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ELECTRIC INSULATING COMPOSITION CONTAINING AN ORGANIC SEMICONDUCTING MATERIAL
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Fig. 1

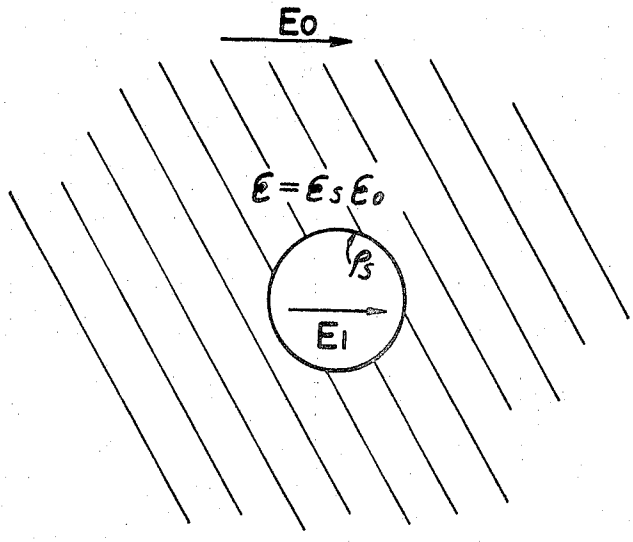


Fig. 2

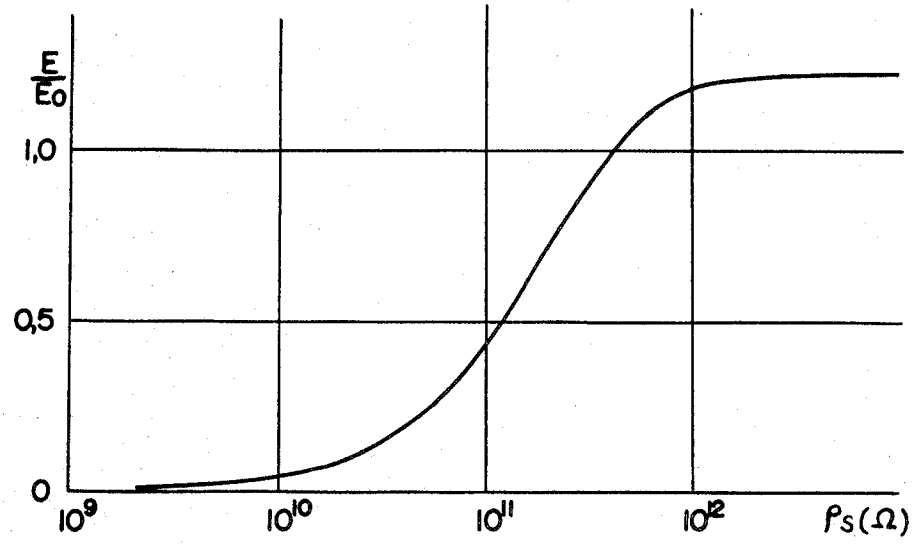
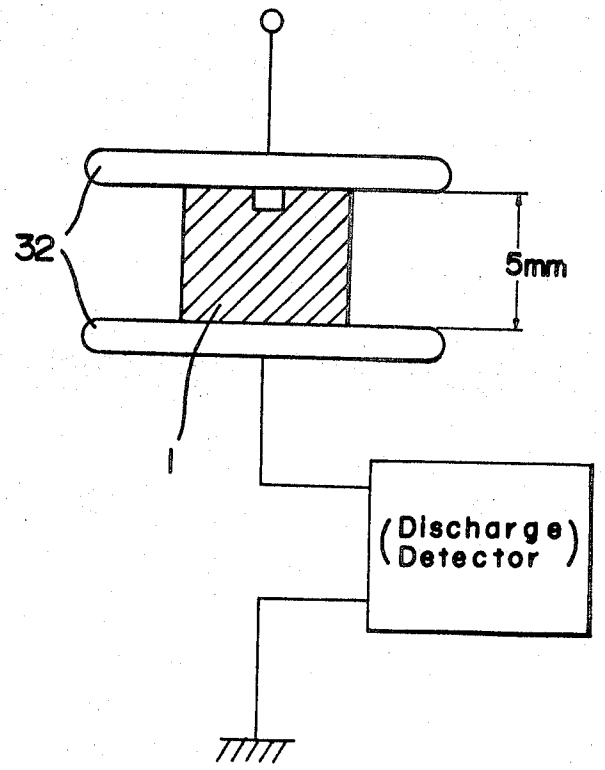


Fig. 3

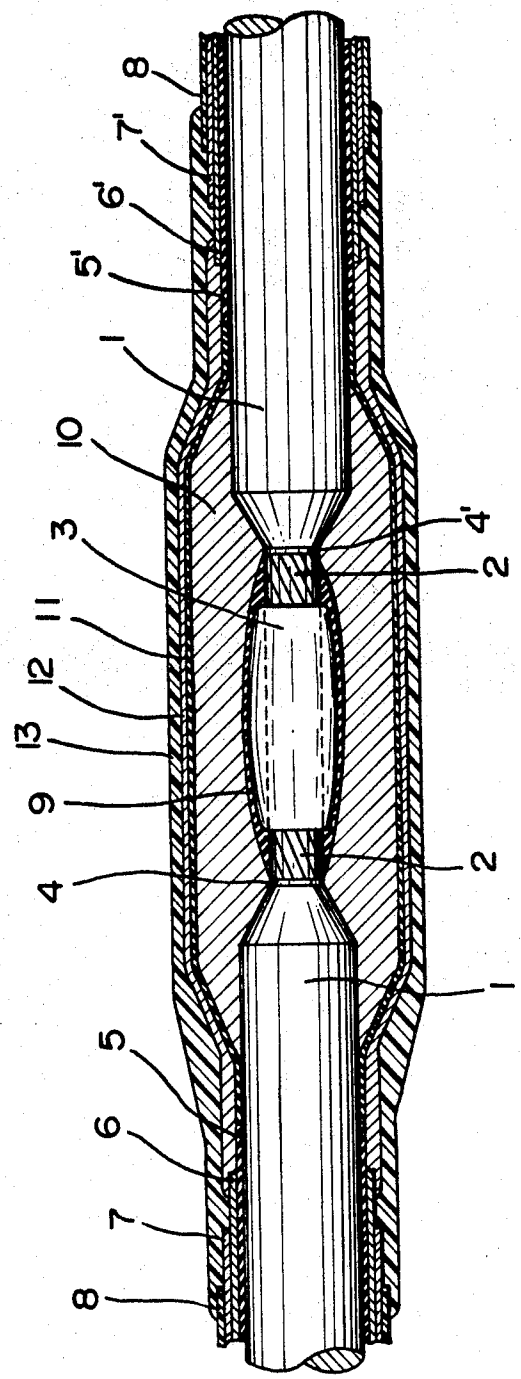


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ELECTRIC INSULATING COMPOSITION CONTAINING AN ORGANIC SEMICONDUCTING MATERIAL

