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**EUROPEAN PATENT APPLICATION**

21 Application number: **86115572.9**

51 Int. Cl.4: **H01B 7/28**

22 Date of filing: **10.11.86**

30 Priority: **12.11.85 US 797106**

43 Date of publication of application:  
**27.05.87 Bulletin 87/22**

84 Designated Contracting States:  
**BE DE FR GB IT NL SE**

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54 **Tree retardant high voltage composition and method.**

57 The present invention relates to a tree retardant composition comprising an oligomer copolymer of at least one alpha-olefin having up to about 8 carbon atom atoms and at least one alpha-unsaturated ester having up to about 10 carbon atoms, the oligomer being combined with a polymeric material ordinarily employed as an insulating material for electric conductors.

**EP 0 223 180 A1**

## TREE RETARDANT HIGH VOLTAGE COMPOSITION AND METHOD

The present invention relates to a novel tree retardant composition comprising an oligomer copolymer combined with a polymeric component employed as an insulating material over an electric conductor.

The loss of electric insulating properties in polymeric dielectric materials is attributable to many factors one of which is manifested as a phenomenon known as treeing. There are generally three causes of treeing one of which is seepage of water into the dielectric material; another of which is caused by electrical overloads and a third is contamination with foreign matter, metal particles or voids. These are referred to respectively as water treeing, electrical treeing and electrochemical treeing. Treeing is caused by a breakdown of the polymeric dielectric material and as the breakdown progresses, the visible damage to the dielectric also progresses through the dielectric in a path that resembles a tree. Treeing usually is a slow type of failure and may take years to cause an eventual breakdown of the polymeric composition so that it is no longer useful as an electric insulator.

Various additives are disclosed in the prior art which when added to polymeric dielectric materials form a tree retardant composition. Ashcraft *et al.*, U.S. Patent 4,144,202 describe certain organic silane compounds which will inhibit water treeing in ethylene polymers whereas McMahon U.S. Patent 4,206,620 describes the use of a 6-24 carbon atom alcohol which imparts electrical tree growth resistance to compositions used as an insulation for high voltage power cables. Both Ashcraft, *et al.* and McMahon go into some detail in describing water treeing and electrical treeing problems in polymer compositions and cite numerous patents that describe attempts to overcome this problem in addition to suitable polymers used as dielectric materials, adjuvants and methods of incorporating the tree retardant compositions into the polymeric dielectric and the preparation of coatings on electrical conductors. Both Ashcraft, *et al.* and McMahon are incorporated herein by reference for these teachings.

Barlow, U.S. Patent 4,499,013 discloses certain fatty acids, esters, and alcohol derivatives useful as electrical tree and water tree resistant compounds in polymeric compositions whereas Braus, Barlow and Maringer U.S. Patent 4,548,865 disclose various silane compounds useful as water tree and electrical tree retardant additives for polymeric compositions. Barlow and Maringer U.S. Patent 4,536,530 describe organophosphorous compounds useful as water tree resistant additives for polymeric compositions.

Otani, *et al.* (Wire Association Meeting, Nov. 1984, Baltimore, MD.) Development of Material for the Very High Performance XLPE Cables, Pages 68-77 describe certain unidentified ethylene copolymers incorporated in crosslinked polyethylene as an additive to reduce water treeing whereas Miyauchi, *et al.* United States Patent 3,929,724 describes the preparation of a crosslinked polyethylene composition having improved aging characteristic obtained by first dispersing antioxidants in an ethylene vinyl acetate copolymer which is then mixed with the polyethylene.

The present invention relates to a tree retardant composition comprising an oligomer copolymer of at least 1 alpha-olefin having up to about 8 carbon atoms and at least 1 alpha-unsaturated ester having up to about 10 carbon atoms, said oligomer having viscosity range as indicated by Brookfield viscosity of about 100 Cps @ 140°C up to a melt index of about 500 by the ASTM D 1238 Condition A method.

Brookfield viscosities are measured with a model RVT Brookfield Viscometer with a thermocell attachment using a SC4-18 spindle and a speed depending on the viscosity as noted in Table II.

The oligomer is combined with a polymeric material employed as an insulating material for electric conductors.

The invention also relates to a method for forming a tree retardant composition by combining the foregoing oligomer copolymer with a polymeric material.

As noted above, tree retardant compositions are known in the art and are employed in combination with polymeric dielectric materials in order to prevent or minimize treeing, e.g. water treeing and/or electrical treeing.

