667430 AUSTRALIA

P/00/001 28/5/91
Section 29

3

Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, being the persons identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

[71]	Applicant:	DOW CORNING CORPORATION
	Address:	MIDLAND, MICHIGAN 48686-0994, UNITED STATES OF AMERICA
[70]	Nominated Person:	DOW CORNING CORPORATION
	Address:	MIDLAND, MICHIGAN 48686-0994, UNITED STATES OF AMERICA
[54]	Invention Title:	METHOD FOR ENHANCING THE DIELECTRICAL STRENGTH OF CABLE USING A FLUID MIXTURE
[72]	Name(s) of actual inventor(s):	DON LEE KLEYER, WAYNE JOSEPH CHATTERTON, MARIS JAZEPS ZIEMELIS, GARY ALLEN VINCENT and GLEN JOHN BERTINI

[74] Address for service in Australia: c/o WATERMARK PATENT & TRADEMARK ATTORNEYS, of The Atrium, 290 Burwood Road, Hawthorn, Victoria 3122, Australia Attorney Code: WM

BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
049,935	UNITED STATES OF AMERICA	US	20 APRIL 1993

Basic Applicant(s): DON LEE KLEYER, WAYNE JOSEPH CHATTERTON, MARIS JAZEPS ZIEMELIS, GARY ALLEN VINCENT and GLEN JOHN BERTINI

Drawing number recommended to accompany the abstract ....

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

....

Ian A. Scott
Registered Patent Attorney

DATED this 18th day of April 1994.

M055 12 8 18 04 94

P/00/008b 12/11/91
Section 29 (1)
Regulation 3.1 (2)

AUSTRALIA

Patents Act 1990

NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, **DOW CORNING CORPORATION** of Midland, Michigan 48686-0994, United States of America, being the applicant in respect of Application No. **60527/94** state the following:-

The person nominated for the grant of the patent has entitlement from the actual inventors as the result of an Assignment dated April 16, 1993.

The person nominated for the grant of the patent has entitlement from the applicants of the basic application listed on the patent request form as the result of an Assignment dated April 16, 1993.

The basic application listed on the patent request form is the first application made in a convention country in respect of the invention.

DOW CORNING CORPORATION
By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

4 December, 1995.

Ian A. Scott
Registered Patent Attorney

AU9460527

(12) PATENT ABRIDGMENT (11) Document No. AU-B-60527/94
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 667430

(54) Title
METHOD FOR ENHANCING THE DIELECTRICAL STRENGTH OF CABLE USING A FLUID MIXTURE

International Patent Classification(s)
(51)^5 **H01B 007/28**

(21) Application No. : **60527/94** (22) Application Date : **18.04.94**

(30) Priority Data

(31) Number	(32) Date	(33) Country
049935	**20.04.93**	**US UNITED STATES OF AMERICA**

(43) Publication Date : **27.10.94**

(44) Publication Date of Accepted Application : **21.03.96**

(71) Applicant(s)
DOW CORNING CORPORATION

(72) Inventor(s)
DON LEE KLEYER; WAYNE JOSEPH CHATTERTON; MARIS JAZEPS ZIEMELIS; GARY ALLEN VINCENT; GLEN JOHN BERTINI

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

(56) Prior Art Documents
US 5200234
US 4766011
US 4372988

(57) Claim

1. A method for enhancing the dielectric properties of an electrical cable having a central stranded conductor encased in a polymeric insulation, the cable having an interstitial void space in the region of the conductor, said method comprising supplying said interstitial void space with a fluid mixture comprising

(A) at least one antitreeing agent; and

(B) a water-reactive compound,

said water-reactive compound (B) having a diffusion coefficient of at least 1×10^{-7} cm^2/second at 50°C. in said polymeric insulation and said fluid mixture having an initial viscosity of ≤ 100 cP (mPa·s) at 25°C.

P/00/011 28/5/91
Regulation 3.2(2)

AUSTRALIA

Patents Act 1990

667430

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:
Lodged:

Invention Title: METHOD FOR ENHANCING THE DIELECTRICAL STRENGTH OF CABLE USING A FLUID MIXTURE

The following statement is a full description of this invention, including the best method of performing it known to us :-

METHOD FOR ENHANCING THE DIELECTRICAL STRENGTH OF CABLE USING A FLUID MIXTURE

The present invention relates to a method for enhancing the dielectric strength of an electrical distribution cable. More particularly, the instant invention relates to a method of contacting the interior of the cable with a fluid mixture which comprises a liquid antitreeing agent and a water-reactive compound, the latter having a diffusion coefficient of at least 1×10^{-7} cm^2/second at 50°C. in the polymeric insulation of the cable.

A major problem associated with electrical distribution cable is its tendency, over a period of time, to fail due to the progressive degradation of its insulation.

"Water treeing," is observed when the insulation material is simultaneously exposed to moisture and an electric field. This mechanism is much more gradual than electrical treeing, requiring an extended period of time to cause the degree of damage that affects the insulation characteristics of the distribution cable. However, since water treeing occurs at considerably lower electrical fields than required for the formation of electrical trees, this phenomenon is thought to be a leading cause of reduced service life of cables. As a partial answer to industry's desire to extend the useful life of existing underground cables, it has been found that certain tree retardants can be introduced into the cable's interior to partially restore the insulation performance.

United States Patent No. 5,200,234, assigned to the assignee of the present invention, disclosed a method for restoration of in-service electrical cable. The cable is first positioned within a surrounding conduit and the space between the cable and the conduit is then filled with a homogeneous mixture of a silane antitreeing agent and a dielectric oil. The dielectric oil is completely miscible with said antitreeing agent and has a solubility in the polymeric insulation of the cable of less than 5 weight percent. This cable reclamation method is effective but typically requires a long exposure time to obtain a fully treated cable. As a consequence, a contractor might find it economically equivalent, or even advantageous, to completely replace a cable once it has deteriorated rather than avail himself of this restorative method.

Applicants have extensively investigated the methods taught by US-A 4,766,011 and US-A 5,200,234 and have found them to be limited by a heretofore undisclosed phenomenon whereby the use of the suggested restorative fluids of these patents results in a highly asymmetric treatment of the cable insulation. This asymmetry, which is further described infra, has been correlated to a lower level of dielectric breakdown strength of the treated cable. Due in part to the finding of this asymmetry, the inventors of the claimed invention now teach a method which overcomes this disadvantage and achieves a much more symmetrical distribution of dielectric enhancing fluid in the treated cable insulation. Moreover, the instant method also produces a significant reduction in overall cable treatment time.

The instant invention therefore relates to a method for enhancing the dielectric properties of an electrical cable having a central stranded conductor encased in a polymeric insulation, the cable having an interstitial void space in the region of the conductor, the method comprising supplying the interstitial void space of the cable with a fluid mixture comprising

(A) at least one antitreeing agent; and
(B) a water-reactive compound,

said compound (B) having a diffusion coefficient of at least $1 \times 10^{-7} cm^2$/second at 50°C. in the insulation polymer and the fluid mixture having an initial viscosity of ≤100 cP (mPa·s) at 25°C.

Figure 1 is a graph showing the (50% probability) dielectric breakdown stress of treated cables as a function of the (log) diffusion coefficient of the treating fluid at 50°C.

Figure 2 is a cross-section depiction of a cable treated with phenylmethyldimethoxysilane.

Figure 3 is a cross-section depiction of a cable treated with a mixture of 70 weight percent phenylmethyldimethoxysilane and 30 weight percent dimethyldimethoxysilane.

Figure 4 is a cross-section of a cable treated with a mixture of 70 weight percent phenylmethyldimethoxysilane and 30 weight percent trimethylmethoxysilane.

