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(54) **Electric wire.**

(57) An electric wire has coating of a gel film which is formed by applying a solution obtained by hydrolyzing and dehydrating/condensing alkoxide onto an outer part of a conductor and thereafter leaving the same.

FIG.1A

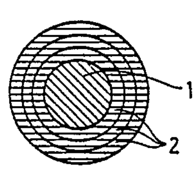


FIG.1B

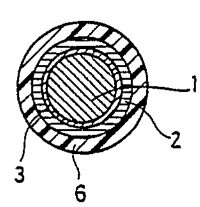


FIG.1C

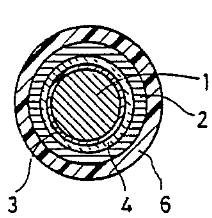
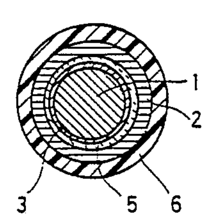


FIG.1D



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Electric Wire

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an electric wire, and more particularly, it relates to an electric wire which is applied to an electric wire requiring fire resistance and heat resistance such as a magnet wire or a wire employed in the vicinity of a nuclear reactor, or a special wire or cable requiring corrosion resistance.

Description of the Prior Art

The aforementioned electric wire requiring heat resistance or corrosion resistance is generally prepared by a covered conductor, which is coated with organic material. However, an organic coating film is insufficient in long-term stability, heat resistance, chemical durability and the like.

Thus, there has been provided a conductor coated with a compound of metal or metalloid, which is different from the material for the conductor, in order to attain heat resistance and corrosion resistance. For example, National Patent Publication Gazette No. 501783/1985 in the name of Raychem Inc., published in Japan on October 17, 1985, discloses a conductor which is coated with an oxide or a nitride by vacuum deposition, in order to provide heat resistance to an electric wire to be utilized under a high temperature. A compound for forming such coating is prepared by an oxide or a nitride of aluminum, silicon etc. Since such oxide is excellent in heat resistance and corrosion resistance, an electric wire coated with the oxide can be provided with high heat resistance and corrosion resistance.

The aforementioned electric wire which is covered with a ceramic film has been studied for improving these characteristics. Such a ceramic film is formed by:

(a) a method of forming a film from a vapor phase (vapor phase thin film growth method), such as CVD (chemical vapor deposition), PVD (physical vapor deposition) or flame coating;

(b) an electrochemical method of forming a film in a solution, such as plating;

(c) a sol-gel method of forming a film from a liquid phase by chemical reaction of reacting alkoxide; or

(d) a method of forming a film by dipping in a melt.

As hereinabove described, it is well known that an oxide of ceramics such as Al_2O_3 or SiO_2 is excellent in heat resistance and corrosion resistance. However, such an oxide formed by vacuum deposition is rather insufficient in adhesion to the material, such as copper, for a conductor. Therefore, when an electric wire coated with an oxide is used under corrosive environment over a long period of time, for example, the oxide film may partially peel off from the copper surface, to result in corrosion from the exposed portion.

The vapor phase thin film growth method such as vacuum deposition is employed as a method of forming an oxide film on the surface of a conductor. However, a film obtained by vacuum deposition or the like may be inferior in flexibility. Therefore, when a wire coated with an oxide by vacuum deposition is used in a bended state, for example, the oxide film may be broken by stress applied to the surface of the conductor, to result in corrosion from the broken portion.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide an electric wire which effectuates excellent heat resistance and corrosion resistance over a long period of time, by forming a film having excellent adhesion and flexibility. Another object of the present invention is to provide an electric wire which can be industrially obtained by simple means in a step of coating an elongated wire conductor.

An electric wire in accordance with the present invention comprises a conductor and a gel film formed by applying a solution obtained by hydrolyzing and dehydrating/condensing alkoxide onto an outer part of the conductor and leaving the same.