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Fig. 4

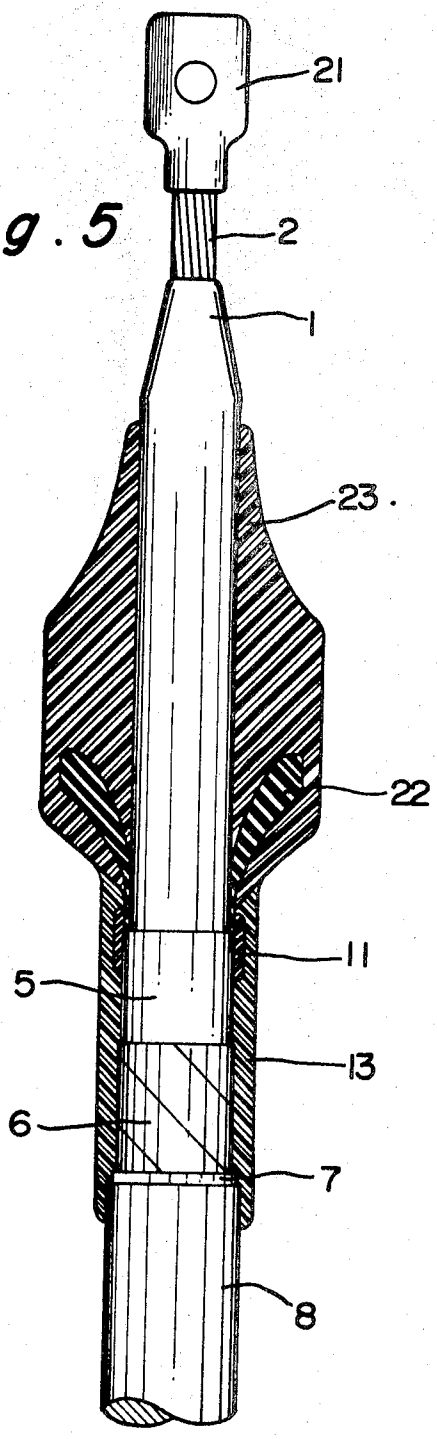


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ELECTRIC INSULATING COMPOSITION CONTAINING AN ORGANIC SEMICONDUCTING MATERIAL

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Fig. 5



United States Patent Office 3,573,210 Patented Mar. 30, 1971

3,573,210

ELECTRIC INSULATING COMPOSITION CONTAINING AN ORGANIC SEMICONDUCTING MATERIAL

Hisatomo Furusawa and Tadaaki Kuhara, Yokohama, and Hironori Matsuba, Kawasaki, Japan, assignors to The Furukawa Electric Company Limited, Tokyo, Japan

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Int. Cl. C08k 1/26; H01b 3/18
U.S. Cl. 252—64 14 Claims

ABSTRACT OF THE DISCLOSURE

An electrical insulating shaped body, free from partial discharge at internal voids which are inevitably formed therein. The shaped body has a volume resistivity larger than 10^{10} ohm-cm., and a surface resistivity smaller than 10^{12} ohms, both at the outer surface of the body and the internal surface of the voids. The surface resistivity is achieved by adding special semiconducting organic compounds, which bleed on the surface of the body by aging.

This invention relates to an insulated conductor, and more particularly to an insulated conductor whose insulation is rubber and/or plastics containing from 0.1% to 10% by weight of an organic semiconducting material selected for improving the dielectric strength. The insulated conductor of the invention is particularly suitable for high voltage apparatus rated at 5 kv. or higher, such as high voltage power cables, cable joints, cable terminals, and the like.

Known cross-linked or non-cross-linked plastic compositions and vulcanized or unvulcanized rubber compositions have heretofore been used as insulating materials of electric apparatuses, and a number of power apparatus insulated by using such plastic or rubber composition are recently installed in high voltage power network, e.g. rated at 5 kv. or higher. With insulation made of such known insulating composition, even though the initial breakdown voltage thereof is generally very high, the insulation sometimes collapses after being used for a long period of time at an A.C. voltage considerably lower than the initial breakdown voltage. Accordingly, such insulation made of the plastic or rubber composition has been used only at a lower voltage, such as a voltage below the discharge inception voltage, which is much lower than the initial breakdown voltage of the material, and the inherent dielectric strength of the material has not been utilized to its full extent.

Recent studies of the behavior of the plastic and rubber insulation at a high voltage have revealed that partial defects of the insulation are caused either during manufacturing process or during operation; namely, formation of unavoidable fine voids, mixing of foreign matters, such as metallic flakes and dust particles, contamination during manufacture, formation of fine air gaps at the boundaries between the surfaces of semiconducting layer and the shaped insulating layer during operation of the

electric apparatus. Upon application of an alternating high voltage to the apparatus, electric discharges take place at such partially defective portions for each alternating polarity of the alternating voltage. Such frequent electric discharges due to partial defects cause deterioration of the whole insulating body, with the resultant dielectric breakdown.

Among the aforesaid causes for partial defects, those due to fine air gap between the surfaces of semiconducting and insulating layers can be prevented by careful processing and those due to foreign matters can be also eliminated by keeping the place of production clean, but the formation of small voids is inevitable with the present techniques for shaping rubber or plastic compositions. It is also very difficult to detect discharges occurring in fine holes or voids having a diameter less than several ten microns. In fact, the partial discharges at such fine voids in the insulation, effected by application of an alternating high voltage, gradually deteriorate or erode the insulating material surrounding the voids to form a "tree," or a growing tree-like deterioration, and finally result in dielectric breakdown.