Figure 5 is a plot of the concentration of phenylmethyldimethoxysilane in the insulation of phase 1 of a treated feeder cable as a function of distance from the conductor shield.

Figure 6 is a plot of the concentration of phenylmethyldimethoxysilane in the insulation of phase 2 of the treated feeder cable of Figure 5 as a function of distance from the conductor shield.

Figure 7 is a plot of the concentration of phenylmethyldimethoxysilane in the insulation of phase 3 of the treated feeder cable of Figure 5 as a function of distance from the conductor shield.

For the purposes of the invention, an in-service cable is generally of the type used in underground residential distribution and typically comprises a central core of a stranded copper or aluminum conductor encased in polymeric insulation. As is well known in the art, there is usually also a semi-conducting polymeric conductor shield positioned between the conductor and insulation as well as a semi-conducting insulation shield covering the insulation. The latter shield is ordinarily wrapped with a wire or metal foil grounding strip and, optionally, is encased in an outer polymeric protective jacket. The insulation is preferably a polyolefin polymer, such as polyethylene or a copolymer of polyethylene and propylene or vinyl acetate. As used herein, the term "in-service" refers to a cable which has been under electrical load and exposed to the elements for an extended period. In such a cable, the electrical integrity of the cable insulation has generally deteriorated to some extent due to the formation of water trees. It is also contemplated, however, that the instant method can be used to enhance the dielectric properties of either a new cable or an in-service cable.

After the cable has been in operation for an extended period, for example 7 to 15 years, the fluid mixture of the invention is introduced into the interstitial void space of the conductor. Alternatively, a representative section of cable can be removed and subjected to dielectric breakdown tests to determine whether a particular installation is a good candidate for the method of the invention.

The method of the present invention can be carried out in the same manner as described in United States Patent No. 4,766,011, assigned to the assignee of the present invention. This patent teaches the dielectric enhancement of a cable by supplying the interstitial void space thereof with an antitreeing fluid and then polymerizing said fluid within said voids. Briefly, the method comprises filling the interstitial void space of the conductor with the fluid mixture according to well known methods. The fluid mixture is then allowed to remain in the cable interior for an appropriate period while it diffuses into the cable's polymeric insulation to fill the water trees, thereby enhancing the dielectric strength of the cable. The time required for treatment is a function of such variables as cable size (insulation thickness), water content of the cable components and treatment temperature. Less time is required when the cable has a thinner insulation and operates at a higher current load. Those skilled in the art will readily determine optimum conditions for a particular situation based on the following disclosure and routine experimentation.

As is also known in the art, the instant method may further comprise a step wherein water present in the conductor interstitial volume may be removed or its quantity reduced prior to the introduction of the fluid mixture. In this operation, a desiccant gas or liquid, such as air, nitrogen, ethanol or isopropanol, is flushed through the cable interior to either physically push out the moisture or mix with the water to facilitate physical removal. Thus, for example, a high velocity dry air stream may be used to blow out bulk water which has accumulated in the void space.

As already noted, the practice of the methods using a fluid according to US-A 4,766,011 or US-A 5,200,234 (e.g., phenylmethyldimethoxysilane) result in an asymmetric distribution of the fluid in the cable's insulation. This asymmetry manifests itself as an irregularly shaped penetration front of the fluid in the insulation cross-section when the cable is cut perpendicular to its longitudinal axis. As used herein, the term "penetration front" is defined as the boundary between untreated polymer and polymer into which at least some fluid has diffused. This asymmetry can be observed visually as a general lightening of the polymer into which the fluid has penetrated. Alternatively, an accurate determination of the penetration front can be made by an infrared micro mapping technique, described infra. Thus, during the early phases of treatment with such a fluid, there can be little or no penetration along a given radial direction. These areas represent weak links in the treatment where dielectric breakdown is more likely to occur than in those areas which have been more extensively penetrated by the fluid. Given sufficient treatment time, the fluid would presumably diffuse into all of the insulation, but it is clearly advantageous to have as symmetric a distribution of the fluid as possible throughout the treatment process.

Although the inventors of the instant method do not wish to be bound by a particular theory or mechanism, it is believed that the degree of the observed asymmetry is related to the compaction of conductor strands during cable manufacture. Thus, when a typical cable is fabricated, its conductor strands are subjected to uneven pressures as the conductor travels between multiple sets of rollers before the shield and insulation are extruded thereover. This can result in significant compaction of some strands such that little fluid can penetrate the strands in this region. On the other hand, where little or no such compaction occurs, the strands form a relatively loose structure and diffusion into the insulation is not impeded. Further compounding this problem, water, which has been absorbed in the narrow regions between conductor strands within the conductor shield, can also retard the penetration of dielectric enhancing fluid.

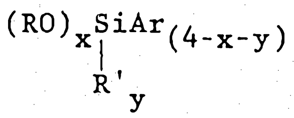
The above described asymmetry can be greatly reduced or eliminated by employing a dielectric enhancing fluid comprising a homogeneous mixture of (A) a conventional antitreeing agent and (B) a water-reactive compound having a diffusion coefficient of at least about 1×10^{-7} cm^2/sec in the cable's insulation at 50°C. Since the fluid must flow through the relatively small cross-sectional area of the cable's interstitial void space, the initial viscosity of this mixture should be no greater than about 100 cP (mPa·s) at 25°C., preferably less than about 20 cP (mPa·s) at 25°C. When the viscosity is greater, filling the cable with the mixture is difficult and/or too time consuming. Further, the skilled artisan will readily appreciate that the fluid mixture must be completely compatible with the materials of construction of the cable. This applies equally to any reaction products it may form with adventitious water. Thus, for example, the fluid must be compatible with both aluminum and copper conductors, must not cause excessive swelling of either the conductor or insulation shields or interact in any untoward manner with the polymeric insulation. It is preferred that the fluid mixture have a vapor pressure below about 30 psi (207 kPa) at the operating temperature of the conductor, which can be as high as 130°C. under emergency conditions, but generally is no more than 90°C.

The conventional antitreeing agent (A) can be selected from compounds known to prevent water trees in polymeric insulation when compounded into the insulation and mixtures thereof. Such compounds are aromatic ketones (e.g., acetophenone), fatty alcohols (e.g., dodecanol) and organoalkoxysilanes and illustrate the range of suitable antitreeing agents which can be employed as component (A). Preferably, component (A) has a diffusion coefficient of at least 1×10^{-8} cm^2/sec and below 1×10^{-7} cm^2/sec in the cable's insulation at 50°C.

It is also preferred that component (A) be capable of reacting with water to polymerize in the cable insulation after diffusing therethrough. This tends to increase the lifetime of the treatment and precludes the need for perpetual maintenance of the dielectric enhancing fluid.

Many such systems have been described in the patent literature and the interested reader is referred to United States Patent No. 4,144,202, United States Patent No. 4,212,756, United States Patent No. 4,299,713, United States Patent No. 4,332,957, United States Patent No. 4,400,429, United States Patent No. 4,608,306 and United States Patent No. 4,840,983, among others.

A particularly preferred silane antitreeing agent is described in United States Patent No. 4,766,011. This compound is represented by the general formula



$$(RO)_x\underset{\underset{R'_y}{|}}{Si}Ar_{(4-x-y)}$$

wherein R is an alkyl radical having 1 to 6 carbon atoms, R' is an alkyl radical having 1 to 6 carbon atoms, Ar is an aromatic group selected from the group consisting of phenyl and benzyl radicals, x is 1, 2 or 3, y is 0, 1 or 2 and $(x + y) \leq 3$. Highly preferred silanes of this type include phenyltrimethoxysilane, diphenyldimethoxysilane, phenylmethyldiethoxysilane and phenylmethyldimethoxysilane, the latter being most preferred.

