyl, diaryl, dialkaryl, or diaralkyl peroxide, having the same or differing alkyl, aryl, alkaryl, or aralkyl moieties. In an embodiment, each of R^1 and R^2 is independently a C_1 to C_{20} or C_1 to C_{12}alkyl, aryl, alkaryl, or aralkyl moiety. In an embodiment, R can be a C_1 to C_{20} or C_1 to C_{12} alkylene, arylene, alkarylene, or aralkylene moiety. In various embodiments, R, R^1, and R^2 can have the same or a different number of carbon atoms and structure, or any two of R, R^1, and R^2 can have the same number of carbon atoms while the third has a different number of carbon atoms and structure.

Organic peroxides suitable for use herein include mono-functional peroxides and di-functional peroxides. As used herein, "mono-functional peroxides" denote peroxides having a single pair of covalently bonded oxygen atoms (e.g., having a structure R-O-O-R). As used herein, "di-functional peroxides" denote peroxides having two pairs of covalently bonded oxygen atoms (e.g., having a structure R-O-O-R-O-O-R). In an embodiment, the organic peroxide is a mono-functional peroxide.

Exemplary organic peroxides include dicumyl peroxide ("DCP");tert-butyl peroxybenzoate; di-tert-amyl peroxide ("DTAP"); bis(alpha-t-butyl-peroxyisopropyl) benzene ("BIPB"); isopropylcumyl t-butyl peroxide; t-butylcumylperoxide; di-t-butyl peroxide; 2,5-bis(t-butylperoxy)-2,5-dimethylhexane; 2,5-bis(t-butylperoxy)-2,5-dimethylhexyne-3; 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane; isopropylcumyl cumylperoxide; butyl 4,4-di(tert-butylperoxy) valerate; di(isopropylcumyl) peroxide; and mixtures of two or more thereof. In various embodiments, only a single type of organic peroxide is employed. In an embodiment, the organic peroxide is dicumyl peroxide.

As noted above, the crosslinkable polymeric composition further comprises a crosslinking coagent. The crosslinking coagent comprises N,N,N',N',N",N"-hexaallyl-1,3,5-triazine-2,4,6-triamine ("HATATA"). HATATA has the following structure:



In various embodiments, the crosslinkable polymeric composition can include one or more additional crosslinking coagents. Examples of such crosslinking coagents include polyallyl crosslinking coagents, such as triallyl isocyanurate ("TAIC"), triallyl cyanurate ("TAC"), triallyl trimellitate ("TATM"), triallyl orthoformate, pentaerythritol triallyl ether, triallyl citrate, and triallyl aconitate; ethoxylated bisphenol A dimethacrylate; α-methyl styrene dimer ("AMSD"); acrylate-based coagents, such as trimethylolpropane triacrylate ("TMPTA"), trimethylolpropane trimethylacrylate ("TMPTMA"), 1,6-hexanediol diacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, tris(2-hydroxyethyl) isocyanurate triacrylate, and propoxylated glyceryl triacrylate; vinyl-based coagents, such as polybutadiene having a high 1,2-vinyl content, and trivinyl cyclohexane ("TVCH"); and other coagents as described in USP 5,346,961 and 4,018,852.

In various embodiments, the crosslinkable polymeric composition can comprise the ethylene-based polymer in an amount ranging from 50 to 99 wt%, from 80 to 99 wt%, from 90 to 99 wt%, or from 95 to 99 wt%, based on the entire crosslinkable polymeric composition weight. Additionally, the crosslinkable polymeric composition can comprise the organic peroxide in an amount ranging from 0.1 to 5 wt%, from 0.1 to 3 wt%, from 0.4 to 2 wt%, from 0.4 to 1.7 wt%, from 0.5 to 1.4 wt%, or from 0.7 to less than 1.0 wt%, based on the entire crosslinkable polymeric composition weight.In various embodiments, the organic peroxide can be present in an amount of less than 1.2 wt%, less than 1.0 wt%, or in the range of from 0.2 to 0.85 wt%,0.3 to 0.7%, 0.4 to 0.6% based on the entire crosslinkable polymeric composition weight. In still further embodiments, the organic peroxide can be present in an amount of less than 1.2 parts per

hundred resin ("phr"), less than 1.0 phr, less than 0.85 phr, or in the range of from 0.2 to 0.85 phr, 0.3 to 0.7 phr, 0.4 to 0.6 phrbased on 100 weight parts of the ethylene-based polymer. Furthermore, the crosslinkable polymeric composition can comprise the HATATA crosslinking coagent in an amount ranging from 0.01 to 15 wt%, from 0.05 to 5 wt%, from0.1 to 3 wt%, from 0.5 to 3 wt%, from 0.7 to 3 wt%, from 1.0 to 3 wt%, from 1.5 to 3 wt%, from 0.2 to 1 wt%, from 0.3 to 0.9 wt%, from 0.4 to 0.8 wt%, or from 0.4 to 0.7 wt% based on the entire crosslinkable polymeric composition weight.

