

(19)



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European Patent Office
Office européen des brevets



(11)

EP 0 735 545 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
16.06.1999 Bulletin 1999/24

(51) Int Cl.⁶: **H01B 7/28, H01B 3/44**

(21) Application number: **96301806.4**

(22) Date of filing: **15.03.1996**

(54) **Tree resistant cable**

Gegen Dendritenbildung widerstandsfähiges Kabel

Câble résistant aux arborescences

(84) Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL
PT SE**

(30) Priority: **30.03.1995 US 413236**

(43) Date of publication of application:
02.10.1996 Bulletin 1996/40

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Description**Technical Field**

5 [0001] This invention relates to electric power cable insulated with a polyethylene composition having an improved resistance to water trees.

Background Information

10 [0002] A typical electric power cable generally comprises one or more conductors in a cable core that is surrounded by several layers of polymeric material that include a first semiconducting shield layer, an insulating layer, a second semiconducting shield layer, a metallic tape or wire shield, and a jacket.

[0003] These insulated cables are known to suffer from shortened life when installed in an environment where the insulation is exposed to water, e.g., underground or locations of high humidity. The shortened life has been attributed to the formation of water trees, which occur when an organic polymeric material is subjected to an electrical field over a long period of time in the presence of water in liquid or vapor form. The net result is a reduction in the dielectric strength of the insulation.

[0004] Many solutions have been proposed for increasing the resistance of organic insulating materials to degradation by water treeing. The most recent solutions involve the addition of polyethylene glycol, as a water tree growth inhibitor, to a heterogeneous low density polyethylene such as described in United States Patents 4,305,849; 4,612,139; and 4,812, 505. Another solution is the use of a homogeneous polyethylene per se as the organic insulating material, i.e., without the addition of a water tree growth inhibitor. See United States Patent 5,246,783. Both of these solutions appear to be steps in the right direction, but there is a continuous industrial demand for improvement partially because power cable is increasingly exposed to harsher environments, and partially because consumers are more concerned with cable longevity, e.g., a service life of 30 to 40 years.

Disclosure of the Invention

[0005] An object of this invention, therefore, is to provide an insulated cable which exhibits a much improved resistance to water trees. Other objects and advantages will become apparent hereinafter.

[0006] According to the invention, an insulated cable has been discovered which meets the above object.

[0007] The cable comprises one or more electrical conductors, each, or a core of one or more electrical conductors, surrounded by an insulating composition comprising

- 35 (i) a homogeneous polyethylene having a polydispersity in the range of about 1.5 to about 3.5 and an essentially uniform comonomer distribution; and, based on 100 parts by weight of component (i),
 (ii) about 0.1 to about 20 parts by weight of a polyethylene glycol having a molecular weight in the range of about 1000 to about 30,000.

Description of the Preferred Embodiment(s)

[0008] Homogeneous polyethylenes are copolymers of ethylene, one or more alpha-olefins, and, optionally, a diene. The alpha-olefins can have 3 to 12 carbon atoms, and preferably have 3 to 8 carbon atoms. Examples of the alpha-olefins are propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. As noted above, they have a polydispersity (Mw/Mn) in the range of about 1.5 to about 3.5 and an essentially uniform comonomer distribution. The homogeneous polyethylenes are characterized by single and relatively low DSC melting points. Heterogeneous polyethylenes (the more common of the two), on the other hand, have a polydispersity (Mw/Mn) greater than 3.5 and do not have a uniform comonomer distribution. Mw is defined as weight average molecular weight and Mn is defined as number average molecular weight. The homogeneous polyethylenes can have a density in the range of 0.86 to 0.93 gram per cubic centimeter, and preferably have a density in the range of 0.87 to about 0.92 gram per cubic centimeter. They also can have a melt index in the range of about 0.5 to about 30 grams per 10 minutes, and preferably have a melt index in the range of about 0.5 to about 5 grams per 10 minutes.

[0009] Homogeneous polyethylenes can be prepared, for example, with vanadium based catalysts such as those described in United States Patents 5,332,793 and 5,342,907, and they can also be prepared with single site metallocene catalysts such as those described in United States Patents 4,937,299 and 5,317,036.