Extensive studies have been made to find some means to remove the above-mentioned defects of rubber or plastic insulation for high voltage apparatus. One of them is the development of insulation material having a high corona resistance. But, so far such material has not been developed, nor has there been established any practical method of testing the corona resistance of insulation materials.

Another means is to use some kinds of additives to prevent "tree" which occurs from discharges in rubber or plastic insulation. This is what Kitchin, Pratt ("Power Apparatus and Systems", June, 1962, pp. 112–121, published by American Institute of Electrical Engineers), and others studied. In their study, they prepared some shaped bodies of various compositions of polyethylene and different additives, stuck a needle into them, applied voltage to it, and measured the voltage at which "tree" started in the bodies. By so doing they selected such additives that gave the highest "tree" initiation voltage and developed an insulation material having good resistance to "tree" by addition of, for example, diphenyl p-phenylene diamine.

Still another means is to mix in an insulation material a liquid substance, such as paraffin oil and alkyl benzene, having substantially the same dielectric constant as that of the insulation material, thereby preventing occurrence of discharges in it (British Pat. No. 1,028,110).

This method, however, has many problems in respect to the processibility of the compositions produced by it and has not been put to practical use.

The inventors noticed the fact that voids in shaped rubber or plastic insulation are inevitable with the present techniques of processing them, but the frequent partial discharges at such fine voids could be prevented if the voltage gradient, or electric field strength, at each such void could be reduced. As a result of theoretical and experimental studies of means for reducing the field strength at the void, the inventors found that if the surface resistivity of the void is reduced to a level lower than 10^{12} ohms, the field strength E_1 inside the void becomes lower

than the field strength E_0 in the rubber or plastic insulation surrounding the void.

In short, the inventors have found that it is possible to produce a semiconducting layer with a surface resistivity smaller than 10^{12} ohms on the surface of each inevitable void in the electric insulation by adding one or more semiconducting organic compounds into a substrate consisting of rubber or plastics or a mixture thereof, at a rate exceeding the solubility of the semiconducting organic compounds in the substrate.

Therefore, an object of the present invention is to provide an insulated electrical conductor for use at a high voltage having a volume resistivity larger than 10^{12} ohm-cm., characterized in that the insulation of the insulated conductor comprises a substrate consisting of rubber, plastics, or a mixture thereof and 0.1 to 10 wt. percent, of organic semiconducting compound, said organic semiconducting compound bleeding out onto boundary surfaces (including those of voids) of the insulation to form semiconducting layers with a surface resistivity smaller than 10^{10} ohms on the boundary surfaces.

The insulated electrical conductor according to the present invention can be shaped in various forms for use at 5 kv. or higher, for instance in the form of power cables, power cable terminals, power cable joints, and the like.

For a better understanding of the invention, reference is made to the accompanying drawings, in which:

FIG. 1 is a diagrammatic illustration of a hypothetical void in an insulating body, assumed for calculation of field strength in the void;

FIG. 2 is a graph representing the relationship between the field strength inside the void and the surface resistivity of the void surface;

FIG. 3 is a simplified schematic diagram of a device for detecting partial discharge within an insulating body;

FIG. 4 is a diagrammatic illustration of a joint of power cables insulated by the insulating shaped body according to the present invention, with a part thereof shown in section; and

FIG. 5 is a diagrammatic illustration of a cable terminal assembly insulated by the insulating shaped body according to the present invention, with a part thereof in section.

Like parts are designated by like reference numerals and symbols throughout the drawings.

Now, referring to FIG. 1, let it be assumed that a spherical void having a diameter a and a surface resistivity ρ_s is formed in an insulating body having a specific inductive capacity ϵ_s, and that a field strength $E_0 \sin \omega t$ (ω: angular frequency, t: time) is applied to the insulating body. Then, the maximum field strength E_1 within each void having a dielectric constant ϵ_0 can be given by the following equation.

$$E_1 = \frac{3E_0}{\sqrt{\left(\frac{1}{\epsilon_s}+2\right)+\left(\frac{2}{\omega\epsilon_s\cdot\epsilon_0 a\cdot\rho_s}\right)^2}} \qquad (1)$$

The Equation 1 based on MKS unit system. The specific inductive capacity ϵ_s of rubber and plastic usable as insulating material is usually 2 to 5, and the diameter of the void to be formed in shaped insulating body is at most 1 mm. The ratio of E_1/E_0 is calculated for different values of the surface resistivity ρ_s, by assuming a specific inductive capacity ϵ_s of 2.2, a void diameter of 1 mm., and an angular frequency of 100π (50 Hz.), and the result is shown in FIG. 2.

It is apparent from FIG. 2 that for a given field strength

E_0, the value of the field strength E_1 in the void becomes smaller when the surface specific resistance ρ_s is as low as 10^{12} ohms, and when the ρ_s is 10^{11} ohms, the field strength is reduced to 0.36 time as much as that for $\rho_s \geqq 10^{12}$ ohms. When the surface resistivity ρ_s is further reduced to the level of 10^{10} ohms, the field strength E_1 is reduced to 0.036 time as much as that for $\rho_s \geqq 10^{12}$ ohms.

In other words, the inventors have found that by reducing the surface resistivity of the void, the field strength within the void can be limited to a very low level enough to prevent partial discharges at such voids.

In calculating the value of E_1 with reference to E_0, the diameter of each void is assumed to be 1 mm., which is larger than that of most actual voids in insulation. Judging from the Equation 1, the smaller the void is, the smaller the field strength E_1 will be, and hence, the values of the E_1/E_0 ratio as shown in FIG. 2 are on the safe side. The value of the specific inductive capacity ϵ_s does not vary extensively for different insulation materials, and hence, the field strength E_1 at such voids is not noticeably affected by the kind of the insulation material used or specific inductive capacity thereof. Therefore, it can be safely concluded that by reducing the surface resistivity of the voids formed in the shaped insulating body to a level below 10^{12} ohms, the partial discharges within the insulating body can be successfully suppressed, regardless of the kind of insulation material.