In various embodiments, the HATATA can constitute at least1 wt%, at least 10 wt%, at least 20 wt%, at least 30 wt%, at least 40 wt%, at least 50 wt%, at least 60 wt%, at least 70 wt%, at least 80 wt%, at least 90 wt%, or at least 99 wt% of the total amount of crosslinking coagent, based on the total weight of the crosslinking coagent present in the crosslinkable polymeric composition. In further embodiments, the HATATA can constitute all or substantially all of the crosslinking coagent, based on the total weight of the crosslinking coagent present in the crosslinkable polymeric composition. As used herein, "substantially all" with respect to the HATATA crosslinking coagent means all other crosslinking coagents are present in an aggregate amount of 10 parts per million by weight ("ppmw") or less. In further embodiments, the organic peroxide and HATATA crosslinking coagent can be present in a coagent-to-peroxide weight ratio of at least 1:1, or greater than 1:1.

In addition to the components described above, the crosslinkable polymeric composition may also contain one or more additives including, but not limited to, antioxidants, processing aids, fillers, coupling agents, ultraviolet absorbers or stabilizers, antistatic agents, nucleating agents, slip agents, plasticizers, lubricants, viscosity control agents, tackifiers, anti-blocking agents, surfactants, extender oils, acid scavengers, flame retardants, and metal deactivators. Additives, other than fillers, are typically used in amounts ranging from 0.01 or less to 10 or more wt% based on total composition weight. Fillers are generally added in larger amounts, although the amount can range from as low as 0.01 or less to 65 or more wt% based on the total composition weight. Illustrative examples of fillers include clays, precipitated silica and silicates, fumed silica, calcium carbonate, ground minerals, aluminum trihydroxide, magnesium hydroxide, and carbon blacks with typical arithmetic mean particle sizes larger than 15 nanometers.

In various embodiments, the crosslinkable polymeric composition can comprise one or more antioxidants. Exemplary antioxidants include hindered phenols (e.g., tetrakis [methylene

(3,5-di-t-butyl-4-hydroxyhydrocinnamate)] methane), less-hindered phenols, and semi-hindered phenols; phosphates, phosphites, and phosphonites (e.g., tris (2,4-di-t-butylphenyl) phosphate); thio compounds (e.g., distearyl thiodipropionate, dilaurylthiodipropionate); various siloxanes; and various amines (e.g., polymerized 2,2,4-trimethyl-1,2-dihydroquinoline). In various embodiments, the antioxidant is selected from the group consisting of distearyl thiodipropionate, dilauryl thiodipropionate, octadecyl-3,5-di-t-butyl-4-hydroxyhydrocinnamate, benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-thiodi-2,1-ehtanediyl ester, stearyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate, 2,4-bis(dodecylthiomethyl)-6-methylphenol, 4,4'-thiobis(6-tert-butyl-m-cresol), 4,6-bis(octylthiomethyl)-o-cresol, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione, pentaerythritol tetrakis(3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate), 2',3-bis[[3-[3,5-di-tert-butyl-4-hydroxyphenyl] propionyl]] propionohydrazide, and mixtures of two or more thereof. Antioxidants, when present, can be used in amounts ranging from 0.01 to 5 wt%, from 0.01 to 1 wt%, from 0.1 to 5 wt%, from 0.1 to 1 wt%, or from 0.1 to 0.5 wt%, based on the total weight of the crosslinkable polymeric composition.

Preparation of Crosslinkable Polymeric Composition

Preparation of the cross-linkable polymeric composition can comprise compounding the above-described components. For example, compounding can be performed by either (1) compounding all components into the ethylene-based polymer, or (2) compounding all the components except for the organic peroxide and crosslinking coagent, which can be soaked in as described below. Compounding of the cross-linkable polymeric composition can be effected by standard equipment known to those skilled in the art. Examples of compounding equipment are internal batch mixers, such as a Brabender™, Banbury™, or Bolling™ mixer. Alternatively, continuous single or twin screw, mixers can be used, such as a Farrel™ continuous mixer, a Werner and Pfleiderer™ twin screw mixer, or a Buss™ kneading continuous extruder. Compounding can be performed at a temperature of greater than the melting temperature of the ethylene-based polymer up to a temperature above which the ethylene-based polymer begins to degrade. In various embodiments, compounding can be performed at a temperature ranging from 100 to 200 °C, or from 110 to 150 °C.