The water-reactive compound (B) of the present invention is a low molecular weight liquid which is different from component (A), which reacts with water and which has a diffusion coefficient of at least about 1×10^{-7} cm^2/sec in the cable's insulation at 50°C. When the diffusion coefficient of this component is considerably less than that stipulated, not only is the treatment time extended, but the aforementioned asymmetry of the fluid in the cable is increased for a reasonable treatment time, for example 30 to 120 days.

Component (B) may be selected from trialkylalkoxysilanes, dialkyldialkoxylsilanes or organoborates. Component (B) can also be an orthoester having the general structure

$R^1C(OCH_3)_3$, where R^1 is selected from hydrogen or a methyl radical. Alternatively, component (B) can be an enol ether of the general structure $R^3R^4C=C(OR^5)R^6$, where R^3, R^4 and R^6 are independently selected from hydrogen or alkyl radicals having 1 to 3 carbon atoms and R^5 is $-SiR^7{}_3$, in which R^7 is an alkyl radical having 1 to 2 carbon atoms. When the above fluids are allowed to diffuse into polymeric insulation materials, such as polyethylene, it has been found that tree formation in the treated materials is retarded relative to a control or when the fluid does not react with water. Specific examples of suitable water reactive compounds and their respective diffusion coefficients (D) at 50°C. in low density polyethylene (wherein Me denotes a methyl radical and OAc denotes an acetoxy group), include:

$Me_3Si(OMe)$	$(D = 2.4 \times 10^{-7})$	cm^2/s at 50°C.
$(MeO)_3CH$	$(D = 1.7 \times 10^{-7})$	cm^2/s at 50°C.
$(MeO)_3CCH_3$	$(D = 1.0 \times 10^{-7})$	cm^2/s at 50°C.
$(MeO)_3B$	$(D = 2.7 \times 10^{-7})$	cm^2/s at 50°C.
$Me_2Si(OMe)_2$	$(D = 1.4 \times 10^{-7})$	cm^2/s at 50°C.
$CH_2=C(Me)-OSiMe_3$	$(D = 1.5 \times 10^{-7})$	cm^2/s at 50°C.

From the above description, one skilled in the art will readily appreciate that there will be certain combinations of component (A) and component (B) which will not be suitable for the instant process due to the chemical interaction therebetween. For example, when component (A) is an alkoxysilane, component (B) can not be a borate since the latter would react with the silane to form products which would retard diffusion of component (A) in the insulation. Routine experimentation can be applied to determine whether a potentially reactive combination of (A) and (B) is suitable.

For the purposes of the present invention, the amount of the water-reactive compound (B) that is included in the fluid mixture is the least amount needed to reduce the asymmetric penetration front of the antitreeing agent (A) and the appropriate range may be determined by routine experimentation based on the instant disclosure. Typically, the weight percent ratio of component (A) to (B) is in the approximate range 90/10 to 10/90 and is preferably in the range of about 70/30.

When components (A) and (B) are selected from compounds which can form oligomers upon reaction with water, it is preferred that these components have a low water equivalent weight, this being defined as the weight of the compound required to react with one mole of water. This preference is suggested by the observation that the oligomers have significantly lower diffusion coefficients relative to the monomers and by recognition that the intent is to limit the extent of oligomerization in the conductor region so that more of the fluid can penetrate the insulation as quickly as possible and react with the water therein.

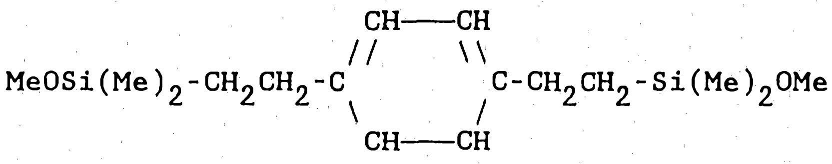
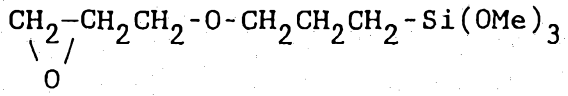
The following examples are presented to further illustrate the method of this invention, but are not to be construed as limiting the invention, which is delineated in the appended claims. All parts and percentages in the examples are on a weight basis and all measurements were obtained at 25°C., unless indicated to the contrary.

Example 1

A cable of the following construction was used in the evaluation of various fluids shown in Table 1: 1/0 AWG stranded aluminum conductor (single strand diameter 0.19 cm), extruded semiconducting conductor shield, 175 mils (4.375 mm) crosslinked polyethylene insulation, extruded semiconducting insulation shield and tinned copper concentric neutral strips. This cable was rated at 15 kV (8.7 kV to ground) and had been aged for 3.5 years while submerged in ambient temperature water. During this aging procedure, the cable was energized at 20 kV to ground (60 Hz AC) and water was also added to the conductor region to further accelerate the aging process.

The aged cable was cut into 90 foot (27.4 m) long sections and each such section was treated with one of the liquids shown in Table 1 according to the following procedure, one untreated section serving as a control. In each case, 0.2 weight percent of a tetraisopropyl titanate catalyst was added to the fluid. Herein, the following notation is used to represent moieties of the chemical structures: Ph = phenyl radical; Me = methyl radical; Et = ethyl radical; Vi = vinyl radical; and AcO = acetoxy group.

Table 1 Fluids Used in Example 1

Fluid	Chemical Structure
3	
5	$(Ph)_2$-$Si(OMe)_2$
6	$ViSi(Me)(OEt)_2$
7	$AcO(-CH_2CH_2O)_4$-$CH_2CH_2CH_2$-$Si(Me)(OMe)_2$
10	NC-CH_2CH_2-$Si(OEt)_3$
13	
14	Ph-CH=N-$CH_2CH_2CH_2$-$Si(OEt)_3$
15	Ph-$Si(Me)(OMe)_2$
16	Ph-C(O)Me
17	CH_2=C(Me)C(O)-$OCH_2CH_2CH_2$-$Si(OMe)_3$
18	CH_2=C(Me)C(O)N(Me)-$CH_2CH_2CH_2$-$Si(OMe)_3$
19	$Me_2Si(OMe)_2$
20	$F_3CCH_2CH_2Si(Me)(OMe)_2$
21	$HO(PhMeSiO)_xH$ where x = 2 to 5
23	$Me_3SiO(Me_2SiO)_2Me_3$

First the interstitial space of the conductor was flushed with isopropanol to remove water therefrom. A volume of the isopropanol equivalent to two interstitial volumes was so employed, one such interstitial volume being allowed to remain in the cable conductor for about 20 hours. A fluid was then injected into the conductor interstitial space. Again, twice the interstitial volume of dielectric enhancing fluid was used to flush out the isopropanol. The final fluid treatment was then introduced to the interstitial space and maintained therein by reservoirs at each end of the cable section, which reservoirs were pressurized using a helium blanket at 12 psi (83 kPa) gauge pressure. This condition was maintained for the first 60 days of treatment, after which the reservoirs were drained of fluid and blanketed with helium at essentially atmospheric pressure. After filling the cable interstices with a dielectric enhancing fluid, the cable was again energized at 20 kV to ground (60 Hz AC) and submersed in ambient temperature water for six months.

At the end of six months, each cable section was cut into five equal test lengths and each length was subjected to alternating current (60 Hz) dielectric breakdown tests. The breakdown tests were performed by increasing the applied voltage in ten percent increments every five minutes until the insulation failed. The results of these tests are presented in Table 2, wherein the statistically calculated breakdown strength is given at 13, 50 and 87% probability, respectively, based on a Weibull distribution.