If an insulation material has a low volume resistivity at commercial power frequency, e.g. a value smaller than 10^{10} ohm-cm. at 50 Hz., the conductive current therethrough will become larger than the displacement current therethrough, and such material actually cannot be dealt with as a true insulation material. Accordingly, the field strength inside the voids formed in such material cannot be improved to any noticeable extent by the reduction of surface resistivity according to the invention.

The inventors carried out a series of experimental studies to find means for achieving surface resistivity of voids smaller than 10^{12} ohms, while maintaining the volume resistivity at a level higher than 10^{10} ohm-cm. Consequently, it has been found that if certain special semiconducting organic compounds are added to a rubber or plastic composition in excess of the solubility of the organic compounds in the rubber or plastic compositions, part of such organic compounds bleed in a few hours or in a few days on both the outer surface of the shaped body and the internal surface of the voids enclosed in it, to form semiconducting layers having a comparatively low surface resistivity. Thus, surface achieved, while maintaining the volume resistivity of the shaped body at a level above 10^{10} ohm-cm.

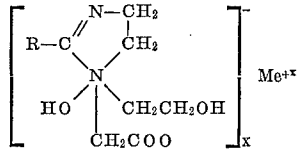
According to the present invention, the aforesaid special semiconducting organic compounds are added to a rubber or plastic insulating composition containing suitable amounts of one or more of known filters, plasticizers, stabilizers, accelerators, and a small amount of cross-linking agents, and the thus incorporated composition is shaped to form insulating body having an excellent discharge inception voltage considerably higher than that of insulating body with known insulating composition, without significantly sacrificing any physical or electrical characteristics or processibility thereof. Furthermore, with the insulating shaped body according to the present invention, partial discharge due to localized strong field do not take place to eliminate the possibility of dielectric breakdown caused by such partial discharges, even after using the insulating shaped body for a prolonged period in the state as subjected to a strong alternating electric field. Thereby, the insulating shaped body according to the present invention can be used at a voltage considerably higher than that applicable to a known insulating shaped body of similar structure.

As described in the foregoing, in order to improve the dielectric strength of insulating composition consisting essentially of rubber or plastic, special semiconducting

organic compounds having a compatibility with and a low solubility in such insulating composition, which compounds have properties to bleed to form a layer having a surface resistivity less than 10^{12} ohms, are added to such insulating composition, and the thus incorporated insulating composition is applied to high voltage apparatus to form an insulating body of the apparatus. Then, the special organic compounds bleed both on the outer surface of the insulating body and on the internal surface of voids, inevitably formed in the insulating body, so that semiconducting layers having a surface resistivity smaller than 10^{12} ohms are bled thereon. The semiconducting layers thus bled effectively prevent partial discharges at the voids, which have been the cause of dielectric breakdown of conventional insulation materials. The insulating composition containing the special semiconducting organic compounds can be applied to high voltage apparatus by extrusion or in tape or preshaped form.

In the shaped body formed of the composition incorporated with the semiconducting organic compounds, said incorporated semiconducting organic compounds bleed partially on the interface of the shaped body gradually depending upon the solubility as time elapses and form a layer having a surface resistivity of less than 10^{12} ohms and the residue remains in the interior in such a state the vicinity of the surface layer of the shaped body has a high concentration, so that even if the bled portion is removed, the semiconducting organic compounds bleed from the interior successively and compensate immediately and therefore a very stable shaped body can be maintained for a long time.

As the semiconducting organic compounds, which have a compatibility with and a low solubility in insulating compositions consisting mainly of rubber, plastic, or mixture thereof and which are capable of forming a layer on all interfaces of the insulating composition whose surface resistivity is less than 10^{12} ohms, mention may be made of alkylamine ethylene oxide adducts, such as laurylamine ethylene oxide adduct (mole ratio 1:2), stearylamine ethylene oxide adduct (mole ratio 1:51) and tallowamine ethylene oxide adduct (mole ratio 1:61); alkyladiamine ethylene dioxide adducts, such as, cocopropylenediamine ethylene oxide adduct (mole ratio 1:7), tallowpropylenediamine ethylene oxide adduct (mole ratio 1:21), imidazoline ethylene oxide adducts, such as, 1-hydroxy-2-heptadecyl-2-imidazoline ethylene oxide adduct (mole ratio 1:3), 1-aminoethyl-2-undecyl-2-imidazoline ethylene oxide adduct (mole ratio 1:1); alkylamine propylene oxide adducts, such as laurylamine propylene oxide adduct (mole ratio 1:1); amphoteric surfactants, for example, metal salts derived from imidazoline type, which are expressed by the general formula



wherein R is hydrocarbon radicals having 8 to 22 carbon atoms and Me is metals other than alkali metals, such as calcium, magnesium, cadmium, binc, barium, aluminium, tin, lead, iron, nickel, manganese, etc., such as calcium salt of (1-hydroxy, 1-hydroxyethylene, 2-heptadecyl imidazolinyl) acetic acid, magnesium salt of (1-hydroxy,

1-hydroxyethylene, 2-undecyl imidazolinyl) acetic acid; alanine type metal salts expressed by the general formula

$$[R—NH\cdot CH_2CH_2COO]^- \text{ or } [R—N(CH_2COO)CH_2COO]^-$$

wherein R is hydrocarbon radicals having 8 to 22 carbon atoms and the metal is metals other than alkali metals, such as calcium, magnesium, cadmium, zinc, barium, aluminium, tin, lead, iron, nickel, manganese, etc., such as lead salt of N-octadecyl β-alanine; zinc salt of N-dodecyl, β-alanine; calcium salt of N-octadecyl, β-alanine; magnesium salt of N-dodecyl, N-carboxyethylene, β-alanine; metal salts derived from amido amine type, such as calcium salt of N-heptyl amidoethylene, N-hydroxyethylene, N-carboxymethylene amine; magnesium salt of N-heptadecylamidoethylene, N-hydroxyethylene, N-carboxyethylene amine; metal salts derived from diamine type, such as barium salt of N-cocopropyl, N-carboxyethylene, trimethylene diamine; zinc salt of N-cocoalkyl-N',N'-di-carboxyethylene trimethylene diamine; aluminium salt of N-cocopropyl, N,N',N'-tricarboxyethylene diamine; and some other surfactants.

