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(54) Title: TREE RESISTANT CABLE INSULATION

(57) Abstract: A polyethylene composition comprising: (i) a homopolymer of ethylene made by a high pressure process, and, based on 100 parts by weight of component (i), (ii) 5 to 20 parts by weight of an elastomer; and (iii) 0.05 to 1 part by weight of a polyethylene glycol having a molecular weight in the range of 1000 to 100,000.

TREE RESISTANT CABLE INSULATION

This invention relates to electric power cable insulated with a polyethylene composition having an improved resistance to water trees and improved flexibility.

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

 These insulated cables are known to suffer from shortened life when
10 installed in an environment where the insulation is exposed to water, for example, 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 formation of water trees is
15 believed to be caused by a complex interaction of the AC electrical field, moisture, time, and the presence of ions. The net result is a reduction in the dielectric strength of the insulation.

 Many solutions have been proposed for increasing the resistance of organic insulating materials to degradation by water treeing. One solution
20 involves the addition of polyethylene glycol, as a water tree growth inhibitor, to a low density polyethylene such as described in United States Patents 4,305,849; 4,612,139; and 4,812, 505. This solution has been successfully applied for many years, but there is a continuous industrial demand for improvement in water tree resistance particularly in combination with
25 improved flexibility partially because power cable is increasingly exposed to harsher environments, and partially because consumers are more concerned with cable longevity, for example, a service life of 40 to 50 years.

 An object of this invention, therefore, is to provide a polyethylene composition useful as the insulating layer for a power cable, the insulating
30 layer of which exhibits an improved resistance to water trees together with improved flexibility. Other objects and advantages will become apparent hereinafter.

According to the invention, a polyethylene composition has been discovered which meets the above object.

The polyethylene composition comprises:

- (i) a homopolymer of ethylene made by a high pressure process, and,
5 based on 100 parts by weight of component (i),
- (ii) 5 to 20 parts by weight of an elastomer; and
- (iii) 0.05 to 1 part by weight of a polyethylene glycol having a molecular weight in the range of 1000 to 100,000.

Component (i) is a homopolymer of ethylene made by a conventional
10 high pressure process. These high pressure processes are typically run at pressures above 15,000 psi (pounds per square inch). The homopolymer can have a density in the range of 0.860 to 0.940 gram per cubic centimeter, and preferably has a density in the range of 0.915 to 0.930 gram per cubic
15 centimeter. The homopolymer can also have a melt index in the range of 1 to 5 grams per 10 minutes, and preferably has a melt index in the range of 0.75 to 3 grams per 10 minutes. Melt index is determined under ASTM D-1238, Condition E. It is measured at 190 degrees C and 2160 grams. It is not an elastomer.

Component (ii) is an elastomer, which is defined as a flexible
20 homopolymer or copolymer of two or more comonomers having a density in the range of 0.860 to 0.915 gram per cubic centimeter and a crystallinity of 0 percent to 25 percent. Many of these polymers are essentially amorphous, that is, having 0 percent crystallinity. The elastomer can be present in an amount of 5 to 20 parts by weight based on 100 parts by weight of component (i), and is
25 preferably present in an amount of 5 to 15 parts by weight. Generally, the elastomers can be prepared under low pressure in the gas phase in a fluidized bed. Examples of useful elastomers are as follows: IR (polyisoprene); BR (polybutadiene); SBR (butadiene copolymerized with styrene); nitrile rubbers (butadiene copolymerized with acrylonitrile); butyl rubbers (isobutylene
30 copolymerized with isoprene); EPM (polymer of ethylene copolymerized with propylene); EPDM (ethylene copolymerized with propylene and a diene such as hexadiene, dicyclopentadiene, or ethylidene norbornene); VLDPE (copolymers of