[0010] Generally, the polyethylene glycol is defined by its molecular weight, which can be in the range of about 1000 to about 30,000, and is preferably in the range of about 5000 to about 25,000. The optimum molecular weight is 20,000. Polyethylene glycol is a polar compound, which can be represented by the formulas $\text{HOCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{OH}$ or

$\text{HO}(\text{C}_2\text{H}_4\text{O})_n\text{H}$ wherein, for example, n can be 225 to 680. This translates into a molecular weight in the range of about 10,000 to about 30,000. The amount of polyethylene glycol that can be in the insulating composition can be in the range of about 0.1 to about 20 parts weight based on 100 parts by weight of the polyethylene component, and is preferably in the range of about 0.1 to about 1 part by weight.

[0011] Conventional additives, which can be introduced into the polyethylene formulation, are exemplified by anti-oxidants, coupling agents, ultraviolet absorbers or stabilizers, antistatic agents, pigments, dyes, nucleating agents, reinforcing fillers or polymer additives, slip agents, plasticizers, processing aids, lubricants, viscosity control agents, tackifiers, anti-blocking agents, surfactants, extender oils, metal deactivators, voltage stabilizers, flame retardant fillers and additives, crosslinking agents, boosters, and catalysts, and smoke suppressants. Fillers and additives can be added in amounts ranging from less than about 0.1 to more than about 200 parts by weight for each 100 parts by weight of the base resin, in this case, polyethylene.

[0012] Examples of antioxidants are: hindered phenols such as tetrakis[methylene(3,5-di-tert-butyl-4-hydroxyhydrocinamate)]methane, bis[(beta-(3,5-ditert-butyl-4-hydroxybenzyl)-methylcarboxyethyl)]sulphide, 4,4'-thiobis(2-methyl-6-tert-butylphenol), 4,4'-thiobis(2-tert-butyl-5-methylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), and thiodiethylene bis(3,5-di-tert-butyl-4-hydroxy)hydrocinamate; phosphites and phosphonites such as tris(2,4-di-tert-butylphenyl)phosphite and di-tert-butylphenylphosphonite; thio compounds such as dilaurylthiodipropionate, dimyristylthiodipropionate, and distearylthiodipropionate; various siloxanes; and various amines such as polymerized 2,2,4-trimethyl-1,2-dihydroquinoline. Antioxidants can be used in amounts of about 0.1 to about 5 parts by weight per 100 parts by weight of polyethylene.

[0013] The resin can be crosslinked by adding a crosslinking agent to the composition or by making the resin hydrolyzable, which is accomplished by adding hydrolyzable groups such as $-\text{Si}(\text{OR})_3$ wherein R is a hydrocarbyl radical to the resin structure through copolymerization or grafting.

[0014] Suitable crosslinking agents are organic peroxides such as dicumyl peroxide; 2,5-dimethyl-2,5-di(t-butylperoxy)hexane; t-butyl cumyl peroxide; and 2,5-dimethyl-2,5-di(t-butylperoxy)hexane-3. Dicumyl peroxide is preferred.

[0015] Hydrolyzable groups can be added, for example, by copolymerizing ethylene with an ethylenically unsaturated compound having one or more $-\text{Si}(\text{OR})_3$ groups such as vinyltrimethoxy silane, vinyltriethoxysilane, and gamma-methacryloxypropyltrimethoxysilane or grafting these silane compounds to the resin in the presence of the aforementioned organic peroxides. The hydrolyzable resins are then crosslinked by moisture in the presence of a silanol condensation catalyst such as dibutyltin dilaurate, dioctyltin maleate, dibutyltin diacetate, stannous acetate, lead naphthenate, and zinc caprylate. Dibutyltin dilaurate is preferred.

[0016] Examples of hydrolyzable copolymers and hydrolyzable grafted copolymers are ethylene/vinyltrimethoxy silane copolymer, ethylene/gamma-methacryloxypropyltrimethoxy silane copolymer, vinyltrimethoxy silane grafted ethylene/ethyl acrylate copolymer, vinyltrimethoxy silane grafted linear low density ethylene/1-butene copolymer, and vinyltrimethoxy silane grafted low density polyethylene.