Table 2 Breakdown Stress at 13, 50 and 87% Probability

Fluid	Breakdown Stress (Volts/mil) (13, 50, 87% probability)
Untreated Control	440, 516, 570
3	635, 966, 1045
5	620, 921, 1085
6	980, 1095, 1185
7	680, 777, 990
10	620, 1042, 1370
13	540, 773, 980
14	400, 738, 980
15	970, 1117, 1170
16	880, 1015, 1210
17	460, 929, 1240
18	550, 725, 975
19	915, 1133, 1320
20	690, 838, 1160
21	465, 509, 560
23	450, 473, 500

In separate experiments, the diffusion coefficient of each fluid of Table 1 was measured at various temperatures in polyethylene. Representative data at 50°C. is shown in Table 3, wherein powers of 10 are written in engineering form such that, for example, 3.6e-8 denotes 3.6×10^{-8}. This table also shows the Arrhenius parameters which can be used to calculate the diffusion coefficient D in the approximate temperature interval of 20 to 70°C. according to the equation: $D = A\ 10^{-Q/T}$ where (A) is the pre-exponential factor, also shown in Table 3 and T is the temperature in degrees Kelvin.

Table 3. Diffusion Coefficient (D) at 50°C. and Arrhenius Factors (A) and (K) for Diffusion of Fluids in Polyethylene.

Fluid	D (cm^2/sec)	Q (K)	A (cm^2/sec)
3	9.4e-9	4004	2.137e4
5	1.6e-8	3742	4.391e3
6	7.7e-8	3676	1.744e4
7	1.1e-8	---	---
10	1.2e-8	4416	6.431e5
14	7.6e-9	4517	7.174e5
15	5.9e-8	3539	5.129e3
16	1.3e-7	5380	3.215e9
17	2.2e-8	4027	6.564e4
18	8.0e-9	5252	1.460e8
19	1.4e-7	3607	1.998e4
20	4.0e-8	3498	3.254e3
21	5.2e-8	2204	3.473e-1
23	7.3e-9	3407	3.671e2

The breakdown data at 50% probability (from Table 2) is plotted as a function of the logarithm of the diffusion coefficient (from Table 3) for the various fluids in Figure 1. All the fluids which do not react with water have been omitted from this plot since these were shown to be inferior with respect to retarding tree formation. Fluids **6** and **10** were also excluded from Figure 1 since it was observed that they interacted with the aluminum conductor to form a gas within the conductor region; these fluids could therefore not be used in the instant method. The data of Figure 1 were used to obtain the least squares linear equation relating the variables: 50% Breakdown Stress = 253.9 (log D) + 2,871 wherein D is the diffusion coefficient and the calculated correlation coefficient (r) is 0.73. From Figure 1 it can be seen that there is a good correspondence between diffusion coefficient of water-reactive fluids and their ability to enhance dielectric strength of the aged cable.

Example 2

Water trees were grown in polyethylene specimens having defects of known dimension as points of initiation. Each polyethylene sample was molded in the shape of a short-walled cup having a 6 mm thick flat bottom. This cup had a diameter of 70 mm and a wall having a height of 16 mm for the purpose of retaining a liquid electrolyte. Simulated defects were created on the inside surface of the cup's bottom by penetrating the surface with a special needle to a depth of 3.2 mm and subsequently withdrawing the needle. The needle had a diameter of 1 mm (+0, -0.03 mm), a tip angle of 30° and a tip radius of 3 ± 1 micrometers. A total of 16 such defects per specimen were created (arranged in a square pattern) in order to provide a basis for statistical analysis.

Each cup containing the simulated defects was treated with one of the fluids shown in Table 4 by total immersion for 7 days at 50°C. Each cup was then partially filled with a saturated aqueous solution of NaCl electrolyte and immersed in a glass dish which also contained some of this electrolyte, the two electrolyte portions being insulated from each other by the wall of the polyethylene cup. A potential of 5,000 volt AC, 3000 Hz, was imposed between the electrolyte in the cup and the electrolyte in the glass dish, the latter being maintained at ground potential.

After a period of 100 hours at room temperature, the defect area was microtomed and stained with methylene blue dye to reveal the resulting trees, the lengths of which were then measured by optical microscopy. The results are presented in Table 4, wherein the standard deviation of tree length is also given.

Table 4

Treatment Fluid	Average Tree Length (Micrometers)	Standard Deviation
None (Control)	242	30.6
Dodecanol	85.8	12.3
Acetophenone	92.8	20.8
$HO(PhMeSiO)_xH$ (x = 2-5)	233.1	43.2
$HO(Me_2SiO)_xH$ (x = 2-5)	199	48.5
$PhSi(Me)(OMe)_2$	20.7	6.8
$Me_2Si(OMe)_2$	21.4	11.8
$(MeO)_3CCH_3$	56.2	12.4
70% $PhSi(Me)(OMe)_2$/ 30% $Me_2Si(OMe)_2$	13.7	5.9
70% $PhSi(Me)(OMe)_2$/ 30% $Me_3Si(OMe)$	26.7	8.5

From Table 4, it can be seen that, while fluids which do not react with water, such as acetophenone, the hydroxy-terminated siloxanes and dodecanol, can retard tree formation relative to an untreated control, their performance is significantly inferior to that obtained from water reactive materials.

Example 3

A 750 kcmil (15 kV rated) crosslinked polyethylene-insulated cable which had been aged under actual field conditions for more than 20 years was removed from service and cut into segments. Each segment was treated by injecting a dielectric enhancing fluid into the interstitial volume of the conductor and maintaining the fluid therein for 20 days at a gauge pressure of 10 psig (69 kPa) and at a temperature of 50°C. The fluids used were:

(a) phenylmethyldimethoxysilane, the preferred fluid of US-A 4,766,011;

(b) a mixture of 30 weight percent dimethyldimethoxysilane and 70 weight percent phenylmethyldimethoxysilane; and

(c) a mixture of 30 weight percent trimethylmethoxysilane and 70 weight percent phenylmethyldimethoxysilane.

To each of these fluids, there was added 0.2 weight percent of tetraisopropyl titanate (TIPT) catalyst just before treating the cable segments.

When the above treatments were completed the cable segments were identically sectioned in a transverse direction and the extent of penetration of the respective fluid in the insulation was determined by micro infrared mapping analysis. According to this procedure, the cable insulation was scanned in a radial direction by microtoming sections thereof perpendicular to the length of the cable and using a Fourier Transform Infrared (FTIR) microscope to determine absorbance at 1260 cm^{-1}. This absorption is due exclusively to the stretching deformation of methyl radicals on silicon in the silane and is therefore related to the silane concentration at a given point in the insulation. Twelve such radial scans were made on each cable section (i.e., at 30° increments about the circumference). In each case, the radial distance at which the treating fluid was no longer detected was recorded, these points defining the fluid's penetration front. This data is presented in Table 5, wherein the outer radius of the cable insulation ranged from about 17,969 to 18,124 micrometers and the inner radius of the insulation was about 13,589 micrometers.