ethylene and a C₃-C₁₂ alpha-olefin having densities up to 0.915 gram per cubic centimeter); terpolymers of ethylene, an alpha olefin (C₃-C₁₂), and a diene (preferably non-conjugated); neoprene (polychloroprene); silicone (polydimethyl siloxane); copolymers of ethylene and vinyltrimethoxy silane; copolymers of
5 ethylene and one or more of acrylonitrile, maleic acid esters, vinyl acetate (EVA), and acrylic (EEA) and methacrylic acid esters (these are generally made by high pressure processes); copolymers of butadiene and isoprene; polystyrene; terpolymers of styrene, butadiene, and isoprene; chlorobutyl rubbers (chlorinated copolymer of isobutylene and isoprene); bromobutyl rubbers
10 (brominated copolymer of isobutylene and isoprene); and brominated copolymer of isobutylene and paramethylstyrene. Ethylene-propylene rubbers (EPM), ethylene-propylene-diene rubbers (EPDM), ethylene-ethyl acrylate (EEA), polyisoprene, polybutadiene, and poly(styrene-butadiene) rubber are preferred. Most preferred are EPM and EPDM, particularly the most amorphous. Some
15 specific examples can be found in the Examples.

Generally, the polyethylene glycol is defined by its molecular weight (weight average molecular weight), which can be in the range of 1000 to 100,000, and is preferably in the range of 5000 to 30,000. The optimum molecular weight is 20,000 (prior to processing). It will be understood by those
20 skilled in the art that processing the polyethylene glycol reduces its molecular weight by one third to one half. Polyethylene glycol is a polar compound, which can be represented by the formulas HOCH₂(CH₂OCH₂)_nCH₂OH or HO(C₂H₄O)_nH wherein, for example, n can be 225 to 680. This translates into a molecular weight in the range of 10,000 to 30,000. The amount of
25 polyethylene glycol that can be in the insulating composition can be in the range of 0.05 to 1 part weight based on 100 parts by weight of component (i), and is preferably in the range of 0.3 to 0.6 part by weight.

Conventional additives, which can be introduced into the formulation, are exemplified by antioxidants, coupling agents, ultraviolet absorbers or
30 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 0.1 to 5
5 parts by weight for additives other than fillers to more than 200 parts by weight for fillers, all for each 100 parts by weight of the base resin, in this case, a homopolymer of ethylene.

Examples of antioxidants are: hindered phenols such as tetrakis[methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]methane,
10 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)hydrocinnamate; phosphites and phosphonites such as tris(2,4-di-tert-butylphenyl)phosphite and di-tert-butylphenyl-phosphonite; thio
15 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 0.1 to 5 parts by weight per 100 parts by weight of the ethylene homopolymer.

20 The resins, that is, components (i) and (ii), 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 hydrocarbonyl radical to the resin structure through copolymerization or grafting. Crosslinking by irradiation can also be used if desired.

25 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.

Hydrolyzable groups can be added, for example, by copolymerizing ethylene with an ethylenically unsaturated compound having one or more -
30 $\text{Si}(\text{OR})_3$ 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.

5 Dibutyltin dilaurate is preferred.

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
10 density ethylene/1-butene copolymer, and vinyltrimethoxy silane grafted low density polyethylene.

The cable using the polyethylene composition of the invention can be prepared in various types of extruders, for example, single or twin screw types. Compounding can be effected in the extruder or prior to extrusion in a
15 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
20 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
25 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 15:1 to 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 130°C to 260°C,
30 and preferably in the range of 170°C to 220°C.

The advantages of the invention lie in the improved water tree growth rate and flexibility, and in the use of less polyethylene glycol and organic

peroxide. The use of the polyethylene composition of the invention can also result in longer screen pack life, ability to use finer screen packs, reduced tooling plate-out, avoidance of sweat-out problems, less contamination, increased cable run lengths, and lower additive costs. Expensive silane cure
5 boosters can also be avoided.

The term "surrounded" as it applies to a substrate being surrounded by an insulating composition, jacketing material, or other cable layer is considered to include extruding around the substrate; coating the substrate; or wrapping around the substrate as is well known by those skilled in the art. The substrate
10 can include, for example, a core including a conductor or a bundle of conductors, or various underlying cable layers as noted above.