The present invention also relates to a tree retardant composition comprising an oligomer copolymer of at least 1 alpha-olefin having up to about 8 carbon atoms and at least 1 alpha-unsaturated ester having up to about 10 carbon atoms and a polymeric material.

Although the term copolymer has sometimes been employed to designate only those polymers in which two monomers are polymerized with one another, as used throughout the specification and claims hereof, the term copolymer is intended to describe polymers based on two or more monomers and generally is employed to describe those polymeric compositions based on 2,3,4, and more monomers being polymerized into a single polymeric composition. The various copolymers employed according to the present invention may be random copolymers, graft copolymers, block copolymers and star copolymers all of which are known in the art.

The alpha-olefin component of the copolymer, as noted previously, can have up to about 8 carbon atoms by which it is meant any alpha-olefin whether an aliphatic or branch chain olefin having from 2 to about 8 carbon atoms may be employed such as ethylene, propylene, isobutylene, 1-pentene, 1-hexene, 1-heptene, 1-octene and the like and the various structural isomers thereof and mixture thereof. The preferred alpha-olefin component is ethylene or propylene or mixtures thereof, said preferred alpha-olefin component optionally containing a four to about eight carbon atom alpha-olefin.

The various alpha-unsaturated esters that may be employed, as noted above, have up to about 10 carbon atoms and comprise the various vinyl esters and acrylic esters and the art known equivalents thereof. Vinyl esters that may be employed in this regard comprise vinyl acetate, vinyl formate, vinyl propionate, vinyl butyrate and the like. The various acrylic esters comprise various esters of acrylic acid, methacrylic acid, ethacrylic acid, and the like such as ethyl acrylate, ethyl methacrylate, methylacrylate, methyl methacrylate, n-butyl acrylate, n-butyl ethacrylate, n-butyl methacrylate, n-pentyl acrylate, n-pentyl ethacrylate, n-hexyl acrylate, n-hexyl ethacrylate, n-hexyl methacrylate and the various isomers thereof as well as various art know equivalents thereof and mixtures thereof.

The alpha unsaturated ester employed in the oligomer is present in an amount from about 10% to about 90% by weight and especially from about 30% to about 80% by weight.

Various oligomers that may be employed in this respect comprise ethylene vinyl acetate copolymers having anywhere from about 10 to about 90% by weight of vinyl acetate and especially from about 30% to about 80% vinyl acetate a weight basis. An especially suitable oligomer in this respect comprises an ethylene vinyl acetate oligomer having about 40% by weight of vinyl acetate and a viscosity of about 800 cps at 140°C as measured by a RVT Brookfield viscosimeter with a thermocell attachment at 3 rpm employing a number SC4-18 spindle.

Oligomers of ethylene and n-butyl acrylate may also be used where the n-butyl acrylate ranges from about 10% to about 90% by weight and especially from about 25% to about 75% by weight.

Terpolymer oligomers of isobutylene ethylene and an alpha-unsaturated ester such as vinyl acetate or n-butyl acrylate are also suitable where the isobutylene in the polymer is from about 0.5% to about 10% and especially from about 1% to about 5% by weight. The range of the alpha-unsaturated ester employed in the terpolymer is from about 1% to 50% and especially from about 10% to about 40% by weight.

Synergistic results are obtained in the minimization or elimination of water treeing and/or electrical treeing with various ethylene propylene rubbers (EPR) when the rubbers are added to the oligomer polymer component in an amount of about 5% by weight of the overall composition or less and especially an amount from about 1% to about 5% and especially from about 2% to about 4% by weight of the overall composition i.e., oligomer, polymer component and EPR.

The EPR materials in this respect comprise those having anywhere from about 40% to about 80% by weight of ethylene and the balance propylene and especially those having from about 50% to about 75% ethylene and the balance propylene on a weight basis. The EPR rubbers employed in this regard have a Mooney Viscosity (127°C) from about 10 to about 70 and especially from about 15 to about 45. Especially suitable EPR rubbers comprise those having an ethylene content of about 65% on a weight basis and the balance propylene and a Mooney Viscosity (127°C) of about 20. The EPR is employed in this regard when the polymeric material of the composition is not an EPR material.

The oligomer is employed with a polymeric component, the oligomer being combined with the polymeric component to form a composition so that the total amount of alpha-unsaturated ester in the composition is anywhere from about 0.2% to about 5% by weight and especially about 0.5% to about 1.7% on a weight basis, it especially being preferred that the amount of alpha-unsaturated ester in the composition be no greater than that to maintain satisfactory electrical properties in the composition.