Table 5

Angle of Scan (degrees)	Penetration of Fluid in Insulation (micrometers)		
	Fluid (a)	Fluid (b)	Fluid (c)
0	14094	17659	18124
30	15664	17504	18124
60	13939	16884	18124
90	17969	15489	18124
120	16574	17814	18124
150	15799	16419	18124
180	13589	15954	18124
210	13939	16419	18124
240	13589	15954	18124
270	14404	16264	18124
300	14404	16729	18124
330	14559	15954	18124

Figure 2 depicts the cross-section of the above described cable and illustrates the diffusion of fluid (a) into the polyethylene insulation thereof. This figure illustrates the cable (10) which comprises a conductor consisting of 61 individual strands (5) of 10 gauge aluminum, a conductor shield (6) covering the conductor and insulation (12) covering the conductor shield, said insulation having an inner surface (9) and an outer surface (13). In this figure, the extent of fluid penetration, as presented in Table 5, is indicated by the circled points (8). The line connecting points (8) represents the penetration front, region (7) illustrating the portion of insulation (12) into which the dielectric enhancing fluid has diffused. In a similar manner, Figures 3 and 4 show the penetration profiles for the above described fluids (b) and (c), respectively. In these latter two figures, the conductor and conductor shields have been omitted for the sake of simplicity.

From Figure 2 and Table 5, it can be seen that the penetration front of fluid (a) had a highly asymmetric pattern. Indeed, this fluid was not even detected in at least two of the radial scans. Such areas of little or no penetration represent weak links in the insulation integrity where breakdown is likely to occur in an energized cable. To the contrary, Figure 3 indicates that the cable treated according to the method of the present invention using fluid (b) under identical conditions had a much more symmetrical penetration front. In this case, all radial directions showed at least some penetration of the treating fluid and the overall penetration was demonstrably greater. This effect was even more pronounced when fluid (c) was used to similarly treat the cable. As shown in Figure 4, the fluid had completely penetrated the insulation to present a symmetrical "front" which, for all practical purposes, was coincident with the outer perimeter of the cable's insulation.

Example 4

A feeder cable comprising three phases (each 1,000 kcmil, 15 kV-rated crosslinked polyethylene insulation, 61 strand aluminum conductor) which had been in the field for about 23 years was removed from service and treated with an antitreeing fluid of the prior art. The conductor interstitial volume was first flushed with methanol, whereupon phenylmethyldimethoxysilane was introduced and allowed to remain therein for 100 days while the cable was in service. After this treatment, each phase of the cable was subjected to dielectric breakdown testing. Each phase was also sectioned in a transverse direction at the same longitudinal location of the cable for comparison purposes. Upon visual inspection, the cross-section of each phase was observed to have an asymmetric penetration front. The above described micro mapping technique was used to scan four radial directions (i.e., at 90° increments) of each cross-section. A quantitative determination of the amount of phenylmethyldimethoxysilane at various points along each radius was made based on previous calibrations using polyethylene samples which contained known concentrations of this fluid. The results of these experiments are presented in graphical form in Figures 5 through 7 for phases 1 through 3, respectively. In these figures, the concentration of the fluid as a weight/volume percent (grams/cm^3 x 100) is plotted against the radial distance from the conductor shield (mils) at 0, 90, 180 and 270 degrees relative to an arbitrary zero. The penetration of fluid in the case of phase 1 is seen to be considerably greater along each radial direction than in the case of either phase 2 or phase 3, wherein at least two of the radial scans showed essentially no penetration. The extent of this penetration and improved symmetry were found to be directly correlated with the breakdown strength of the three phases, these being 284 (phase 1), 196 (phase 2) and 202 (phase 3) volts/mil, respectively.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:
~~Claims:~~

1. A method for enhancing the dielectric properties of an electrical cable having a central stranded conductor encased in a polymeric insulation, the cable having an interstitial void space in the region of the conductor, said method comprising supplying said interstitial void space with a fluid mixture comprising

(A) at least one antitreeing agent; and

(B) a water-reactive compound,

said water-reactive compound (B) having a diffusion coefficient of at least 1×10^{-7} cm^2/second at 50°C. in said polymeric insulation and said fluid mixture having an initial viscosity of ≤100 cP (mPa·s) at 25°C.

2. The method according to claim 1, wherein said water-reactive compound (B) is selected from the group consisting of trialkylalkoxysilanes and dialkyldialkoxylsilanes.

3. The method according to claim 1, wherein said water-reactive compound (B) is an orthoester having the general structure $R^1C(OCH_3)_3$, where R^1 is selected from hydrogen or a methyl radical.

4. The method according to claim 1, wherein said water-reactive compound (B) is an enol ether having the general structure $R^3R^4C=C(OR^5)R^6$, where R^3, R^4 and R^6 are independently selected from hydrogen or alkyl radicals having

1 to 3 carbon atoms and R^5 is $-SiR^7{}_3$, in which R^7 is an alkyl radical having 1 to 2 carbon atoms.

5. The method according to claim 1, wherein said water-reactive compound (B) is an organoborate.

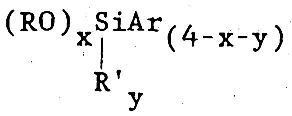
6. The method according to claim 2, wherein said water-reactive compound (B) is selected from trimethylmethoxysilane or dimethyldimethoxysilane.

7. The method according to claim 3, wherein said water-reactive compound (B) is $(MeO)_3CCH_3$, wherein Me denotes a methyl radical.

8. The method according to claim 4, wherein said water-reactive compound (B) is $CH_2=C(Me)-OSiMe_3$, in which Me denotes a methyl radical.

9. The method according to claim 5, wherein said water-reactive compound (B) is $(MeO)_3B$, in which Me denotes a methyl radical.

10. The method according to claim 1, wherein the antitreeing agent (A) is represented by the general formula



$$(RO)_x\underset{R'_y}{\underset{|}{Si}}Ar_{(4-x-y)}$$

wherein R is an alkyl radical having 1 to 6 carbon atoms, R' is an alkyl radical having 1 to 6 carbon atoms, Ar is an aromatic group selected from the group consisting of phenyl and benzyl radicals, x is 1, 2 or 3, y is 0, 1 or 2 and $(x + y) \leq 3$.

11. The method according to claim 10, wherein said antitreeing agent (A) is selected from of phenyltrimethoxysilane, diphenyldimethoxysilane, phenylmethyldiethoxysilane and phenylmethyldimethoxysilane.

12. The method according to claim 11, wherein said antitreeing agent (A) is phenylmethyldimethoxysilane and said water-reactive compound (B) is selected from the group consisting of dimethyldimethoxysilane and trimethylmethoxysilane.

DATED this 18th day of April 1994.

DOW CORNING CORPORATION

WATERMARK PATENT & TRADEMARK ATTORNEYS
"THE ATRIUM"
290 BURWOOD ROAD
HAWTHORN. VIC. 3122.