[0017] The cable of the invention can be prepared in various types of extruders, e.g., single or twin screw types. Compounding can be effected in the extruder or prior to extrusion in a conventional mixer such as a Brabender™ mixer or a Banbury™ mixer. A description of a conventional extruder can be found in United States patent 4,857,600. A typical extruder has a hopper at its upstream end and a die at its downstream end. The hopper feeds into a barrel, which contains a screw. At the downstream end, between the end of the screw and the die, is a screen pack and a breaker plate. The screw portion of the extruder is considered to be divided up into three sections, the feed section, the compression section, and the metering section, and two zones, the back heat zone and the front heat zone, the sections and zones running from upstream to downstream. In the alternative, there can be multiple heating zones (more than two) along the axis running from upstream to downstream. If it has more than one barrel, the barrels are connected in series. The length to diameter ratio of each barrel is in the range of about 15:1 to about 30:1. In wire coating, where the material is crosslinked after extrusion, the die of the crosshead feeds directly into a heating zone, and this zone can be maintained at a temperature in the range of about 130°C to about 260°C, and preferably in the range of about 170°C to about 220°C. The advantage of the invention lies in the much improved water tree growth rate. The patents mentioned in this specification are incorporated by reference herein. The invention is illustrated by the following examples.

Examples 1 to 8

[0018] The resistance of insulating compositions to water treeing is determined by the method described in United States Patent 4,144,202. This measurement leads to a value for water tree resistance relative to a standard polyethylene insulating material. The term used for the value is "water tree growth rate" (WTGR). From experience in laboratory tests of materials and for accelerated tests of cables, it has been established that the value for WTGR should be equal to or less than about 20 percent, preferably 10 percent, of the standard to provide a useful improvement in cable performance, i.e., in the life of a cable, which is in service and in contact with water during the period of the service.

[0019] Parts are by weight.

[0020] 100 parts of each of the polyethylenes described below are compounded with 0.61 part of polyethylene glycol (PEG) having a molecular weight of 20,000 (if the PEG is used); 0.76 part of p-oriented styrenated diphenylamine; and 0.4 part of vinyl modified polydimethyl siloxane in a two roll mill operating at 24 revolutions per minute (rpm) on the front roll and 36 rpm on the back roll and a temperature of 125 to 130 degrees C on the two rolls for a period of time (minutes). The procedure involves preheating the resin to 70 degrees C in an oven; fluxing the resin as quickly as possible on the two roll mill (about 3 to 4 minutes); adding all of the non-peroxide additives and fluxing for an additional 3 to 4 minutes; and then adding the peroxide and fluxing, peeling, and folding until well mixed. Sufficient dicumyl peroxide is introduced into each composition to provide an oscillating disk rheometer (5 degree arc at 182,2°C (360 degrees F)) reading of 5,42 Nm (48 inch-pound). Each composition is then removed from the two roll mill as a crepe and diced and molded into one inch discs which are 0,64 cm (0.25 inch) thick in a press in two steps:

	initial step	final step
pressure N/m ² (psi)	low	high
temperature (°C)	120	175
residence time (minutes)	9	15 to 20

Each plaque is tested for WTGR and the results compared with a control polyethylene composition, which exhibits 100 percent WTGR. Variables and results are set forth in the following Table:

Table

Example	polyethylene	PEG incorporated?	WTGR (percent) *
1	A	No	40.5
2	A	Yes	16.4
3	B	No	81.0
4	B	Yes	6.2
5	C	No	179.2
6	C	Yes	12.5
7	D	No	68.5
8	D	Yes	10.8

*The lower value reflects the improved WTGR in the examples in which the PEG is incorporated.

[0021] A description of the polyethylenes follows (each polyethylene is prepared with a single site metallocene catalyst):

[0022] A = a copolymer of ethylene and 1-octene having an Mw/Mn ratio of about 2; a narrow comonomer distribution; 9.5 percent by weight 1-octene; a melt index of 3.5 grams per 10 minutes; and a density of 0.910 gram per cubic centimeter.