In general the polymeric material suitable for the practice of this invention includes any normally solid synthetic organic polymeric thermoplastic resin. Included are polyolefins and copolymers thereof, vinyls, olefin-vinyl copolymers, olefin-allyl copolymers, polyamides, acrylics, polystyrenes, cellulosics, polyesters and flouorocarbons.

The polyolefins include normally solid polymers of olefins, particularly mono-alpha-olefins, which comprise from about 2 to about 6 carbon atoms, e.g., polyethylene, polypropylene, polybutene, polyisobutylene, poly(4-methyl-pentene), and the like. Preferred polyolefins are polyethylene and polypropylene. Polyethylene is especially preferred. Specific polyethylenes include linear low density polyethylene, high density polyethylene and low density polyethylene. Especially preferred polyethylenes because of their demonstrated effectiveness are low density polyethylenes such as NA 310 sold by National Distillers and Chemical Corporation.

Copolymers of ethylene, and other compounds interpolymerizable with ethylene such as butene-1, pentene-1, styrene and the like may be employed. In general the copolymer will comprise about 50 weight % or more ethylene. Other copolymers, such as ethylene-propylene rubber (EPR) and ethylene-propylene-diene monomer (EPDM) are also contemplated herein.

5 Suitable vinyl polymers include polyvinyl chloride, polyvinyl acetate, vinyl chloride/vinyl acetate copolymers, polyvinyl alcohol and polyvinyl acetal.

Suitable olefin-vinyl copolymers include ethylene-vinyl acetate, ethylene-vinyl propionate, ethylene-vinyl isobutyrate, ethylene-vinyl alcohol, ethylene-methyl acrylate, ethylene-ethyl acrylate, ethylene-ethyl methacrylate, and the like. In general the ethylene constitutes at least about 25% of the copolymer by weight.

10 Olefin-allyl copolymers include ethylene-allyl benzene, ethylene-allyl ether, ethylene-acrolein, and the like.

When it is desired to use a polymeric composition which can be crosslinked, crosslinking can be accomplished by any of the known procedure such as chemical means including peroxide crosslinking; by high energy radiation using an electron accelerator, gamma-rays, x-rays, microwaves and the like. The basic procedures for crosslinking polymers are extremely well known to the art and need not be described herein in detail.

Conventional crosslinking agents such as organic peroxides may be suitably employed. Typical organic peroxide free radical generators include dicumyl peroxide; 2,5-bis (tert-butylperoxy)-2,5-dimethylhexane; di-tert-butyl peroxide; benzoyl peroxide;  $\alpha$   $\alpha$ 'bis(t-butylperoxy) diisopropyl benzene and the like, as discussed in U.S. Pat. No. 3,287,312. The amount of organic peroxide, when employed, will range from about 0.5 to 5.0 by weight based on the total weight of the composition, or about 0.5 to 10 phr, preferably 3 to 6 phr.

Other tree retardants such as silanes, stannates, titanates, phosphorus compounds, and the like may be employed in combination with the oligomer of the present invention in amounts of from about 1% to about 95% by weight of the oligomer. The tree retardants that may be used in combination with the oligomers described herein are more fully disclosed in U.S. Patent Nos. 4,299,713; 4,332,957; 4,400,429; 4,483,954; 4,514,535; 4,536,530 all of which are incorporated herein by reference.

Minor amounts of other additives may also be employed in conventional amounts to obtain the desired results. Conventional antioxidants such as the hindered phenols, polyquinolines and the like may be employed. Other ingredients that may be included are plasticizers, dyes, pigments, heat and light stabilizers, antistatic agents and the like.

The compositions of this invention are generally unfilled polymer compositions. The term "unfilled" as applied to the instant composition shall mean a composition which contains less than 10% of a conventional polymer filler. For certain applications and to meet particular specifications the unfilled compositions herein may contain no filler. The compositions of this invention may contain, therefore, 0 to less than 10% filler. When the polymers such as ethylene-propylene rubber (EPR) and ethylene-propylene-diene monomer - (EPDM) are employed however, from about 20% to about 30% fillers are generally used. Such compositions are also intended to be within the scope of this invention. Accordingly, fillers such as mineral fillers, may be employed to this limited extent in preparing the compositions of the invention, but in the particularly preferred embodiment and for certain uses, these compositions contain no fillers.