METHOD FOR ENHANCING THE DIELECTRICAL STRENGTH OF CABLE USING A FLUID MIXTURE

ABSTRACT

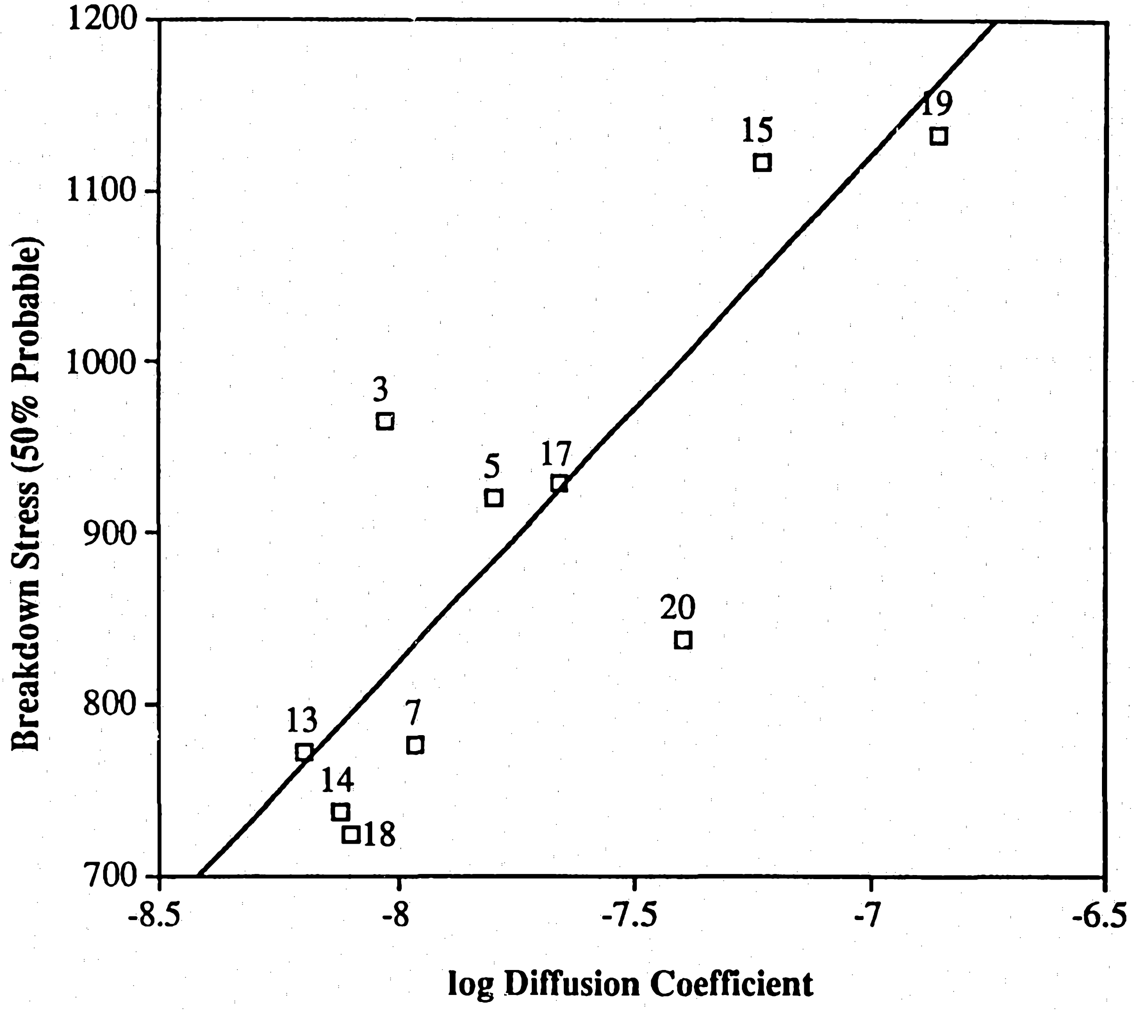
A method for enhancing the dielectric properties of new or in-service electrical cable is disclosed, the method comprising supplying the interstitial void space of the cable's conductor with a fluid mixture comprising

(A) an antitreeing agent; and

(B) a water-reactive compound,

wherein (B) has a diffusion coefficient of at least 1×10^{-7} cm^2/second at 50°C. in the insulation of the cable and the mixture has an initial viscosity of ≤ 100 cP (mPa·s) at 25°C. The instant method provides a more symmetrical distribution of dielectric enhancing fluid in the insulation than prior art approaches and results in a significant reduction in cable treatment time.

Figure 1.


1200
1100
1000
900
800
700
Breakdown Stress (50% Probable)
-8.5
-8
-7.5
-7
-6.5
log Diffusion Coefficient
15
19
3
5
17
20
13
7
14
18