[0023] B = a copolymer of ethylene and 1-octene having an Mw/Mn ratio of about 2; a narrow comonomer distribution; 12 percent by weight 1-octene; a melt index of 1 gram per 10 minutes; and a density of 0.902 gram per cubic centimeter.

[0024] C = a copolymer of ethylene and 1-octene having an Mw/Mn ratio of about 2; a narrow comonomer distribution; 24 percent by weight 1-octene; a melt index of 1 gram per 10 minutes; and a density of 0.870 gram per cubic centimeter.

[0025] D = a copolymer of ethylene and 1-octene having an Mw/Mn ratio of about 2; a narrow comonomer distribution; 24 percent by weight 1-octene; a melt index of 5 grams per 10 minutes; and a density of 0.870 gram per cubic centimeter.

Claims

1. A cable comprising one or more electrical conductors, each, or a core of electrical conductors, surrounded by an insulating composition comprising (i) a homogeneous polyethylene having a polydispersity in the range of 1.5 to 3.5 and an essentially uniform comonomer distribution; and, based on 100 parts by weight of component (i), (ii) 0.1 to 20 parts by weight of a polyethylene glycol having a molecular weight in the range of 1000 to about 30,000.

2. The cable defined in claim 1 wherein the polyethylene is a copolymer of ethylene, one or more alpha-olefins, each

having 3 to 12 carbon atoms, and, optionally, a diene.

3. The cable defined in claim 1 wherein the polyethylene is made with a single site metallocene based catalyst.

4. The cable defined in claim 1 wherein the polyethylene has a density in the range of 0.86 to 0.93 gram per cubic centimeter and a melt index in the range of 0.5 to 30 grams per 10 minutes.

5. The cable defined in claim 1 wherein the alpha-olefin is 1-butene, 1-hexene, 4-methyl-1-pentene, or 1-octene.

6. The cable defined in claim 1 wherein the polyethylene glycol has a molecular weight in the range of 5000 to 25,000.

7. The cable defined in claim 1 wherein the polyethylene glycol is present in an amount of 0.1 to 1 part by weight.

8. The cable defined in claim 1, wherein the insulating composition comprises :

(i) a homogeneous copolymer of a mixture comprising ethylene and one or more alpha-olefins, each having 3 to 8 carbon atoms, said copolymer having a polydispersity in the range of 1.5 to 3.5; an essentially uniform comonomer distribution; a density in the range of 0.87 to 0.92 gram per cubic centimeter; and a melt index in the range of 0.5 to 5 grams per 10 minutes, said copolymer having been prepared with a single site metallocene based catalyst; and, based on 100 parts by weight of component (i),

(ii) 0.1 to 1 part by weight of a polyethylene glycol having a molecular weight in the range of 5000 to 25,000.

Patentansprüche

1. Kabel, umfassend einen oder mehrere elektrische Leiter, von denen jeder oder eine Seele aus elektrischen Leitern von einer isolierenden Zusammensetzung umgeben ist, welche umfaßt (i) ein homogenes Polyethylen mit einer Polydispersität im Bereich von 1,5 bis 3,5 und einer im wesentlichen gleichmäßigen Comonomer-Verteilung; und, bezogen auf 100 Gewichtsteile der Komponente (i), (ii) 0,1 bis 20 Gewichtsteile eines Polyethylenglycols mit einem Molekulargewicht im Bereich von 1000 bis etwa 30000.

2. Kabel nach Anspruch 1, in welchem das Polyethylen ein Copolymer von Ethylen, einem oder mehreren alpha-Olefinen, von denen jedes 3 bis 12 Kohlenstoffatome aufweist, und gegebenenfalls einem Dien ist.

3. Kabel nach Anspruch 1, in welchem das Polyethylen mit einem Einzelstellen-Katalysator auf Metallocen-Basis hergestellt ist.