The polymer compositions of this invention can be prepared by mixing the various ingredients. When the organic compound and the polymeric component are mixed together to form the instant compositions, the organic compound and the polymeric component are homogeneously dispersed in each other. The order of mixing and specific procedure employed are not critical except to the extent that from the time the peroxide is added, if employed, the temperature is less than about 130°C in order to prevent premature curing of the composition. This precaution, however, is conventional in the art.

The components may be mixed on a variety of apparatus including multi-roll mills, screw mills, continuous mixers, compounding extruders and Banbury mixers.

After being extruded onto wire or cable, or other substrate the crosslinkable compositions are vulcanized at elevated temperatures, e.g., above about 180°C using conventional vulcanizing procedures.

In order to determine the utility and effectiveness of the polymeric compositions of the present invention with regard to its inhibiting effect of the water treeing thereof, the compositions were evaluated by the use of accelerated tests.

Electrical tree tests were performed using the DNCV (Double Needle Characteristic Voltage) method  
55 ASTMD3756-79.

The water tree test is performed using a procedure similar to that described in U.S. Pat. No. 4,144,202. A compression molded disc about 150 millimeters (mm.) in diameter having 10 conical depressions was prepared for each composition. The geometry of the disc and dimensions of the depressions are substantially the same as shown in U.S. Pat. No. 4,144,202. The base of the disc is sprayed with silver paint which serves as the ground electrode. An acrylic tube 6" long is clamped to the upper face forming a test cell. About 150ml. of 0.01N sodium chloride solution is poured into the cell and the air bubbles trapped on the surface of the sample are removed. A platinum wire ring is then immersed in the electrolyte and connected to the electrical supply which provides 5 KV at a frequency of 3KHz. Samples are energized for 22 hours after which time they are removed from the test cell and washed with distilled water. The ten depressions are cut from the disc and stained to make the water trees more visible. The sections are obtained with a microtone, examined microscopically (at 200X) and the tree size measured. Normally four discs are made for each sample so that the average tree size is calculated from forty individual measurements. In evaluating different tree retardants, the relative tree size is determined by comparing the average tree size obtained on a standard high voltage insulation material containing no tree retardant additives.

The following Examples are illustrative.

#### EXAMPLES 1-30

Various mixtures of a low density polyethylene (NA 310) and an oligomer were prepared, the molecular weight of the oligomer being indicated by the Brookfield viscosity, melt index (MI) or melt flow rate (MFR) measured as noted herein. The oligomers are based on ethylene and alpha unsaturated ester and optionally isobutylene.

Oligomers that are liquids at room temperature were blended with the polyethylene in a Bankury mixer and then fed into twin screw extruder, pelletized and evaluated for electrical treeing and/or water treeing according to the procedures set forth herein. Oligomers that are solids at room temperature were blended directly with the polyethylene in a twin screw extruder and evaluated in the same way.

The results obtained are listed in Table I.

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TABLE 1

<u>No.</u>	<u>Oligomer wt. %</u>	<u>wt. % of co-monomer in oligomer</u>	<u>Brookfield Visc. at 40°C (unless otherwise noted) cps.</u>	<u>Water Tree Size in Microns</u>	
1	1	79 VA (vinyl acetate)	315	78	
2	2	79 VA	315	75	
3	4	79 VA	315	66	
4	2	40 VA	750	82.5	
5	2	60 VA	0.3 MFR (ASTM D1238 Cond. B)	75.5	
6	2	28 VA	1000 MI (ASTM D1238 Cond. A)	79.5	
7	2	69.1 nBA (n-butyl acrylate)	958	55 (123)	
8	2	35.1 nBA	3080	106	
9				93.5	
10	2	74 VA	315	99.5	
11	2	40 VA	750	87	Aged
12	2	41.8 VA 2-5 iso-butylene	142	117	504 Hr @ 90°C 122
13	2	39.9 VA	140	97	98.5
14	2	28 VA	8.5 MFR	144	172.5
15	2	28 nBA	7 MFR	221	163.5
16	2	14 VA/13 nBA	6 MFR	145	204

