

[54] HIGH VOLTAGE INSULATED ELECTRIC CABLE HAVING OUTER SEMICONDUCTIVE LAYER

[72] Inventors: Hirokazu Miyauchi; Hironaga Mat-subara, both of Osaka, Japan

[73] Assignee: Sumitomo Electric Industries, Ltd., Osaka, Japan

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Primary Examiner—E. A. Goldberg  
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[57] ABSTRACT

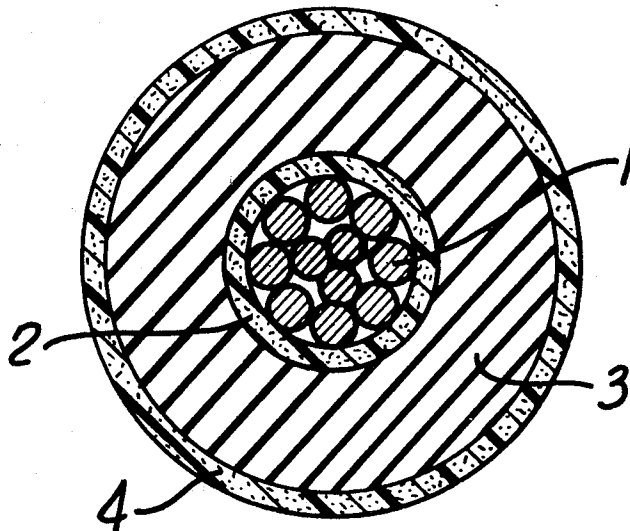
This invention relates to an insulated cable having an outer semiconductive layer, and more particularly relates to the structure of an insulated cable chiefly consisting of a crosslinked polyethylene or a crosslinked polyethylene copolymer, having an outer semiconductive layer. The composition is a mixture of 10 - 90 percent by weight of ethylene-vinyl acetate copolymer having 15 - 55 percent by weight of vinyl acetate content with 90 - 10 percent by weight of ethylene-vinyl acetate-vinyl chloride terpolymer, said mixture being used as a base, said base being mixed with a cross-linking agent and a conductivity imparting agent such as carbon black.

[56] References Cited

7 Claims, 1 Drawing Figure

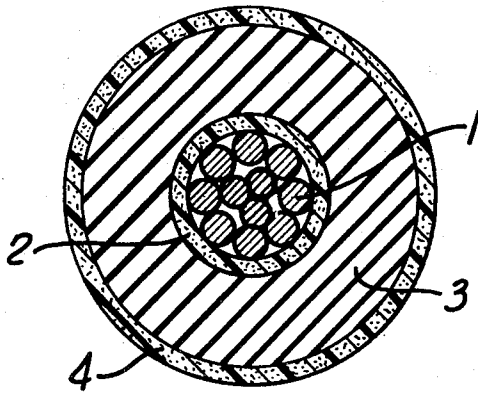
UNITED STATES PATENTS

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## HIGH VOLTAGE INSULATED ELECTRIC CABLE HAVING OUTER SEMICONDUCTIVE LAYER

In the conventional art, when covering the insulating layer of a crosslinked polyethylene insulated cable with an extruded semiconductive layer, wherein low density polyethylene, an ethylene-vinyl acetate copolymer or a polymer mainly consisting of these substances is used as the base thereof, to which are further added talcum, clay, calcium-carbonate or the like inorganic fillers, and also various antioxidants, processing aids and the like as required, it is a usual practice to use a composition such as a mixture of a ethylene-vinyl acetate copolymer, di- $\alpha$ -cumyl peroxide or like crosslinking agents and electric-conductive carbon black, or a mixture of a ethlene-ethyl acrylate copolymer, di- $\alpha$  cumyl peroxide or the like crosslinking agents, and electric-conductive carbon black. When splicing and treating the end of a cross-linked polyethylene insulated cable having an outer semi-conductive layer, it is necessary to strip the semiconductive layer in the range from the end of the cable to a certain length thereof, and in this case the semiconductive layer must be completely removed, and when it is removed, caution must be exercised not to impair the insulator. Moreover, in recent years an art of splicing and terminating the cable by the use of premolded accessories has been developed in making connections and end disposition with the cross-linked polyethylene insulated cable having an outer semiconductive layer. The advantage of the art in that it makes it possible to provide a product more uniform in quality and to deal or labor with the cable in shorter time than a conventional process in which tape winding and heat molding are carried out, has brought about a trend toward generalizing such a process. In this case, as it is necessary that the premolded accessories and cable must be assembled without allowing any electrical faults, there is an increasing demand that the semiconductive layer must be stripped in a shorter period of time and in a more simple manner so as not to impair the insulator.