In one or more embodiments, the ethylene-based polymer and any optional components can first be melt compounded according to the above-described procedure and pelletized. Next, the organic peroxide and the cross-linking coagent can be soaked into the resulting ethylene-based polymer compound, either simultaneously or sequentially. In an embodiment, the organic peroxide and coagent can be premixed at the temperature above the melting temperature of the organic peroxide and coagent, whichever is greater, followed by soaking the ethylene-based polymer compound in the resulting mixture of the organic peroxide and cross-linking coagent at a temperature ranging from 30 to 100 °C, from 50 to 90 °C, or from 60 to 80 °C, for a period of time ranging from 1 to 168 hours, from 1 to 24 hours, or from 3 to 12 hours.

The resulting crosslinkable polymeric composition can have certain enhanced properties. Though not wishing to be bound by theory, it is believed that use of an HATATA crosslinking coagent can surprisingly provide superior resistance to coagent migration out of the crosslinkable polymeric composition. Thus, in various embodiments, the crosslinkable polymeric composition can exhibit a crosslinking coagent migration to the surface of the crosslinkable polymeric composition of less than 1,000 parts per million ("ppm"), less than 750 ppm, less than 500 ppm, or less than 350 ppm, based on the total weight of the crosslinkable polymeric composition, when stored at 23 °Cand 1 atm over a period of four weeks. Furthermore, the crosslinkable polymeric composition can exhibit a crosslinking coagent migration to the surface of the crosslinkable polymeric composition in the range of from 1 to 1,000 ppm, from 10 to 750 ppm, from 50 to 500 ppm, or from 200 to 400 ppm, based on the total weight of the crosslinkable polymeric composition, when stored at 23 °C and 1 atm over a period of four weeks. The method for determining coagent migration is detailed in the Test Methods section, below, at a coagent loading of 2.50 wt% based on the entire weight of the crosslinkable polymeric composition.

Crosslinked Polymeric Composition

The above-described crosslinkable polymeric composition can be cured or allowed to cure in order to form a crosslinked ethylene-based polymer. Such curing can be performed by subjecting the crosslinkable polymeric composition to elevated temperatures in a heated cure zone, which can be maintained at a temperature in the range of 175 to 260 °C. The heated cure zone can be heated by pressurized steam or inductively heated by pressurized nitrogen gas. Thereafter, the crosslinked polymeric composition can be cooled (e.g., to ambient temperature).

The crosslinking process can create volatile decomposition byproducts in the crosslinked polymeric composition. Following crosslinking, the crosslinked polymeric composition can undergo degassing to remove at least a portion of the volatile decomposition byproducts. Degassing can be performed at a degassing temperature, a degassing pressure, and for a degassing time period to produce a degassed polymeric composition. In various embodiments, the degassing temperature can range from 50 to 150 °C, or from 60 to 80 °C. In an embodiment, the degassing temperature is 65 to 75 °C. Degassing can be conducted under standard atmosphere pressure (i.e., 101,325 Pa).

Coated Conductor

A cable comprising a conductor and an insulation layer can be prepared employing the above-described crosslinkable polymeric composition. "Cable" and "power cable" mean at least one wire or optical fiber within a sheath, e.g., an insulation covering and/or a protective outer jacket. Typically, a cable is two or more wires or optical fibers bound together, typically in a common insulation covering and/or protective jacket. The individual wires or fibers inside the sheath may be bare, covered or insulated. Combination cables may contain both electrical wires and optical fibers. Typical cable designs are illustrated in USP 5,246,783, 6,496,629 and 6,714,707. "Conductor" denotes one or more wire(s) or fiber(s) for conducting heat, light, and/or electricity. The conductor may be a single-wire/fiber or a multi-wire/fiber and may be in strand form or in tubular form. Non-limiting examples of suitable conductors include metals such as silver, gold, copper, carbon, and aluminum. The conductor may also be optical fiber made from either glass or plastic.

Such a cable can be prepared with various types of extruders (e.g., single or twin screw types) by extruding the crosslinkable polymeric composition onto the conductor, either directly or onto an interceding layer. A description of a conventional extruder can be found in USP 4,857,600. An example of co-extrusion and an extruder therefore can be found in USP 5,575,965.

Following extrusion, the extruded cable can pass into a heated cure zone downstream of the extrusion die to aid in crosslinking the crosslinkable polymeric composition and thereby produce a crosslinked polymeric composition. The heated cure zone can be maintained at a temperature in the range of 175 to 260 °C. In an embodiment, the heated cure zone is a

continuous vulcanization ("CV") tube. In various embodiments, the crosslinked polymeric composition can then be cooled and degassed, as discussed above.