If the content of these semiconducting organic compounds based on the composition is less than 0.01% by weight, it is impossible to make the surface resistivity of the overall interfaces of the insulation less than 10^{12} ohms and when the content is more than 10.0% by weight, the slipping property increases and it is often difficult to effect extrusion process and further, even if the amount is increased, the effect is not improved and the cost only rises, so that the content of the semiconducting organic compounds in the composition is 0.01 to 10.0% by weight, preferably, 0.05 to 5.0% by weight.

The insulation materials used under the present invention are natural or synthetic rubbers, for example, butyl rubber, ethylene propylene rubber, ethylene-propylene-diene terpolymer rubber or natural rubber and plastic, for example, high density polyethylene, low density polyethylene, ethylene-metal salt of acrylic acid copolymer, ethylene ethylacrylate copolymer, ethylene vinyl acetate copolymer and polyvinyl chloride. If necessary, the substrate of the insulating materials may be compounded, with sulphur, quinone dioximes, cross-linking agents of organic peroxides such as dicumyl peroxide and 2,5-dimethyl 2,5-ditertiary butyl peroxy hexyne; fillers such as clay, talc, and carbon black; plasticizer or softner such as polybutene, aromatic hydrocarbon, paraffinic hydrocarbon, dioctylphthalate, and diisodecylphthalate; antioxidant or stabilizer such as 4,4'-thio bis(6-tertiary-butyl-m-cresol), phenylisopropyl-p-phenylenediamine, antimony trioxide, and tribasic lead maleate; accelerators, for example, thiazole series such as mercaptobenzothiazole, thiuram series such as tetramethylthiuram disulfide, dithiocarbamate series such as copper dimethyl dithiocarbamate, and lead oxide series such as red lead and litharge; and activator such as zinc oxide, in an amount which is usually used for insulating compositions.

EXAMPLE 1

Various substrates were prepared by using ingredients, as shown in Table 1. Different semiconducting organic compounds were added to the substrates at different ratios, as shown in Table 2, respectively. The insulating compositions thus prepared were formed into 1 mm. thick sheets of 10 cm. x 10 cm. by press-molding. The obtained sheets were left to stand for 48 hours, and then the surface resistivity and volume resistivity of the sheets were measured by applying a DC 500 volt across electrodes spaced by 10 mm. at a relative humidity of 40%. The results are shown in Table 2.

TABLE 1

Substrate	Ingredients	Parts by weight
Polyethylene	Polyethylene "NUC 2005" (made by Nippon Unicar Co.)	100
Ionomer	Ionomer "Surlyn A 1600" (du Pont)	100
Cured polyethylene	Polyethylene "NUC 2005" (made by Nippon Unicar Co.)	100
	Dicumyl peroxide	3.0
	4,4-thio bis 6-tert. butyl p-methyl cresol	0.5
Butyl rubber	Butyl rubber (Polymer corp. "Polysar butyl 100")	100
	Zinc oxide	5
	Stearic acid	0.5
	Calcined hard clay "Whitetex No. 2" (made by Freeport Kaolin Co.)	10.0
	Medium thermal carbon black "MT carbon black"	10
	Red lead	10
	Dibenzo quinone dioxime	6
	Sulfur	0.5
	Liquid aromatic hydrocarbon (Kenrich Petro Chemicals, Inc. "Kenflex n").	7
Ethylene propylene rubber	Ethylene propylene rubber "Dutral N" (made by Montecatini Soc. Gen. Ind.).	100
	Zinc oxide	5
	Polymerized trimethyldihydroquinoline "Age Rite Resin D"	1.5
	Lead oxide	3
	SRF Black	5
	Calcined clay	11.0
	Triallyl cyanurate	1.5
	Dicumyl peroxide (40% active) "Di-cup 40C" (made by Hercules Co.)	7
Polyvinyl chloride	Polyvinylchloride	100
	Dioctylphthalate	50
	Tribasic lead sulfate	5
	Dibasic lead stearate	1
	Calcined clay	10
	Antimony trioxide	3

TABLE 2

Substrate	Semiconducting organic compound	Shaped body: Surface resistivity, ohm	Shaped body: Volume resistivity, ohm-cm.	Quantity added, (part by weight based on 100 parts of substrate)
Polyethylene	Laurylamine ethylene oxide adduct (mole ratio 1:2)	3.2×10^{3}	$>10^{13}$	1.0
	Stearylamine ethylene oxide adduct (mole ratio 1:100)	1.8×10^{9}	$>10^{13}$	1.0
	Cocopropylenediamine ethylene oxide adduct (mole ratio 1:7)	1.0×10^{9}	$>10^{13}$	1.0
	Tallowpropylenediamine ethylene oxide adduct (mole ratio 1:21)	3.8×10^{9}	$>10^{13}$	1.0
	1-hydroxy-2-heptadecyl-2-imidazoline ethylene oxide adduct (mole ratio 1:3)	1.4×10^{9}	$>10^{13}$	1.0
	1-aminoethyl-2-undecyl-2-imidazoline ethylene oxide adduct (mole ratio 1:1)	9.2×10^{3}	$>10^{13}$	1.0
	"Denon-331-L" (made by Marubish Yuka Co., Ltd.)	1.2×10^{9}	$>10^{13}$	1.0
	Calcium salt of (1-hydroxy, 1-hydroxyethylene, 2-heptadecyl, imidazolinyl) acetic acid.	3.0×10^{3}	$>10^{13}$	1.0
	Lead salt of N-octadecyl β-alanine	4.0×10^{9}	$>10^{13}$	1.0
Cured polyethylene	"Denon-331-L"	1.2×10^{10}	$>10^{13}$	1.0
	Laurylamine ethylene oxide adduct (mole ratio 1:2)	1.0×10^{9}	$>10^{13}$	1.0
	Magnesium salt of (1-hydroxy, 1-hydroxyethylene, 2-undecyl, imidazolinyl) acetic acid.	3.5×10^{9}	$>10^{13}$	1.0
Polyvinyl chloride	Stearylamine ethylene oxide adduct (mole ratio 1:100)	8.8×10^{10}	$>10^{13}$	4.0
	Calcium salt of N-heptylamidoethylene, N-hydroxyethylene, N-carboxymethylene amine.	2.0×10^{9}	$>10^{13}$	2.0
Ethylene propylene rubber	Tallowpropylenediamine ethylene oxide adduct (mole ratio 1:21)	6.5×10^{10}	$>10^{13}$	4.0
	Calcium salt of N-heptylamidoethylene, N-hydroxyethylene, N-carboxyethylene amine.	3.4×10^{10}	$>10^{13}$	2.0
Butyl rubber	Stearylamine ethylene oxide adduct (mole ratio 1:100)	9.8×10^{10}	$>10^{13}$	4.0
	Barium salt of N-cocopropyl, N'-carboxyethylene, trimethylene diamine	7.9×10^{10}	$>10^{13}$	2.0

As seen from the above Table 2, the insulating compositions of this example had surface resistivities lower than 10^{12} ohms and volume resistivities higher than 10^{10} ohm-cm.