When the described compositions in conventional use are extruded over the insulator to cover the same therewith, it is not only very difficult and takes much time but also tends to impair the insulator to strip the covered compositions from the cable. Therefore, such compositions cannot meet the requirements described above. In contrast thereto, the inventors previously made an application Ser. No. 77,918 filed Oct. 5, 1970, for a U.S. Pat. for an invention that provided a cross-linked polyethylene insulated cable having a semiconductive layer capable of being stripped simply and positively without leaving a part of the semiconductive layer over the insulator and without impairing the insulator.

The previous invention related to a cross-linked polyethylene insulated cable having a semiconductive layer by extrusion-covering the insulator, and provides the cable which has the property of making itself very easy to strip the semiconductive layer from the cable, and is characterized in that the semiconductive layer is extrusion-covered with a composition of a mixture of 2.5-dimethyl-2'.5'-di(tertiary-butyl peroxy)-3 with ethylene-vinyl acetate copolymer having 25-55 percent by weight of vinyl acetate content preferably in a ratio of 0.3-5.0 parts by weight of the former to 100 parts by weight of the latter copolymer. But in that in-

vention there was the limitation that the strippable strength could not be reduced beyond a certain degree.

An object of the present invention is to obtain an excellent insulated cable, and more particularly, to obtain an insulated cable having an easily strippable semiconductive layer, consisting of cross-linked polyethylene or cross-linked polyethylene copolymer as a main constituent.

A detailed explanation will now be made of this invention in conjunction with the accompanying single leaf of drawing showing an embodiment of the invention.

The inventors have made researches into the strippable strength in order to eliminate the disadvantages of the kind described, with the result that they have succeeded in obtaining a cross-linked polyethylene cable having an improved type semiconductive layer capable of being easily stripped. Namely, this invention is characterized in that a conductive layer having a composition of a mixture of 90 - 10 percent by weight of ethylene-vinyl acetate copolymer having 15 - 55 percent by weight of vinyl acetate content and 10 - 90 percent by weight of ethylene-vinyl acetate-vinyl chloride terpolymer with an ordinary cross-linking agent such as dicumyl peroxide or 2.5-dimethyl-2'.5'-di(tertiary-butyl peroxy)-hexine-3, preferably in a ratio of 0.3 - 50 parts by weight of the latter to 100 parts by weight of the former copolymer, and terpolymer.

Of course, since the composition is to be made into a semiconductive layer, all that is necessary is to mix a suitable amount of carbon black for imparting conductivity to the composition, and if necessary, other agents such as antioxidant, processing aids, etc. in accordance with conditions of use.

The results of experiments obtained by the inventors have demonstrated that the amount of carbon black (25 - 70 parts by weight as against 100 parts by weight of polymer) and amine-based, or phenol-based antioxidant and processing aids such as zinc stearate have nothing to do with a tendency of the composition toward easy stripping.

An embodiment of the invention in an insulated cable having an outer semiconductive layer will now be described in the drawing in which the numeral 1 designates a conductor; 2 an inner semiconductive layer; 3 an insulated layer; and 4 designates an outer semi-conductive layer. Examples and references are shown below. The material and method of experiment used in the examples are as follows: An ordinary inner semiconductive layer was extruded over a stranded cable conductor of 100 mm<sup>2</sup> in cross-section to cover the conductor therewith, and the cable conductor thus covered was then further covered by extrusion with the insulated layer and semiconductive layer shown in Table 1. and the layer was subjected to a cross-linking reaction in saturated steam of 15 atm. An adhesion test was conducted by making a cut 10 mm wide and running in the axial direction in the thus obtained semiconductive layer covering the surface of the conductor. The results obtained are shown in Table 1.