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TABLE 1 CONT'D

<u>No.</u>	<u>Oligomer wt. %</u>	<u>wt. % of co-monomer in oligomer</u>	<u>Brookfield Visc. at 40°C (unless otherwise noted)</u>	<u>Water Tree Size in Microns</u>	
17	1 (EVA)*	Total in Mixture			
	1 (EnBA)*	14 VA-14 nBA		124	139
18	2	18 VA	7.5 MFR	203	187.8
19	2	40 VA	750 cps	82.5	103
20	2	49.1 n BA	315 cps	130	
21	5	Vistalon 707 (TM)EPR 35% propylene	20 Mooney at 127°C	209.5	
22	2	Vistalon 707 (TM)	20 Mooney at 127°C	232	
23	4 1	Vistalon 707 (TM) Oligomer of Ex. 20		143	
					<u>Electrical Tree Size in microns</u>
24	2	74 VA	315 cps	86 (80.5)	15.7
25	2	69.1 nBA	958 cps	75 (84.5)	16.2
26	2	40 VA	750 cps	90.5 (82)	16.4
27	2	28 VA	1000 MI	87	
28 VE 636	2	28 VA	43 MI	95	
29 NA 310		N.A.		230	11.2
30 Cross Linked NA 310		N.A.		130	15.3

\* Mixture of ethylene vinyl acetate oligomer of Ex. 14 and ethylene n-butyl acrylate oligomer of Ex. 15.

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TABLE II

<u>BROOKFIELD THERMOSEL</u> <u>MODEL LVT VISCOMETER</u>			
5	Spindle Number	SC4-18	
10	Sample Volume, cc 0.8 Density)	8.0	
15	Sample Wgt. gms. 0.9 Density)	6.4	
	Sample Wgt. gms,	7.2	
20	Spindle Speed, RPM	Maximum Range, Centipoise	Conversion Factor
	60	50	0.5
25	30	100	1.0
	12	250	2.5
	6	500	5.0
30	3	1000	10.0
	1.5	2000	20.0
	0.6	5000	50.0
35	0.3	10,000	100.0

**Claims**

- 40 1. A tree retardant composition comprising an oligomer copolymer of at least 1 alpha-olefin having up to about 8 carbon atoms and at least 1 alpha-unsaturated ester having up to about 10 carbon atoms, said oligomer having a viscosity range as indicated by a Brookfield Viscosity of about 100 centipoises @ 140°C to melt index of about 500 as indicated by the ASTM D1238 Condition A method and a polymeric material.
- 45 2. The composition of Claim 1 where the oligomer is a copolymer of an alpha-olefin comprising ethylene and at least 1 alpha-unsaturated ester selected from vinyl esters or acrylic esters.
3. The composition of Claim 1 or 2 where the oligomer contains isobutylene.
4. The composition of any Claims 1-3 where the alpha-unsaturated ester is present in the oligomer in an amount from about 10% to about 90% on a weight basis.
- 50 5. The composition of any Claims 1-4 where the tree retardant composition contains up to about 5% by weight of an ethylene propylene rubber with the proviso that the polymeric material is not an ethylene-propylene rubber.
6. The composition of any of Claims 2-5 where the oligomer is based on an alpha-olefin comprising ethylene and an alpha-unsaturated ester comprising vinyl acetate.
- 55 7. The composition of any of Claims 2-5 where the oligomer is based on an alpha-olefin comprising ethylene and an alpha-unsaturated ester comprising n-butylacrylate.

8. The composition of Claim 2 where said oligomer is based on an alpha-olefin comprising ethylene, an alpha-unsaturated ester comprising vinyl acetate and/or n-butyl acrylate in an amount from about 1% to about 50% by weight of said oligomer and an unsaturated compound comprising isobutylene in an amount of from about 0.5% to about 10% by weight of said oligomer.

5 9. The composition of any of Claims 1-8 where the polymeric material is an alpha-olefin.

10. The composition of any of Claims 1-8 wherein polymeric material is a thermoplastic resin.

11. The composition of any of Claims 1-10 where said ester of said oligomer is present in said composition in an amount of from about 0.5% to about 3% by weight.

10 12. A method for improving the fire retardant properties of a polymeric material which comprises adding to the polymeric material the composition of any of Claims 1-10.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	IEEE TRANSACTIONS ON POWER APPARATUS AND SYSTEMS, vol. PAS-103, no. 3, March 1984, pages 536-544, IEEE, New York, US; S. NAGASAKI et al.: "Development of water-tree-retardant XLPE cables"	1-12	H 01 B 7/28
A	US-A-4 370 517 (HITACHI CABLE LTD.)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			H 01 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 06-02-1987	Examiner STANGE
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			