60527/94

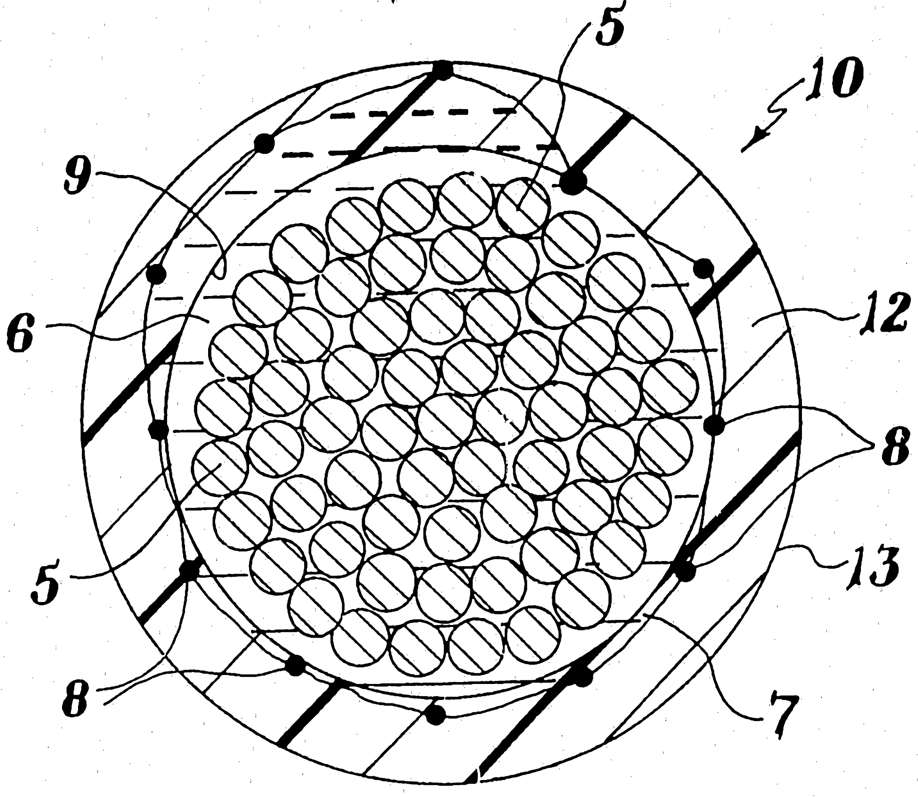


FIG. 2

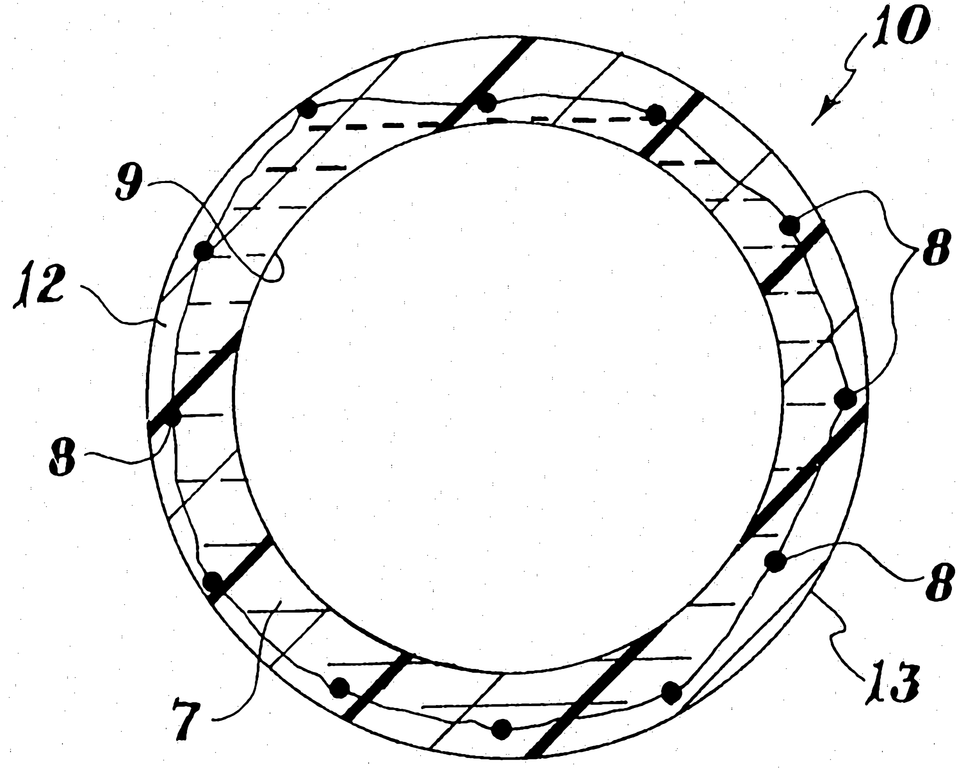


FIG. 3

605527/94

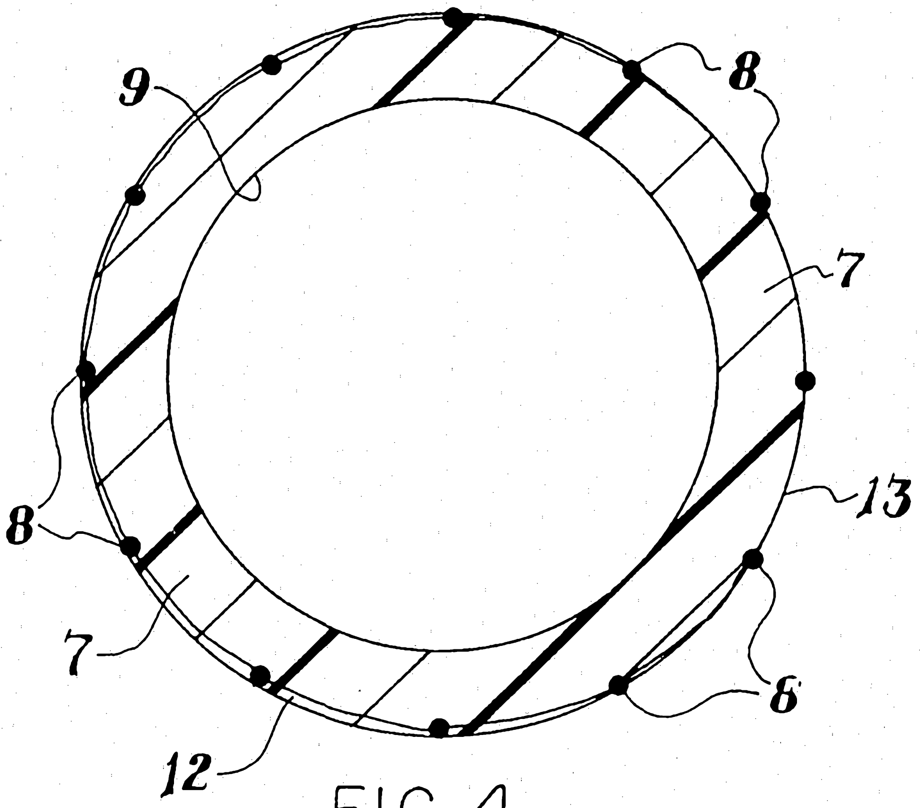


FIG. 4

Figure 5.

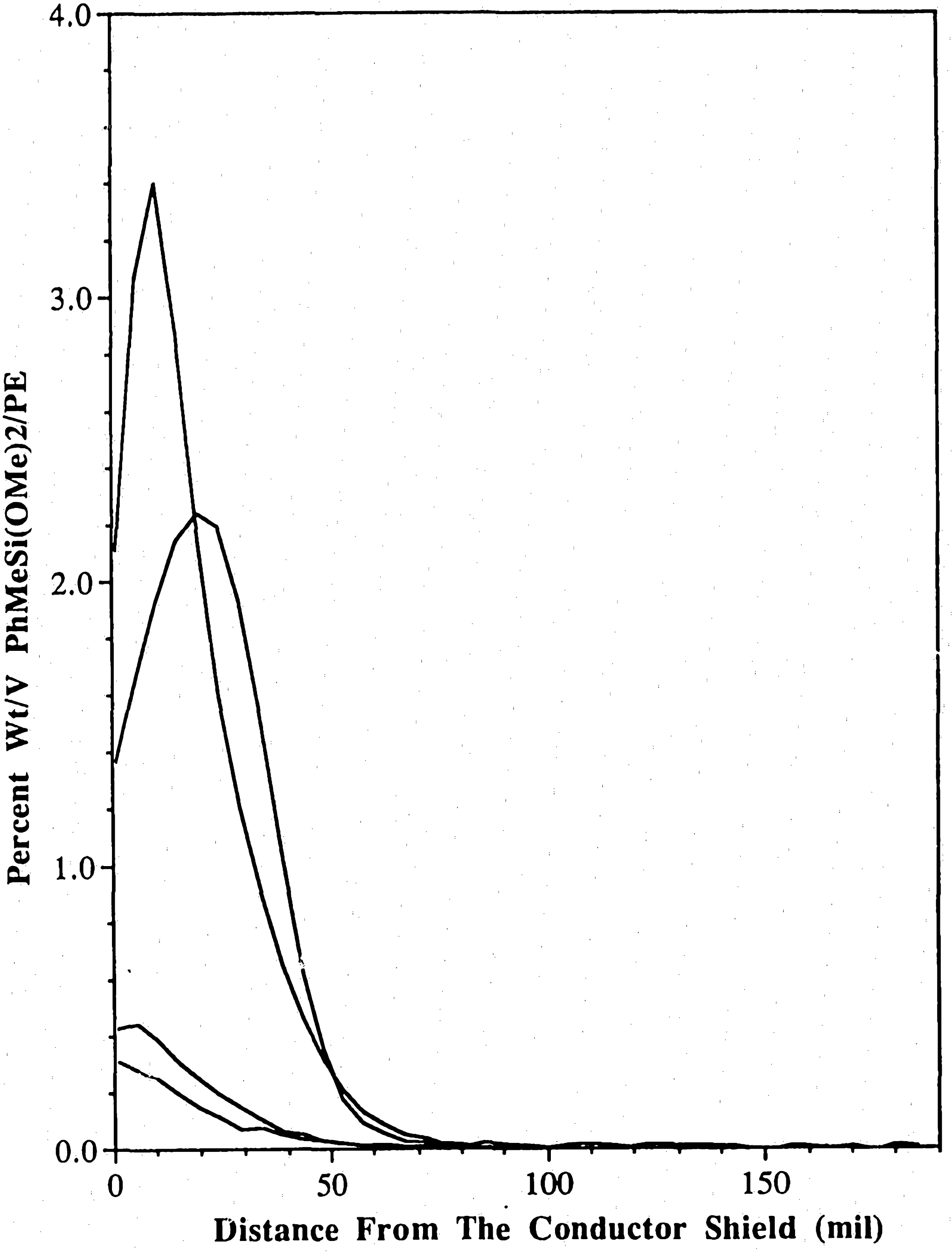

4.0
3.0
2.0
1.0
0.0
0
50
100
150
Percent Wt/V PhMeSi(OMe)2/PE
Distance From The Conductor Shield (mil)

Figure 6.