In the semiconductive layer in the table 50 parts by weight of acetylene carbon black, 1 part by weight of antioxidant, and 1 part by weight of zinc stearate were mixed with 100 parts by weight of base polymer (of course, including mixtures of various polymers) and

the cross-linking agent was varied in type and amount, and the semiconductive layer was varied in thickness.

TABLE 1

No.	Insulated layer	Semiconductive layer (over insulator)			Peeling strength (kg/10 mm)							
		Base polymer	cross-linking agent	Thickness (mm)								
Ref. 1	Polyethylene Specific gravity=0.92g/cc * -3 MI=2 * -4 DCP= 2.5% Antioxdant = 0.3%	E.VA*-1 Vinyl acetate =15% MI=6	X* -2 1%	0.5	More than 5	10	Ref. 9	Same as Ref. 1	Same as Ref. 3	X 0.5%	0.5	3.5
Ref. 2	Same as Ref. 1	E.VA Vinyl acetate = 25% MI=6	X*-2 1%	0.5	3.9	20	Ref. 10	Same as Ref. 1	Same as Ref. 3	X 1.0%	0.5	3.5
Ref. 3	Same as Ref. 1	E, VA Vinyl acetate = 35% MI=6	X*-2 1%	0.5	3.5	25	Ref. 11	Same as Ref. 1	Same as Ref. 3	X 5.0%	0.5	3.0
Ref. 4	Same as Ref. 1	E.VA Vinyl acetate = 50% MI=6	X*-2 1%	0.5	2	30	Ref. 12	Same as Ref. 1	Same as Ref. 3	X 6.0%	0.5	0.3
Ex. 1	Same as Ref. 1	E.VA Vinyl acetate = 10% MI=6 * -5 +SUMI-GRAFT 10%	X*-2 1%	0.5	More than 5	35	Ex. 7	Same as Ref. 1	Same as Ex. 3	X 0.3%	0.5	2.7
Ex. 2	Same as Ref. 1	Ref. 1 +SUMI-GRAFT 10%	X*-2 1%	0.5	3.0	40	Ex. 8	Same as Ref. 1	Same as Ex. 3	X 5.0%	0.5	2.0
Ex. 3	Same as Ref. 1	Ref. 2 +SUMI-GRAFT 10%	X*-2 1%	0.5	2.8	45	Ref. 13	Same as Ref. 1	Same as Ex. 3	X 6.0%	0.5	0
Ex. 4	Same as Ref. 1	Ref. 3 +SUMI-GRAFT 10%	X*-2 1%	0.5	1.3	50	Ref. 14	Same as Ref. 1	Same as Ref. 3	X 1.5%	0.1	Semiconduc-tive layer is cut and not stripped
Ex. 5	Same as Ref. 1	Ref. 2 +SUMI-GRAFT 10%	X 1%	0.5	2.0	55	Ex. 9	Same as Ref. 1	Same as Ex.3	X 1.5%	0.2	2.7
Ex. 6	Same as Ref. 1	Ref. 2 +SUMI-GRAFT 90%	X 1%	0.5	0.5	60	Ex. 10	Same as Ref. 1	Same as Ex.3	X 1.5%	0.5	2.6
Ref. 5	Same as Ref. 1	SUMI-GRAFT 100%	X 1%	0.5	0	65	Ex. 11	Same as Ref. 1	Same as Ex.3	X 1.5%	1.0	2.7
Ref. 6	Same as Ref. 1	Same as Ref. 3	None	0.5	Semiconduc-tive layer is cut and not stripped	70	Ref. 19	Polyethylene Specific gravity = 0.92g/cc MI=4 DCP = 2.5% Antioxdant = 0.5%	Same as Ref. 3	X 2.0%	0.7	3.5
Ref. 7	Same as Ref. 1	Same as Ref. 3	X 0.2%	0.5	"	75	Ref. 20	30 parts by weight of talc is added to 100 parts by weight of composition of Ref. 19.	Same as Ref.3	X 2.0%	0.7	3.0
Ref. 8	Same as Ref. 1	Same as Ref. 3	X 0.3%	0.5	3.5	80	Ref. 21	30 parts by weight of clay is added to 100 parts by weight of composition of Ref. 19.	Same as Ref. 3	X 2.0%	0.7	3.1
Ref.						85	Ref. 22	E.VA Vinyl acetate = 15% MI= 3 DCP = 2% Age-resistor = 0.5%	Same as Ref. 3	X 1.5%	1.0	4.3
						90	Ref. 23	30 parts by weight of talc is added to 100 parts by weight of composition of Ref. 22.	Same as Ref. 3	X 1.5%	1.0	3.9
						95	Ex. 12	Same as Ref. 19	Same as Ex.3	X 2.0%	0.7	2.7
						100	Ex. 13	Same as Ref. 20	Same as Ex. 3	X 2.0%	0.7	2.3
						105	Ex. 14	Same as Ref. 21	Same as Ex. 3	X 2.0%	0.7	2.4