Alternating current cables can be prepared according to the present disclosure, which can be low voltage, medium voltage, high voltage, or extra-high voltage cables. Further, direct current cables can be prepared according to the present disclosure, which can include high or extra-high voltage cables.

TEST METHODS

Density

Determine density according to ASTM D792.

Melt Index

Measure melt index, or I_2, in accordance with ASTM D1238, condition 190 °C / 2.16 kg, and report in grams eluted per 10 minutes.

Moving Die Rheometer ("MDR")

Curing behavior is recorded by MDR at 180 °C according to ASTM D5289. Similar tests are conducted at a temperature of 140 °C and 150 °C in order to characterize a scorch time (the time required for the sample to achieve a unit increase in torque). Unless otherwise noted, MH and ML are reported as measured at 180 °C.

Migration

The pellets samples were sealed in a bottle and aged at certain temperature, 23 °C and 60 °C. After aging is complete, weigh 3.000±0.001 g pellet sample and place into a 40-mL vial. Add 14.5 mL of acetonitrile into the vial, seal the vial, and shake in a shaker for 5 minutes. Collect the liquid in the 40-mL vial and place into a 2-mL sample vial for high-pressure liquid chromatography ("HPLC") analysis. Analyze the samples by HPLC according to the following conditions:

LC Parameter	**Details**	
Column	Agilent Extend-C18, 5 μm particle, 4.6 mm x 150 mm	
Column Oven	40 °C	
Flow rate	1.000 mL/min.	
Injection volume	10 μL	
Detector	UV absorbance at 210 nm	
Mobile Phase A	Water	
Mobile Phase B	Acetonitrile	
Time (min.)	**B%**	**Flow Rate (mL/min.)**

0.00	60	1.000
8.00	80	1.000
10.00	95	1.000
12.00	100	1.000
25.00	100	1.000
25.10	60	1.000

The co-agent content in acetonitrile ("ACN") solution is calculated from pre-established calibration curve. A calibration curve is established by plotting UV absorbance response from the HPLC detector against acetonitrile solutions of a certain co-agent at five different concentrations ranging from 2 ppm to 500 ppm, using the conditions in the above table. Then the concentration of a sample co-agent solution can be determined from this pre-established curve. With the known content of co-agent in a sample solution, the migration level from the sample can be back-calculated. The numerical value is given in ppm of total weight of the sample.

Curing

Cured plaques are prepared with 1-mm thickness by the following steps:

1. Preheat the sample at 130°C for 5min.;
2. Release the air trapped in the sample by the operation of plate open/close for 8 times;
3. Allow another 5 minutes to increase the plate temperature to 182°C;
4. Complete the curing under a pressure of 100kN for 15minutes;
5. Allow another 5 minutes to decrease the plate temperature to 45°C.

Mechanical properties

Conduct tensile test at a speed of 500mm/min on Instron5565 according to ASTM D638;

Heat Aging

Age the samples in a UL oven at 150°C for 10 and 14days. Then measure the mechanical property after 24 hours of conditioning at room temperature.

Dissipation Factor

Prepare cured plaques with a thickness of about 0.35 mm according to the curing steps outlined above. Degas the plaques in a vacuum oven for 3 days. Measure the dissipation factor at 60 °C and 1KV by Soken Automated Schering Bridge, DAC-PSC-UA.

MATERIALS

The following materials are employed in the Examples, below.

A first low-density polyethylene ("LDPE") is employed that has a melt index (I_2) of 2 g/10 min. and a density of 0.920 g/cm^3. The LDPE ("LDPE 1") is produced by The Dow Chemical Company, Midland, MI.

A second LDPE ("LDPE 2") employed has a melt index (I_2) of 2 g/10 min. and a density of 0.920 g/cm^3. The LDPE is produced by The Dow Chemical Company, Midland MI, USA. LDPE 2 contains 0.14 wt% Cyanox 1790 (from Cytec Industries), 0.23 wt% distearyl thiodipropionate ("DSTDP") (from Reagens) and 0.008 wt% Cyasorb UV 3346 (from Cytec Industries).

Dicumyl peroxide is commercially available from Shanghai Fangruida Chemicals Co., Ltd.

The ethylene vinyl acetate ("EVA") employed is ELVAX™ 265, which has a vinyl acetate content of 28 weight percent, a density of 0.951 g/cm^3, and a melt index (I_2) of 3 g/10 min. ELVAX™ 265 is commercially available from E. I. du Pont de Nemours and Company, Wilmington, DE, USA.