EXAMPLE 2

A sample having a thickness of 5 mm. and a dimension of 15 mm. x 15 mm., and further a hole of a diameter of 1 mm. and a depth of 1 mm. in the center as shown in FIG. 3, was prepared from polyethylene composition obtained by adding 1% by weight of the semiconducting organic compounds as described in the following Table 3 to polyethylene ("NUC 2005") and said sample was put between brass electrodes having a diameter of 50 mm. and a thickness of 3 mm. and the electrodes and the samples were immersed completely in silicon oil in order to avoid creeping discharge and then the upper electrode was connected to a high voltage transformer and the lower electrode was connected to a discharge detector. To this was applied 50 Hz. sine wave A.C. voltage and the sensitivity of the discharge detector was adjusted to 10pc. (picocoulombs) and the voltage, which is applied to the upper electrode, was increased at a rate of 50 v./sec. and the voltage, at which partial discharges occur in the hole of the center of the sample, was determined. The results obtained are shown in the following Table 3.

TABLE 3

Semiconducting organic compound added	Discharge inception voltage, kv. r.m.s.	Surface resistivity, ohm
Polyethylene (NUC 2005) only	15	$>10^{16}$
Stearylamine propylene oxide adduct (mole ratio 1:2)	26.3	3.2×10^{11}
Laurylamine ethylene oxide adduct (mole ratio 1:2)	40 over	3.2×10^{8}
Stearylamine ethylene oxide adduct (mole ratio 1:100)	40 over	1.8×10^{9}
Tallowpropylenediamine ethylene oxide adduct (mole ratio 1:21)	40 over	3.8×10^{9}
Cocopropylenediamine ethylene oxide adduct (mole ratio 1:7)	40 over	1.0×10^{9}
"Denon-331-L" (Marubishi Yuka Co., Ltd.)	40 over	1.2×10^{10}
Calcium salt (1-hydroxy, 1-hydroxyethylene, 2-heptadecyl imidazolinyl) acetic acid	40 over	3×10^{8}
Lead-salt of N-octadecyl β-alanine	40 over	4×10^{9}

NOTE: The amount of the semiconducting organic compounds added is 1% by weight.
The term "40 kv. over" in the above table means that the partial discharge does not occur even at 40 kv.

The sample consisting only of polyethylene (NUC 2005), not containing semiconducting organic compound, developed partial discharges at 15 kv., while the sample containing stearylamine propylene oxide adduct (mole ratio 1:2) developed the partial discharges at 26.3 kv. Moreover, the other samples having lower surface resistivity did not develop the partial discharges even at 40 kv.

From the results of Examples 1 and 2, it is apparent that the partial discharge inception voltage in the void depends upon the surface resistivity of the surface in the void and it can be proved that the above described result of the theoretical analysis is correct.

EXAMPLE 3

Referring to FIG. 4, sample cables with different insulating layers were manufactured by successively extruding on stranded conductors **2**, each having 250 mm.^{2} cross-sectional area, (a) a 0.8 mm.-thick strand shielding layer **4**, (b) a 4 mm.-thick insulation layer **1** consisting of one of substrates as shown in Table 4 and one of semiconducting organic compounds added in the quantity as shown in Table 5, and (c) a 0.8 mm.-thick semiconducting insulation shield layer **5**. A 0.1 mm.-thick and 35 mm.-wide copper tape **6** was wound on the semiconducting insulation shield layer **5**, as a conductive shield layer, with ¼ lap. and a 0.2 mm.-thick cotton tape **7** was wound on the conductive shield layer **6** to form a holding layer, and then a 3 mm.-thick sheath **8** was made by extruding polyvinyl chloride on the holding layer.

Each power cable thus manufactured was left to stand for three days, and about 20 meter-long samples were cut off from the cables, respectively. Both ends of the sample were stripped in a step-like form and provided with bellmouthed stress cones. The outer shield was grounded through a discharge detector of sensitivity of 1 pc. The discharge inception voltage was determined by applying a 50 Hz. alternating voltage of sinusoidal waveform across the central conductor and the ground. The results are shown in Table 5.

TABLE 5

Sample No.	Substrate as shown in Table 4	Semi-conducting organic compound [1]	Added amount, percent by weight	Discharge inception voltage (kv.) RMS
1	Polyethylene	None	0	13.2
2	do	1	1.0	70.1
3	do	2	1.0	68.8
4	do	3	0.5	72.1
5	do	4	1.0	65.9
6	Cured polyethylene	None	0	14.6
7	do	1	1.0	74.9
8	do	2	1.0	80.5
9	do	3	0.5	71.1
10	do	4	1.0	76.5
11	Butyl rubber	None	0	15.7
12	do	1	3.0	77.4
13	Ethylene propylene rubber	1	3.0	79.6
14	Ionomer ("Surlyn A")	None	0	16.8
15	do	1	1.0	84.3
16	Polyvinyl chloride	None	0	16.3
17	do	1	4.0	65.0

[1] 1=Laurylamine ethylene oxide adduct (mole ratio 1:2); 2=Cocopropylenediamine ethylene oxide adduct (mole ratio 1:7); 3=Calcium salt of (1-hydroxy, 1-hydroxyethylene, 2-heptadecyl imidazolinyl) acetic acid; 4="Denon-331-L" (made by Marubishi Yuka Co.).

In Table 5, the cable of sample No. 1, the insulation of which was composed only of polyethylene and did not contain the semiconducting organic compounds, had a discharge inception voltage of 13.2 kv., while the cable of sample No. 2, the insulation of which was composed of polyethylene and 1% by weight of laurylamine ethylene oxide adduct (mole ratio 1:2), had a high discharge inception voltage of 70.1 kv.