All molecular weights mentioned in this specification are weight average molecular weights unless otherwise designated.

The patents mentioned in this specification are herein.

15 The invention is illustrated by the following examples.

Examples 1 to 15

The resistance of insulating compositions to water treeing was measured in terms of water tree length (WTL) described in United States
20 Patent 4,144,202. This measurement leads to a value for water tree length relative to a standard tree retardant crosslinked polyethylene insulating material. From experience in laboratory tests of materials and for accelerated tests of cables, it has been established that the value for relative WTL should be equal to or less than the 100 percent control to provide a useful improvement
25 in cable performance, that is, in the life of a cable, which was in service and in contact with water during the period of the service. The examples simulate an insulating layer, which would be used in a cable construction.

Each formulation contains 100 parts by weight of an ethylene homopolymer. The formulation also contains an elastomer.

30 The homopolymer and the elastomer are compounded with polyethylene glycol (PEG) 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 10 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 (3 to 4 minutes); adding all of the non-peroxide additives and fluxing for 5 minutes; and then adding the peroxide at a temperature of less than 140 degrees C and fluxing, peeling, and folding until well mixed. Sufficient dicumyl peroxide was introduced into each composition to provide an oscillating disk rheometer (5 degree arc at 360 degrees F) reading of 46 inch-pound. Each composition was then removed from the two roll mill as a crepe and diced and molded into one inch discs which are 0.25 inch thick in a press in two steps:

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

Each plaque was tested for relative WTL and the results compared with a control tree retardant crosslinked polyethylene composition, which exhibits 100 percent WTL. All the formulations contain antioxidant and peroxide. Further, pph = parts by weight per 100 parts by weight of ethylene homopolymer (all examples). In these examples, the relative WTL effect of 4 elastomers on a crosslinked high pressure low density homopolymer of ethylene containing 0.6 part by weight PEG was demonstrated.

The components of the formulations are as follows:

Homopolymer = a homopolymer of ethylene having a density of 0.92 gram per cubic centimeter and a melt index of 2 grams per 10 minutes, said homopolymer being prepared by a conventional high pressure process.

PEG = a polyethylene glycol having a molecular weight of 20,000.

Elastomer A = a semicrystalline hydrocarbon rubber copolymer containing 72 weight percent ethylene; 22 weight percent propylene; and 6

weight percent 1,4-hexadiene having a density of 0.88 gram per cubic centimeter and a molecular weight of 180,000.

Elastomer B = an amorphous hydrocarbon rubber copolymer containing 54 weight percent ethylene; 42 weight percent propylene; and 4 weight percent
5 1,4-hexadiene having a density of 0.86 gram per cubic centimeter and a molecular weight of 290,000.

Elastomer C = a very low density polyethylene, which was a copolymer of ethylene and 1-butene (VLDPE) having density of 0.885 gram per cubic centimeter and a melt index of 0.8 gram per 10 minutes. This copolymer can be
10 considered semi-crystalline.

Elastomer D is a copolymer of ethylene and ethyl acrylate having a density of 0.930 gram per cubic centimeter and a melt index of 6 grams per 10 minutes.

A/O A = an antioxidant, that is, a diphenylamine alkylated with alpha-methyl styrene.
15

A/O B = an antioxidant, that is, thiodiethylene-bis-(3,5-di-tert-butyl-4-hydroxyhydrocinnamate).

A/O C = an antioxidant, that is, distearyl ester of beta,beta thiodipropionic acid.

20 Melt index was determined under ASTM D 238, Condition E, at 190 degrees C and 2.16 kilograms. It was reported in grams per 10 minutes. The variables and results are set forth in the Table.