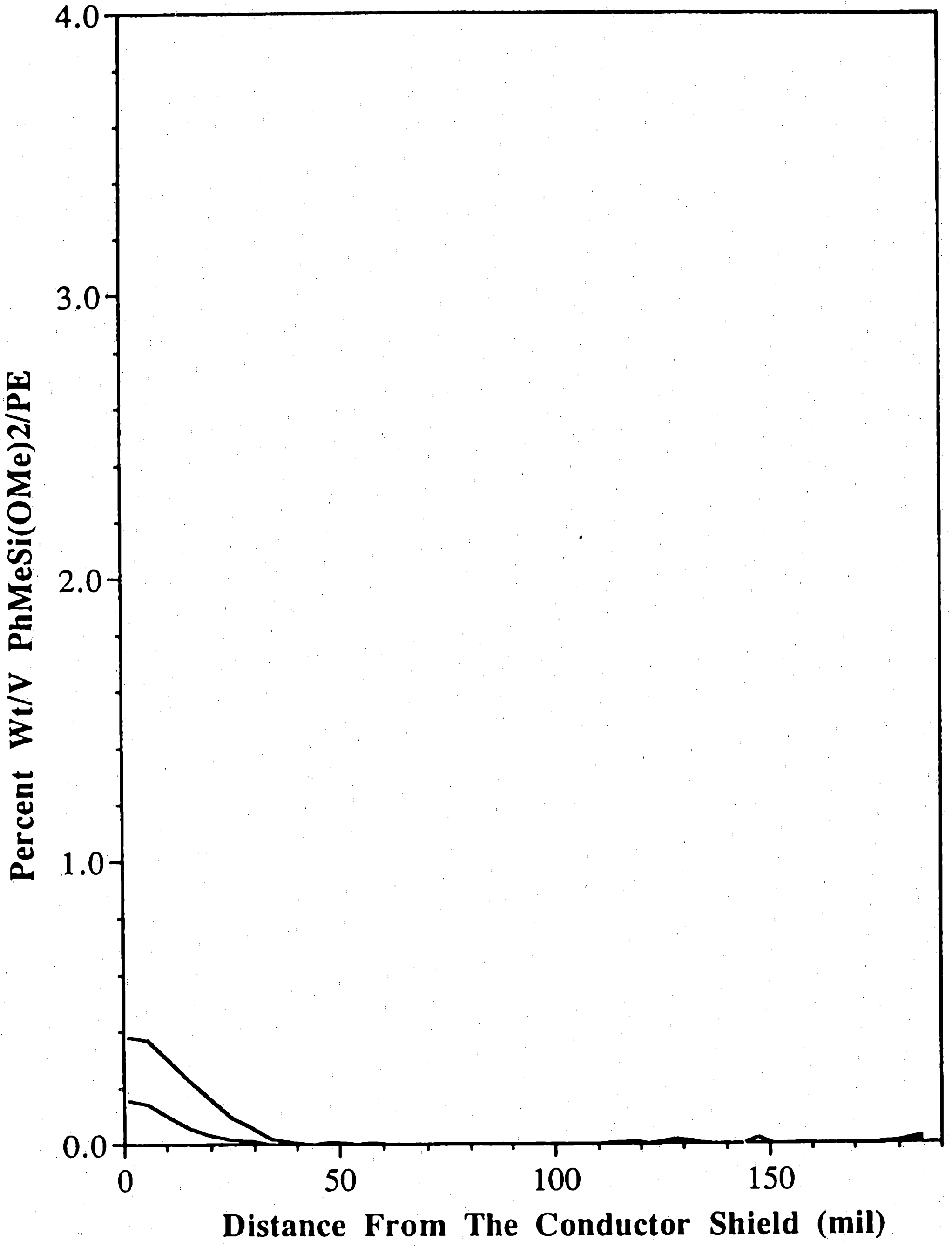
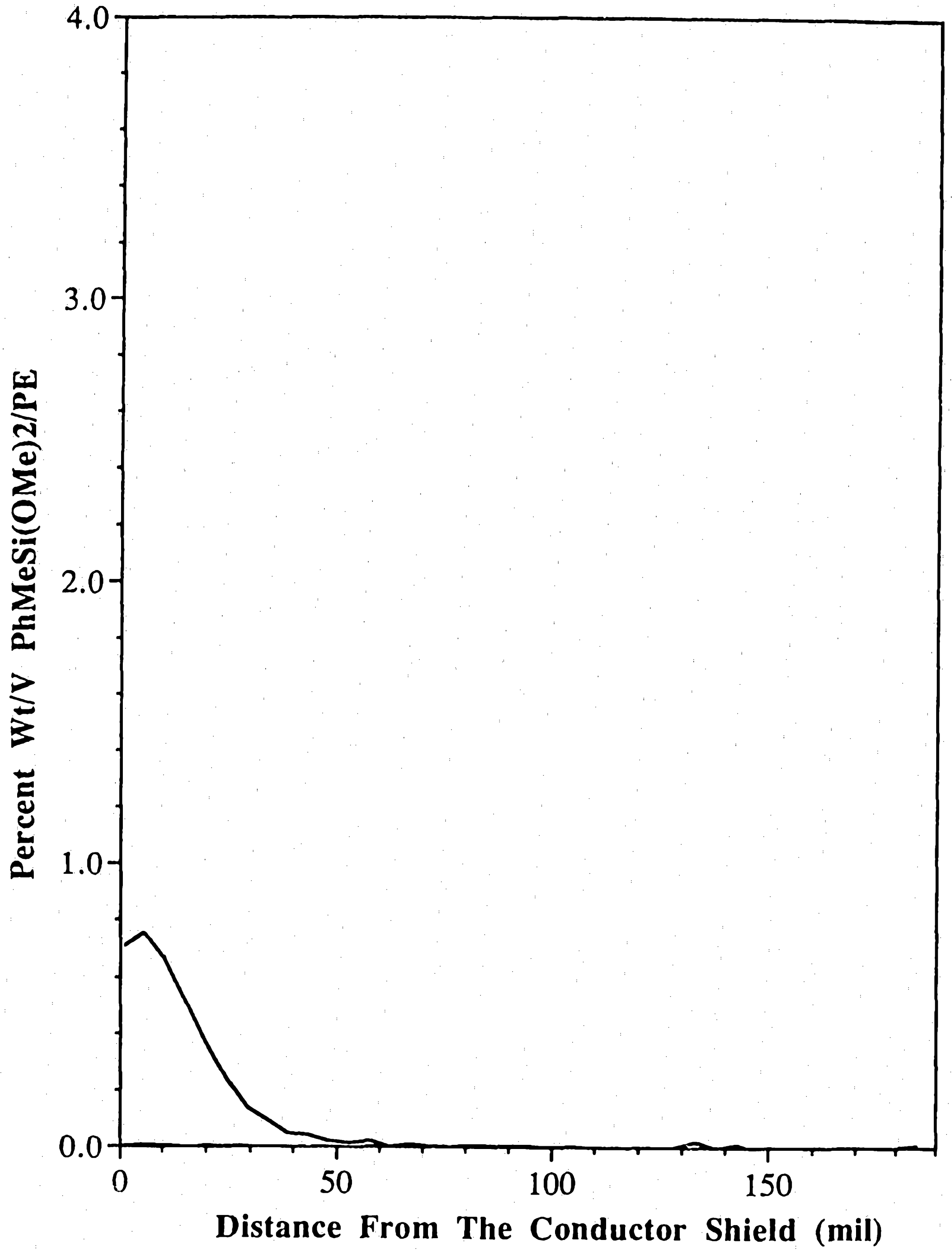

4.0
3.0
2.0
1.0
0.0
Percent Wt/V PhMeSi(OMe)2/PE
0
50
100
150
Distance From The Conductor Shield (mil)

Figure 7.


4.0
3.0
2.0
1.0
0.0
Percent Wt/V PhMeSi(OMe)2/PE
0
50
100
150
Distance From The Conductor Shield (mil)