Stabilizer Preblend is a melt blend of 37:61:2 wt% mixture of Cyanox 1790 (from Cytec Industries), DSTDP (from Reagens) and Cyasorb UV 3346 (from Cytec Industries).

Triallyl isocyanurate ("TAIC") is commercially available from Shanghai Fangruida Chemicals Co., Ltd.

Cyanuric chloride is commercially available from Sinopharm Chemical.

Sodium carbonate is commercially available from Sinopharm Chemical.

1,4-Dioxane is commercially available from Sinopharm Chemical.

Diallylamine is commercially available from Sinopharm Chemical.

Sodium hydroxide is commercially available from Sinopharm Chemical.

EXAMPLES

Coagent Preparation Procedure

Prepare N,N,N',N',N",N"-hexaallyl-1,3,5-triazine-2,4,6-triamine ("HATATA") by adding 3.69 g (0.02 mol) cyanuric acid and 8.90 g (0.064 mol) sodium carbonate into 30 g of 1,4-dioxane in a three-neck flask. While stirring, heat the mixture to 75 °C, and stir for an additional 5 minutes upon reaching 75 °C. Next, gradually add 10.22 g (0.1 mol) diallylamine dropwise over about 15 minutes, then add 2.8 g of sodium hydroxide (0.07 mol) and raise the temperature to about 90 °C. Keep the reaction mixture at 90 °C for 5 hours. Thereafter, cool the

reaction mixture to room temperature and filter using vacuum filtration with a sand-core funnel to remove insoluble salts. The resulting filtrate is distilled under reduced pressure to recover the solvent, and the residue is dissolved in petroleum ether and further purified through silica gel column. This is performed by first transferring the liquid filtrate from the flask to the silica gel column and use 2 mL of petroleum ether to wash the flask and transfer the solution to the silica gel. The silica gel is 300 mesh and is used as the stationary phase; the petroleum ether is used as the eluent.

Sample Compounding

Compounding Procedure 1

Sample S1 and Comparative Samples CS1 and CS2 are prepared according to Compounding Procedure 1. Polyethylene pellets are fed into a Brabender mixer at 125 °C with a rotor speed of 30 rpm to melt the polyethylene. Next, antioxidant, DCP, and the coagents (if present) are added into the mixer respectively. The blend is mixed for 3 minutes. The compound is then pelletized through a single-screw extruder.

Compounding Procedure 2

Comparative Samples CS3-CS8 and S2-S3 are prepared according Compounding Procedure 2. Premix the DCP and coagent at 60 °C for about 20 minutes to form a substantially homogeneous liquid mixture. Inject the DCP/coagent liquid mixture onto the EVA or polyethylene pellets and soak at 70 °C for 8 hours.

Compounding Procedure 3

Samples S4-S7 are prepared according Compounding Procedure 3. Polyethylene pellets, LDPE 1 and LDPE 2 with a certain ratio to achieve certain antioxidant level, are fed into a Brabender single screw extruder at 125 °C for mixing and pelletizing the polyethylene intermediate. Premix the DCP and coagent at 60 °C for about 20 minutes to form a substantially homogeneous liquid mixture. Inject the DCP/coagent liquid mixture onto the polyethylene intermediate pellets and soak at 70 °C for 8 hours.

Example 1 – Comparison of HATATA to TAIC in Polyethylene

Prepare a Sample (S1) and two Comparative Samples (CS1 and CS2) according to the formulations provided in Table 1, below, and using Compounding Procedure 1, described above.

Table 1 – Compositions of S1, CS1, and CS2

Component	CS1	CS2	S1
LDPE 1 (g)	97.94	97.66	96.76

TAIC (g)	-	1.60	-
HATATA (g)	-	-	2.50
DCP (g)	1.70	0.50	0.50
Stabilizer Preblend (g)	0.36	0.24	0.24
Total:	100.00	100.00	100.00

Analyze S1, CS1, and CS2 for curing behavior and coagent migration using the above-described Test Methods. The results are provided in Table 2, below.