Ex. 15	Same as Ref. 22	Same as Ex. 3	X 1.5%	1.0	3.6
Ex. 16	Same as Ref. 23	Same as Ex. 3	X 1.5%	1.0	3.2
Ref. 24	Same as Ref. 1	Same as Ref. 3	DCP 1.0%	0.5	More than 5 Slightly left on insulator
Ref. 25	Same as Ref. 1	Same as Ref. 3	DCP 5.0%	0.5	More than 5 Slightly left on insulator
Ref. 26	Same as Ref. 1	E.VA in Ref.3 was changed into * -6 DPD-6169	X 1.0%	0.5	"
Ex. 17	Same as Ref. 1	Same as Ex. 3	DCP 1.0%	0.5	2.8
Ex. 18	Same as Ref. 1	Same as Ex. 3	DCP 5.0%	0.5	2.0
Ref. 27	Same as Ref. 1	E.VA in ex. 3 was changed into DPD -6169	X 1.0%	0.5	More than 5

\* - 1 EVA : Ethylene vinyl acetate copolymer Vinyl acetate: amount of vinyl acetate in copolymer

\* - 2 X : 2.5-dimethyl-2'.5'-di-(tertiary butyl peroxy)-hexine-3

\* - MI : Melt flow index (g/10 min)(ASTM-D-)

\* - DCP : Di- $\alpha$ -cumyl peroxide

\* - 5 SUMIGRAFT: Ethylene-vinyl acetate-vinyl chloride terpolymer manufactured by the Sumitomo Chemicals Manufacturing Company in Japan

\* - DPD-6169: Ethylene-ethylacrylate copolymer manufactured by UCC in U.S. America.

In the previous application, it was possible to obtain an intended easily and completely strippable semiconductive layer only when 2.5-dimethyl-2'.5'-di-(tertiary butyl peroxy)-hexine-3 was mixed with an ethylene-vinyl acetate copolymer having 25 - 55 percent by weight of vinyl acetate content, but as is apparent from the examples shown, it is possible to obtain an intended easily and completely strippable semiconductive layer and also to reduce the strippable strength in a substantial degree even by the use of not only 2.5-dimethyl-2'.5'-di-(tertiary butyl peroxy)-hexine 3, but also an ordinary cross-linking agent such as di- $\alpha$ -cumyl peroxide only when an ethylene-vinyl acetate-vinyl chloride tertiary copolymer is mixed with an ethylene-vinyl acetate copolymer having 15 - 55 percent by weight of vinyl acetate content.