4. Kabel nach Anspruch 1, in welchem das Polyethylen eine Dichte im Bereich von 0,86 bis 0,93 Gramm pro Kubikzentimeter und einen Schmelzindex im Bereich von 0,5 bis 30 Gramm pro 10 Minuten aufweist.

5. Kabel nach Anspruch 1, in welchem das alpha-Olefin 1-Buten, 1-Hexen, 4-Methyl-1-penten oder 1-Octen ist.

6. Kabel nach Anspruch 1, in welchem das Polyethylenglycol ein Molekulargewicht im Bereich von 5000 bis 25000 aufweist.

7. Kabel nach Anspruch 1, in welchem das Polyethylenglycol in einer Menge von 0,1 bis 1 Gewichtsteil anwesend ist.

8. Kabel nach Anspruch 1, in welchem die isolierende Zusammensetzung umfaßt:

(i) eine homogenes Copolymer einer Mischung, die Ethylen und ein oder mehrere alpha-Olefine mit jeweils 3 bis 8 Kohlenstoffatomen umfaßt, wobei das Copolymer eine Polydispersität im Bereich von 1,5 bis 3,5; eine im wesentliche gleichmäßige Comonomer-Verteilung; eine Dichte im Bereich von 0,87 bis 0,92 Gramm pro Kubikzentimeter; und einen Schmelzindex im Bereich von 0,5 bis 5 Gramm pro 10 Minuten aufweist; wobei das Copolymer hergestellt wurde mit einem Einzelstellen-Katalysator auf Metallocen-Basis; und, bezogen auf 100 Gewichtsteile der Komponente (i),

(ii) 0,1 bis 1 Gewichtsteil eines Polyethylenglycols mit einem Molekulargewicht im Bereich von 5000 bis 25000.

Revendications

1. Câble comprenant un ou plusieurs conducteurs électriques dont chacun, ou dont une âme de conducteurs électriques, est entouré par une composition isolante comprenant (i) un polyéthylène homogène ayant une polydispersité comprise entre 1,5 et 3,5 et une distribution sensiblement homogène des comonomères ; et, pour 100 parties en poids de composant (i), (ii) de 0,1 à 20 parties en poids d'un polyéthylèneglycol ayant un poids moléculaire compris entre 1000 et environ 30 000.
2. Câble selon la revendication 1, dans lequel le polyéthylène est un copolymère d'éthylène, d'une ou plusieurs alpha-oléfinés ayant chacune de 3 à 12 atomes de carbone et éventuellement d'un diène.
3. Câble selon la revendication 1, dans lequel le polyéthylène est préparé avec un catalyseur à base de métallocène à site unique.
4. Câble selon la revendication 1, dans lequel le polyéthylène a une densité comprise entre 0,86 et 0,93 gramme par centimètre cube et un indice de fusion compris entre 0,5 et 30 grammes par 10 minutes.
5. Câble selon la revendication 1, dans lequel l'alpha-oléfine est le 1-butène, le 1-hexène, le 4-méthyl-1-pentène ou le 1-octène.
6. Câble selon la revendication 1, dans lequel le polyéthylèneglycol a un poids moléculaire compris entre 5000 et 25 000.
7. Câble selon la revendication 1, dans lequel le polyéthylèneglycol est présent en une quantité de 0,1 à 1 partie en poids.
8. Câble selon la revendication 1, dans lequel la composition isolante comprend :
 - (i) un copolymère homogène formé d'un mélange comprenant de l'éthylène et une ou plusieurs alpha-oléfinés ayant chacune de 3 à 8 atomes de carbone, ledit copolymère ayant une polydispersité comprise entre 1,5 et 3,5, une distribution sensiblement homogène des comonomères, une densité comprise entre 0,87 et 0,92 gramme par centimètre cube et un indice de fusion compris entre 0,5 et 5 grammes pour 10 minutes, ledit copolymère étant préparé avec un catalyseur à base de métallocène à site unique ; et, pour 100 parties en poids de composant (i),
 - (ii) de 0,1 à 1 partie en poids d'un polyéthylèneglycol ayant un poids moléculaire compris entre 5000 et 25 000.