Table 2 – Properties of S1, CS1, and CS2

Property	CS1	CS2	S1
ML (dN·m)	0.22	0.17	0.16
MH (dN·m)	4.06	3.87	3.85
MH-ML (dN·m)	3.84	3.70	3.69
ts1@180 °C (min.)	1.16	1.32	1.57
T90@180 °C (min.)	4.41	4.91	5.31
ts1@140 °C (min.)	36.71	55.68	84.50
ts0.5@140 °C (min.)	20.92	35.65	51.54
Migration after storage at 23 °C for 4 weeks (ppm)	N/A	3010	306
Migration after storage at 60 °C for 4 weeks (ppm)	N/A	1831	335
Dissipation factor (%) 1 kV(2.9kv/mm), 60 °C	-	-	0.022

The results from Table 2 show that both TAIC (CS2) and HATATA (S1) achieve comparable curing potential and improved scorch performance. However, of the two, HATATA provides superior scorch performance, as evidenced by the increase of ts1@140 °C from about 55 minutes to about 84 minutes. Additionally, HATATA surprisingly provides much greater coagent migration resistance than TAIC.

Example 2 (comparative) – Effect of HATATA in EVA Matrix

Prepare four Comparative Samples (CS3-CS6) according to the formulations provided in Table 3, below, and using Compounding Procedure 2, described above.

Table 3 – Compositions of CS3-CS6

Component	CS3	CS4	CS5	CS6
EVA (g)	98.30	98.10	98.55	97.15
TAIC (g)	0.40	-	0.95	-
HATATA (g)	-	0.60	-	2.35
DCP (g)	1.30	1.30	0.50	0.50
Total:	100.00	100.00	100.00	100.00

Analyze CS3-CS6 for curing behavior using the above-described Test Methods. The results are provided in Table 4, below.

Table 4 – Curing Properties of CS3-CS6

Property	CS3	CS4	CS5	CS6
Condition: 180 °C, 20 min.				
ML (dN·m)	0.24	0.22	0.19	0.17

MH (dN·m)	7.92	7.26	7.78	7.87
T10 (min.)	0.42	0.41	0.52	0.67
T30 (min.)	0.55	0.53	0.72	0.91
T50 (min.)	0.70	0.67	0.93	1.14
T90 (min.)	2.30	2.14	2.25	2.35
Condition: 150 °C, 15 min.				
ML (dN·m)	0.26	0.25	0.25	0.24
MH (dN·m)	5.76	5.62	5.63	4.78
ts0.5 (min.)	1.96	1.70	3.18	4.65
ts1 (min.)	2.73	2.29	4.432	6.52
T50 (min.)	5.06	4.11	7.79	9.73
T90 (min.)	10.89	9.76	12.96	13.83
Condition: 140 °C, 45 min.				
ML (dN·m)	0.31	0.31	0.31	0.29
MH (dN·m)	6.07	6.15	5.37	4.97
ts0.5 (min.)	4.84	3.58	9.343	13.31
ts1 (min.)	7.14	5.15	13.67	18.37
T50 (min.)	14.46	10.70	24.25	28.42
T90 (min.)	31.78	29.07	39.70	41.28

Looking at the results in Table 4, at higher DCP loading (CS3 and CS4) the HATATA accelerates the curing speed to achieve comparable MH (i.e., the maximum torque value recorded on a vulcanization curve after crosslinking). Additionally, HATATA accelerates curing speed even more at 150 °C compared to TAIC. In fact, at all three different temperatures (140 °C, 150 °C, and 180 °C), HATATA accelerates curing speed compared to TAIC.

Surprisingly, however, at lower DCP loading (CS5 and CS6) TAIC accelerates the premature curing speed at processing temperatures (i.e., 140 and 150 °C) more than HATATA. This indicates inferior scorch resistance by TAIC at lower processing temperatures.

Example 3 – Curing Efficiency and Scorch Performance of HATATA in LDPE

Prepare two Samples (S2 and S3) and two Comparative Samples (CS7 and CS8) according to the formulations provided in Table 5, below, and using Compounding Procedure 2, described above.

Table 5 – Compositions of CS7, CS8, S2, and S3

Component	CS7	S2	CS8	S3
LDPE2 (g)	98.3	98.1	98.55	97.15
TAIC (g)	0.4	-	0.95	-
HATATA (g)	-	0.60	-	2.35
DCP (g)	1.30	1.30	0.50	0.50
Total:	100.00	100.00	100.00	100.00

Analyze CS7, CS8, S2, and S3 for curing behavior and scorch improvement using the above-described Test Methods. The results are provided in Table 6, below.

Table 6 – Properties of CS7, CS8, S2, and S3

Property	CS7	S2	CS8	S3
ML (dN·m)	0.19	0.20	0.18	0.17
MH (dN·m)	3.88	3.89	2.02	2.13
T90@180 °C (min.)	4.20	3.90	5.69	5.93
ts0.5@140 °C (min.)	27.1	29.9	>45	>45
ts1@140 °C (min.)	41.4	45.0	>45	>45

As shown in Table 6, at higher DCP loading, the curing speed of the HATATA-containing sample (S2) is faster than the sample containing TAIC (CS7). Surprisingly, the scorch times at 140 °C for S2 are longer than for CS7, which is the opposite of what one would expect based on the high-DCP-loading EVA samples (CS3 and CS4, above). At lower DCP loadings, HATATA provides comparable curing potential as TAIC (compare CS8 and S3).