Furthermore, in the cables of sample Nos. 6, 11, 14 and 16 consisting only of cured polyethylene, butyl rubber, ethylene acrylic acid metal salt copolymer, polyvinyl chloride, which did not contain the semiconducting compounds, the discharge inception voltages were from 14.6 kv. to 16.8 kv., while in the cables of sample Nos. 2, 3, 4, 5, 7, 8, 9, 10, 12, 15, and 17 using the compositions which contain the semiconducting organic compounds, the discharge inception voltages were remarkably high as 65.9 kv. to 84.3 kv. and improved to about four times.

TABLE 4

Substrate	Ingredients	Part by weight
Polyethylene	Polyethylene "NUC 2005" (made by Nippon Unicar Co.)	100
Ionomer	Ionomer "Surlyn A 1600" (made by du Pont)	100
Cured polyethylene	Polyethylene "NUC 2005" (made by Nippon Unicar Co.)	100
	Dicumyl peroxide	3.0
	4,4-thio bis-6-tert butyl p-methyl cresol	0.5
Butyl rubber	Butyl rubber (polymer corp. "Polysar butyl 100")	100
	Zinc oxide	5
	Stearic acid	0.5
	Calcined hard clay "Whitetex No. 2" (made by Freeport Kaolin Co.)	10.0
	Medium thermal carbon black "MT carbon black"	10
	Red lead	10
	Dibenzo quinone dioxime	6
	Sulfur	0.5
	Liquid aromatic hydrocarbon ("Kenflex n" made by Kenrich Petro Chemicals, Inc.)	7
Ethylene propylene rubber	Ethylenepropylene rubber "Dutral N" (made by Montecatini Soc. Gen. Ind.)	100
	Zinc oxide	5
	Polymerized trimethyldihydro quinoline "Age Rite Resin D"	1.5
	Lead oxide	3
	SRF black	5
	Calcined clay	11.0
	Triallyl cyanurate	1.5
	Dicumyl peroxide (40% active) "Di-cup 40C" (made by Hercules Co.)	7
Polyvinyl chloride	Polyvinylchloride	100
	Dioctylphthalate	50
	Tribasic lead sulfate	5
	Dibasic lead stearate	1
	Calcined clay	10
	Antimony trioxide	3

In Example 3, the insulation layers were formed by the extrusion process, and the insulation layer can be formed not only by one-layer extrusion but also by multi-layer extrusion.

Furthermore, in cables, the insulation of which is formed by winding or covering conductor with an insulating tape manufactured by the compositions according to the present invention, it is apparently expected from the theory of the present invention, that the same effect as that of the cable manufactured by the above extrusion process can be obtained.

EXAMPLE 4

From the power cable insulated by the cured polyethylene of sample No. 7 manufactured in Example 3, six samples each having a length of 5 meters, were cut oc and as shown in FIG. 4, the insulation layer **1** of one end of each sample was stripped in a tapered shape to expose 50 mm. of the conductor **2**, and a sleeve **3** was put over the stripped ends of two samples and then compressed to connect the two conductors electrically and mechanically. Then, the semiconducting insulation shield layers **5** and **5'**, shield copper tapes **6** and **6'**, holding layers of cotton tapes **7** and **7'** and polyvinyl chloride sheaths **8** and **8'** were stripped in a step-like manner successively in the vicinity of connecting portions of each cable. Thereafter, a semiconducting insulation shield layer **9** composed of semiconductive cured polyethylene was provided surrounding the sleeve and across the inner semiconducting insulation layers of the cables **4** and **4'**. An insulating layer **10**, according to the present invention, was formed around the semiconducting shield layer **9** and the exposed portions of the insulation layers **1**, **1** of the two cable ends, by winding a 0.15 mm.-thick and 20 mm.-wide vulcanizable polyethylene tape. The tape was prepared by using the composition No. 6, 7 or 9 in Table 5. The tape was wound until the thickness of the insulation layer **10** on the conneceing sleeve **3** became the same as that of the insulation layer **1** of both the cables being connected.

Thereafter, a mold of desired shape was attached to said insulating layer **10**, and pressed while being heated at 160° C.±2° C. for 50 minutes to vulcanize the insulating layer **10**. Then, the mold was cooled while maintaining the pressure.

Then the mold was removed and a semiconductive rubber tape was wound on the pressed portion and across both the outer semiconducting insulation shield layers of the left and right cables to form a semiconducting insulation shield layer **11** and then in the same manner a shield layer **12** and a sheath layer **13** were provided successively by using a copper tape and a polyvinyl chloride tape. The discharge inception voltage of the cable joint thus formed was measured, and the results are shown in Table 6.

TABLE 6

Insulating tape used in the connected portion	Discharge inception voltage of the connected portion (kv.) (RMS)
Cured polyethylene tape containing no semiconducting organic compound	11.7
Cured polyethylene tape containing 1% by weight of laurylamine ethylene oxide adduct (mole ratio 1:2)	70.0
Cured polyethylene tape containing 0.5% by weight of calcium salt of (1-hydroxyl, 1-hydroxyethlyene, 2-heptadecyl imidazolinyl) acetic acid	68.4

The cable joints using insulating tapes composed of the compositions according to the present invention did not develop any partial discharges in the interior, so that the discharge inception voltage of the joint portion was considerably higher than that of known cable joint of similar dimension.

EXAMPLE 5

One end of the power cable insulated with the cured polyethylene of sample No. 7 manufactured in Example 3 was sharpened in a pencil form as shown in FIG. 5 so that the conductor **2** was exposed from the insulation layer **1** and further the semiconducting insulation shield layer **5**, the copper tape layer **6**, the holding layer of cotton tape **7** and the polyvinyl chloride sheath layer **8** were stripped in a step-like manner successively and then an insulating reinforcing body **23**, which contained a bell-mouthed stress cone **22** composed of semiconductive rubber and was made of cured polyethylene composition containing 2% by weight of laurlyamine ethylene oxide adduct (mole ratio 1:2), was put over the stripped portion until one end of the stress cone **22** contacts with the semiconducting insulation shield layer **5** on the cable, and on the contacted portion was wound a cured semiconductive rubber tape **11** to connect stress cone **22** and shield layer **5** tightly and electrically. A polyvinyl chloride tape **13** was wound on the semiconducting rubber tape layer **11**, the remaining portion of the shield layer **5**, the copper tape layer **6**, the cotton tape layer **7**, and the edge portion of the sheath **8**, so that the connection between the cable and the insulating reinforcing body **23** is strengthened. Thereafter, the top of the conductor **2** exposed from the insulation layer **1** was provided with a terminal **21**, whereby a plug-in type end portion of cable was accomplished.