Namely, when an ethylene-vinyl acetate copolymer is less than 15 percent in its vinyl acetate content, ethylene-vinyl acetate-vinyl chloride ternary copolymer is deprived of its effect and the layer made thereof becomes difficult to strip, and when the copolymer exceeds 55 percent, its adhesion to the insulator is reduced too much to be suited for use in a cable.

Accordingly, when the vinyl acetate content is 15 - 55 percent, SUMIGRAFT proves effective and shows its readily improved strippability. Now, when the content of 2.5-dimethyl-2'.5'-di-(tertiary butyl peroxy)-hexine-3 is less than 0.3 part by weight on 100 parts by weight of said copolymer and terpolymer mixture, the semiconductive layer is relatively small in strength, and when the content exceeds 5 parts by weight, it becomes too poor in adhesion with respect to the insulator to be suitable enough for use in the cable.

When it is within the range of 0.3 - 5 parts by weight, it shows an especially good result. As for the thickness of the layer, it should be preferably more than 0.2 mm, because a layer of a thickness of less than 0.2 mm tends to be cut off in stripping.

As described above, only when ethylene-vinyl acetate copolymer is 15 - 55 percent in vinyl acetate content and ethylene-vinyl acetate-vinyl chloride terpolymer is added to said copolymer and 2.5-dimethyl-2'.5'-di-(tertiary butyl peroxy)-hexine-3 or DCP is preferably in a ratio of 0.3 - 5.0 parts by weight to 100 parts by weight of said copolymer and terpolymer mixture, it is possible to obtain a readily and completely strippable semiconductive layer. It has been demonstrated by experiments that the use of other types of cross-linking agents has produced no such semiconductive layer of desirable quality.

When ethylene-vinyl acetate-vinyl chloride terpolymer is less than 10 percent by weight in quantity in copolymer and terpolymer mixture, it has no effect and when it is more than 90 percent by weight, it cannot provide the required peeling strength. On the other hand, even when ethylene-vinyl acetate-vinyl chloride terpolymer is added to a high molecular (weight polymer or) copolymer other than an ethylene-vinyl acetate copolymer, and even when 2.5-dimethyl-2'.5'-di-(tertiary butyl peroxy)-hexine-3 or DCP is used as a cross-linking agent, it has become apparent that no good result can be obtained. Only the use of the formula provided by the invention can produce a semiconductive layer excellent in strippability.

Also, it should be understood that, irrespective of the size of the cable and the purpose for which the cable is used, the invention can be used in the cable, the insulated layer of which consists of cross-linked polyethylene or a cross-linked polyethylene copolymer as a chief constituent.

What we claim:

1. An insulated electric cable having an easily strippable outer semiconductive layer comprising an electric conductor having an insulation layer thereon consisting of crosslinked polyethylene or a crosslinked polyethylene copolymer as a chief constituent, and characterized by an outer semiconductive layer extruded over said insulation layer and composed of a mixture of 90 - 10 percent by weight of an ethylene-vinyl acetate-vinyl chloride terpolymer with 10 - 90 percent by weight of ethylene-vinyl acetate copolymer having 15-55 percent by weight of vinyl acetate content, a cross-linking agent and a conductivity imparting agent.

2. An insulated cable as claimed in claim 1 characterized by the use of Di- $\alpha$ -cumyl peroxide as a cross-linking agent of the semiconductive layer.

3. An insulated cable as claimed in claim 1 characterized by the use of 2.5-dimethyl-2'.5'-di-(tertiary butyl peroxy)-hexine-3 as a cross-linking agent of the semiconductive layer.

4. An insulated cable as claimed in claim 1 wherein the insulation layer is made of crosslinked polyethylene.

5. An insulated cable as claimed in claim 1 wherein the insulation layer is made of crosslinked polyolefine consisting of ethylene-vinyl acetate copolymer.

6. An insulated cable as claimed in claim 1 wherein an inorganic filler is added to the composition of said insulation layer.

7. The insulated electric cable of claim 1 wherein antioxidant and processing aids are included in the composition of said outer semiconductive layer as required.

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