Example 4 – Performance of HATATA at Various Loading Levels

Prepare four additional Samples (S4 to S7) according to the formulations provided in Table 7, below, and using Compounding Procedure 3, described above.

Table 7 Compositions of S4 to S7

Component	S4	S5	S6	S7
LDPE 1 (g)	44.35	33.51	58.05	57.93
LDPE 2(g)	53.75	64.34	40.5	40.42
TAIC (g)	0.40	0.45	0.45	0.45
HATATA (g)	1.00	1.00	0.50	0.80
DCP (g)	0.50	0.70	0.50	0.40
Total:	100.00	100.00	100.00	100.00

Analyze S4-S7 for curing behavior and mechanical properties using the above-described Test Methods. The results are provided in Table 8, below.

Table 8 Properties of S4 to S7

Property	S4	S5	S6	S7
ML (dN·m)	0.19	0.19	0.19	0.18
MH (dN·m)	3.23	4.25	3.32	3.01
MH-ML (dN·m)	3.04	4.06	3.13	2.83
ts1@180 °C (min.)	1.52	1.11	1.25	1.58
T90@180 °C (min.)	4.96	4.14	4.16	4.86
ts1@140 °C (min.)	76.39	53.25	53.09	72.11
ts0.5@140 °C (min.)	46.45	33.96	34.25	45.00
Migration after storage at 23 °C for 4 weeks (ppm),	190/221*	351/366*	214/74*	N/A
TE, %, initial	477.4	470.7	503.1	528.4
std	22.7	18.2	31.3	15.9
TS, MPa, initial	19.6	21.2	19.1	20.4
std	2	2.14	1.8	0.9
TE, %, aged at 150 °C for 10days	486.6	480.7	542.3	538.3
std	30.1	15.4	40.4	10.8
TS, MPa, aged at 150 °C for 10days	19.6	21.2	21.3	21.5
std	1.8	0.4	2.3	1.0

TE Retention, aged at 150 °C for 10days	101.9%	102.1%	107.8%	101.9%
TS Retention, aged at 150 °C for 10days	100.0%	100.1%	111.7%	105.5%
TE, %, aged at 150 °C for 14days	474.2	455.2	547.4	545.9
Std	31.1	44.1	15.6	27.7
TS, MPa, aged at 150 °C for 14days	19.1	19.1	21.6	21.1
Std	1.4	2.5	0.9	1.3
TE retention, aged at 150 °C for 14days	99.3%	96.7%	108.8%	103.3%
TS Retention, aged at 150 °C for 14days	97.5%	90.3%	113.3%	103.2%

*TAIC/HATATA

CLAIMS

1. A crosslinkable polymeric composition, comprising:

(a) a thermoplastic, non-elastomer ethylene-based polymer;

(b) an organic peroxide; and

(c) a crosslinking coagent comprising N,N,N',N',N",N"-hexaallyl-1,3,5-triazine-2,4,6-triamine.

2. The crosslinkable polymeric composition of claim 1, wherein said ethylene-based polymer is non-polar.

3. The crosslinkable polymeric composition of claim 2, wherein said ethylene-based polymer has no fluoromonomers incorporated therein.

4. The crosslinkable polymeric composition of any one of the foregoing claims, wherein said N,N,N',N',N",N"-hexaallyl-1,3,5-triazine-2,4,6-triamine and said organic peroxide are present in a coagent-to-peroxide weight ratio of greater than 1:1.

5. The crosslinkable polymeric composition of any one of the foregoing claims, wherein said ethylene-based polymer comprises a high-pressure low-density polyethylene; wherein said organic peroxide comprises dicumyl peroxide; wherein said crosslinkable polymeric composition further comprises one or more antioxidants.

6. The crosslinkable polymeric composition of any one of the foregoing claims, wherein said ethylene-based polymer is present in an amount ranging from 50 to 99 weight percent, based on the entire crosslinkable polymeric composition weight; wherein said organic peroxide is present in an amount of less than 1.2 weight percent, based on the entire crosslinkable polymeric composition weight; wherein said crosslinking coagent is present in an amount ranging from 0.01 to 15 weight percent, based on the entire crosslinkable polymeric composition weight.