Table

example	1	2	3	4	5
Formulation in percent by weight:					
Homo-polymer	balance	balance	balance	balance	balance
PEG	0.6	0.6	0.6	0.6	0.6
Elasto-mer A	0	5	10	15	20
A/O A	0.1875	0.1875	0.1875	0.1875	0.1875
A/O B	0.1875	0.1875	0.1875	0.1875	0.1875
A/O C	0.375	0.375	0.375	0.375	0.375
dicumyl peroxide	2.0	1.9	1.85	1.80	1.75
Result:					
Relative WTL (%)	100	76.9	84.6	76.9	107.7

Table (continued)

example	6	7	8	9
Formulation in percent by weight				
Homo-polymer	balance	balance	balance	balance
PEG	0.6	0.6	0.6	0.6
Elastomer B	0	20	0	0
Elastomer C	0	0	20	0
Elastomer D	0	0	0	20
A/O A	0.1875	0.1875	0.1875	0.1875
A/O B	0.1875	0.1875	0.1875	0.1875
A/O C	0.375	0.375	0.375	0.375
dicumyl peroxide	1.9	1.8	1.8	2.2
Result:				
Relative WTL (%)	100	50.8	114.5	79.8

Notes to Table:

- 5 Relative WTL (%) = relative water tree length in percent. The controls, examples 1 and 6, are 100 percent.

WHAT IS CLAIMED IS:

1. A polyethylene composition comprising:
 - (i) a homopolymer of ethylene made by a high pressure process, and, based on 100 parts by weight of component (i),
5 (ii) 5 to 20 parts by weight of an elastomer; and
 (iii) 0.05 to 1 part by weight of a polyethylene glycol having a molecular weight in the range of 1000 to 100,000.
2. The composition defined in claim 1 wherein the elastomer has a
10 density in the range of 0.860 to 0.915 gram per cubic centimeter and a crystallinity of 0 to 25 percent.
3. The composition defined in claim 1 wherein the elastomer is present in an amount of 5 to 15 parts by weight per 100 parts by weight of
15 component (i).
4. The composition defined in claim 2 wherein the elastomer is an EPM or an EPDM.
- 20 5. The composition defined in claim 1 wherein the polyethylene glycol has a molecular weight in the range of 5000 to 30,000 and is present in an amount of 0.3 to 0.6 part by weight.
- 25 6. A cable comprising one or more electrical conductors or a core of electrical conductors, each conductor or core being surrounded by an insulating composition comprising:
 - (i) a homopolymer of ethylene made by a high pressure process, and, based on 100 parts by weight of component (i),
 (ii) 5 to 20 parts by weight of an elastomer; and, optionally,
30 (iii) 0.05 to 1 part by weight of a polyethylene glycol having a molecular weight in the range of 1000 to 100,000.

7. The composition defined in claim 6 wherein the elastomer is present in an amount of 5 to 15 parts by weight per 100 parts by weight of component (i).

5 8. The cable defined in claim 6 wherein the elastomer has a density in the range of 0.860 to 0.915 gram per cubic centimeter and a crystallinity of 0 to 25 percent.

9. The cable defined in claim 8 wherein the elastomer is an EPM
10 or an EPDM.

10. The cable defined in claim 6 wherein the polyethylene glycol has a molecular weight in the range of 5000 to 30,000 and is present in an amount of 0.3 to 0.6 part by weight.

15 11. A cable comprising one or more electrical conductors or a core of electrical conductors, each conductor or core being surrounded by an insulating composition comprising:

(i) a homopolymer of ethylene made by a high pressure process
20 having a density in the range of 0.860 to 0.940 gram per cubic centimeter and a melt index in the range of 1 to 5 grams per 10 minutes, and, based on 100 parts by weight of component (i),

(ii) 5 to 15 parts by weight of an EPM or an EPDM, each having a density in the range of 0.860 to 0.915 gram per cubic centimeter and a
25 crystallinity of 0 to 25 percent.

(iii) 0.3 to 0.6 part by weight of a polyethylene glycol having a molecular weight in the range of 5000 to 30,000.