Furthermore, in order to compare with the above described product, another end portion of cable having the same structure as described above was manufactured in the same manner, except that insulating reinforcing body made of cured polyethylene composition alone was used.

The discharge inception voltages were determined with respect to these two end portions of cables, to obtain the results as shown in the following Table 7:

TABLE 7

Cable end:	Discharge inception voltage (RMS)
With insulation according to the present invention	[1] 30 over
Without insulation according to the present invention	14

[1] The term "30 over" means that partial discharge did not occur even at 30 kv.

EXAMPLE 6

To 100 parts by weight of polyethylene added was 0.5 parts by weight of semiconducting organic compound (trademark "Denon–331–L" made by Marubishi Yuka Co., Ltd.), and the mixture was milled until the semiconducting organic compound was homogeneously mixed. The mixture was formed into 0.15 mm.-thick films by a calender roll, and 0.35 mm.-thick adhesive layers composed of compositions as shown in Table 8 were applied on the films, respectively. The films with the adhesive layers were cut into 20 mm.-wide insulating tapes A. For comparison with these tapes A, another insulating tape B was prepared, which had the same structure as the tape A except that the semiconducting organic compound "Denon–331–L" was not included in either the composition of the film of the adhesive.

The two insulating tapes A and B, thus manufactured, were used for forming the insulation layers **10** of cable joints of the construction as described in Example 4. More particularly, two cable joints of the construction of FIG. 4 were prepared by forming their insulating layers **10** by winding the insulating tape A and the insulating tape B, respectively. The discharge inception voltages of the cable joints were measured, and the results are shown in Table 9.

TABLE 8

Composition of adhesive layer	Content, percent by weight
Butyl rubber	44
Polyethylene	25
Polyisobutylene	21.5
Light oil	8.0
Aldole α-naphthyl diamine	1.0
Denon–331–L	0.5

TABLE 9

Insulating tape used for formation of insulation layer on the connected portion of conductors:	Discharge inception, voltage (kv.)
Insulating tape:	
A	[1] 25 over
B	10.2

[1] The term "25 over" means that the partial discharge did not occur even at 25 kv.

It is apparent from the above examples that the electric insulated conductor according to the present invention, such as cables, cable joints, and cable ends, have a much higher discharge inception voltage than that of conventional insulated conductor of the corresponding dimensions. In Examples 4 and 5, cured polyethylene was used as the substrate, but the present invention is not restricted to such substrate. In fact, any other rubber or plastics material can be used as the substrate of the present invention, as long as one or more of the aforesaid semiconducting organic compounds are added in excess of their solubility in the substrate.

What is claimed is:

1. An insulated electrical conductor rated at higher than about 5 kv, wherein the electric insulation of the conductor consists mainly of rubber, plastic insulating composition, or mixture thereof, and contains 0.1% to 10% by weight of an organic semiconducting material, said insulation having a surface resistivity of less than 10^{12} ohms on all surfaces including the surfaces of voids and a volume resistivity of greater than 10^{10} ohms-cm.

2. An insulated electrical conductor according to claim 1, characterized in that said rubber is selected from the group conseisting of natural rubber, butyl rubber, ethylene-propylene rubber, and ethylene-propylene-diene ternary copolymerized elastomer.

3. An insulated electrical conductor according to claim 1, characterized in that said plastic is selected from the group consisting of high density polyethylene, low density polyethylene, ethylene-acrylic acid metal salt copolymer, ethylene-vinyl acetate copolymers, and polyvinyl chloride.

4. An insulated electrical conductor according to claim 1, characterized in that said mixture consists of rubber selected from the group consisting of natural rubber, butyl rubber, ethylene-propylene rubber, and ethylene-propylene-diene ternary copolymerized elastomer, and plastic composition selected from the group consisting of high density polyethylene, low density polyethylene, ethylene acrylic acid metal salt copolymer, and ethylene-vinyl acetate copolymers.

5. An insulated electrical conductor according to claim 1, charaterized in that said insulation contains at least one cross-linking agent, said insulation being cured by the cross-linking agent.

6. An insulated electrical conductor according to claim 5, characterized in that said cross-linking agent used for the curing of said insulation is selected from the group consisting of organic peroxides, sulfur, and quinone dioxime.

7. An insulated electrical conductor according to claim 1, characterized in that said insulation contains at least one filler to be compounded with the insulation.

8. An insulated electrical conductor according to claim 1, characterized in that said insulation contains at least one plasticizer to be compounded with the insulation.

9. An insulated electrical conductor according to claim 1, characterized in that said insulation contains at least one stabilizer to be compounded with the insulation.

10. An insulated electrical conductor according to claim 1, characterized in that said insulation contains at least one accelerator to be compounded with the insulation.

11. An insulated electrical conductor according to claim 1, characterized in that said semiconducting organic material is selected from the group consisting of alkylamine ethylene oxide adducts, alkyldiamine ethylene oxide adducts, imidazoline ethylene oxide adducts, alkylamine propylene oxide adducts, metal salts derived from alanine-type amphoteric surfactants, metal salts derived from diamine-type amphoteric surfactants, metal salts derived from imidazoline-type amphoteric surfactants, metal salts derived from amido-amino-type amphoteric surfactants, and a mixture thereof.

12. An insulated electrical conductor according to claim 1, characterized in that said insulated electrical conductor is an electric power cable.

13. An insulated electrical conductor according to claim 1, characterized in that said insulated conductor is an electric power able connector assembly having a pair of conductor elements being connected thereby.

14. An insulated electrical conductor according to claim 1, characterized in that said electrical conductor is an electric power cable terminal assembly.

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HAROLD ANSHER, Primary Examiner

M. E. McCAMISH, Assistant Examiner

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