7. The crosslinkable polymeric composition of any one of the foregoing claims, wherein said N,N,N',N',N",N"-hexaallyl-1,3,5-triazine-2,4,6-triamine constitutes at least 1 weight percent of the total amount of said crosslinking coagent, based on the total weight of said crosslinking coagent.

8. The crosslinkable polymeric composition of any one of the foregoing claims, wherein said crosslinkable polymeric composition exhibits a crosslinking coagent migration to the surface of said crosslinkable polymeric composition of less than 1,000 parts per million when stored for 4 weeks at 23 °C and 1 atm.

9. A crosslinked article prepared from the crosslinkable polymeric composition according to any one of the foregoing claims.

10. A coated conductor, comprising:

a conductive core; and

a polymeric layer at least partially surrounding said conductive core, wherein at least a portion of said polymeric layer comprises said crosslinked article of claim 9.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2014/074376

A. CLASSIFICATION OF SUBJECT MATTER

C08L 23/06(2006.01)i; C08L 23/08(2006.01)i; C08K 5/3492(2006.01)i; C08K 5/14(2006.01)i; C08J 3/24(2006.01)i

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; C08K; C08J

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)

CNABS;VEN;CNKI;万方;CA on web:hexaallyl, diallylamine, triazine, hexaallylmelamine, melamine, ethylene, ethene, polyethylene, polyethene, HATATA, crosslink, cure, harden, 2830-12-8

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2011162634 A (NIPPON KASEI CHEM) 25 August 2011 (2011-08-25) see description paragraphs 9,15-18,22,28,32	1-10
X	WO 2011096477 A1 (NIPPON KASEI CHEM ET AL.) 11 August 2011 (2011-08-11) see example 1	1,4,6-10
A	US 2011147041 A1 (SENGUPTA SAURAV S ET AL.) 23 June 2011 (2011-06-23) see the whole document	1-10
A	WO 2012049093 A1 (SOLVAY SPECIALTY POLYMERS IT ET AL.) 19 April 2012 (2012-04-19) see the whole document	1-10
A	US 2004014900 A1 (3M INNOVATIVE PROPERTIES CO) 22 January 2004 (2004-01-22) see the whole document	1-10
A	CN 1749303 A (SHANGHAI FUNCTIONAL POLYMER MATERIAL RES) 22 March 2006 (2006-03-22) see the whole document	1-10

☐ 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	Date of mailing of the international search report
22 December 2014	**31 December 2014**

Name and mailing address of the ISA/CN	Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA(ISA/CN) **6,Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088 China**	**WANG,Jinfeng**
Facsimile No. **(86-10)62019451**	Telephone No. **(86-10)62084498**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2014/074376

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
JP	2011162634	A	25 August 2011		Non	e	
WO	2011096477	A1	11 August 2011	EP	2535371	A4	17 July 2013
				JP	2011178993	A	15 September 2011
				EP	2535371	A1	19 December 2012
				KR	20120115975	A	19 October 2012
				US	2013053520	A1	28 February 2013
				TW	201202326	A	16 January 2012
				CN	102753614	A	24 October 2012
US	2011147041	A1	23 June 2011	KR	20120097542	A	04 September 2012
				JP	2013515134	A	02 May 2013
				MX	2012007319	A	08 March 2013
				CA	2784871	A1	14 July 2011
				US	8455580	B2	04 June 2013
				WO	2011084219	A2	14 July 2011
				CN	102762651	B	21 May 2014
				EP	2765158	A1	13 August 2014
				WO	2011084219	A3	06 October 2011
				CN	102762651	A	31 October 2012
				EP	2516544	A2	31 October 2012
				TW	201139542	A	16 November 2011
WO	2012049093	A1	19 April 2012	CN	103282392	A	04 September 2013
				EP	2627683	A1	21 August 2013
				JP	2013539807	A	28 October 2013
				US	2013197163	A1	01 August 2013
				EP	2627683	B1	13 August 2014
US	2004014900	A1	22 January 2004	CN	1297577	C	31 January 2007
				AU	2003232114	A1	09 February 2004
				JP	2005533162	A	04 November 2005
				WO	2004009660	A1	29 January 2004
				RU	2005101073	A	20 January 2006
				KR	101005244	B1	04 January 2011
				US	6803435	B2	12 October 2004
				DE	60317530	T2	18 September 2008
				EP	1539844	B1	14 November 2007
				RU	2326907	C2	20 June 2008
				KR	20050030629	A	30 March 2005
				JP	2010242105	A	28 October 2010
				AT	378359	T	15 November 2007
				CN	1668658	A	14 September 2005
				DE	60317530	D1	27 December 2007
				EP	1539844	A1	15 June 2005
CN	1749303	A	22 March 2006	CN	100398595	C	02 July 2008