The gel film contributing to heat resistance, which is formed by a sol-gel method in the present invention, is excellent in flexibility and adhesion since the same is left not to be completely changed into a ceramic state but to remain in a gel state. This gel film is changed into a ceramic state by heating, to be improved in heat resistance. However, it has been recognized that its flexibility is reduced as much as it is changed into a ceramic state. On the basis of such a viewpoint of the inventors, the gel film is formed as a main heat resisting layer in the present invention. The conductor is preferably left in an atmosphere being at a temperature not less than 25 °C, not more than 400 °C, in order to form the gel film as a main heat resisting layer.

When the outer surface of a conductor coated with the solution obtained by hydrolyzing and dehydrating/condensing alkoxide and left is oxidized by heat, an oxide thus produced is so fragile that adhesion between the gel film and the conductor surface is lost to cause peeling of the film. In order to prevent this, the conductor surface is preferably plated with Ni or Cr for attaining oxidation resistance, before the same is coated with the solution and left in the aforementioned manner.

Upon heating, the gel film is considerably shrunk to be reduced in thickness. Such shrinkage of the film may result in inferior durability of insulation. While a conductor subjected to low voltage may be simply coated with a gel film alone, a problem is caused in durability of insulation when such a simple coated wire is applied to a power cable. Therefore, particulates of a metal oxide, a metal nitride or a metal boride are preferably dispersed/mixed in the gel film as ceramic filler for suppressing shrinkage of the gel film.

Although the gel film is considerably flexible in a natural state, such flexibility may be lost when the gel film is heated to be changed into a ceramic state. Even if the electric wire is utilized in a portion exposed to strong vibration, the film changed into a ceramic state must not peel off from the conductor by cracking caused by the strong vibration. Thus, particularly strong adhesion may be required between the gel film and the conductor. In this case, an adhesion layer may be provided between the gel film and the conductor, or between the gel film and a plating layer formed on the surface of the conductor. The adhesion layer may be prepared by a film completely changed into a ceramic state by applying a solution obtained by hydrolyzing and dehydrating/condensing alkoxide and thereafter heating the same. Alternatively, the adhesion layer may be prepared by a ceramic layer formed by CVD, on the basis of such a viewpoint of the inventors that a layer formed by CVD is larger in adhesion to a substrate than a gel film.

The inventive wire may be provided with an outermost layer of organic material, in order to improve slipperiness in winding and durability of insulation under the room temperature. In this case, the particulates of a metal oxide etc. may be dispersed/mixed in the organic material layer to improve durability of insulation. Further, the organic material layer may be formed from a solution of organic material, added to which is a solution obtained by hydrolyzing and dehydrating/condensing alkoxide with addition of tetraalkylammonium halide to be mixable into the solution of organic material, in order to improve heat resistance.

A gel film in accordance with the present invention may be formed as a multilayer film having two or more layers, in order to improve heat resistance, corrosion resistance and durability of insulation. In the process of forming the gel film in accordance with the present invention, alkoxide may be hydrolyzed by moisture contained in the atmospheric air, without directly adding water to an alkoxide solution.

These and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A, 1B, 1C and 1D are sectional views showing electric wires in accordance with the present invention; and

Fig. 2 illustrates an apparatus for performing a heat resistance test on samples of the electric wires in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Figs. 1A to 1D are sectional views showing electric wires in accordance with the present invention.

Fig. 1A shows an electric wire, which comprises a conductor 1 of copper etc. coated with a gel film 2 of one or more layers. Fig. 1B shows an electric wire which comprises a conductor 1, a plating layer 3 of Ni or Cr formed on the surface thereof, a gel film 2 covering the plating layer 3 and a covering layer 6 of organic material. Fig. 1C shows an electric wire which has a gel film 2 and a ceramic film 4 formed under the gel film 2 by CVD to serve as an adhesion layer. Fig. 1D shows an electric wire which has a ceramic film 5 formed by a starting raw material of alkoxide, to serve as an adhesion layer. This ceramic film 5 is formed by applying a solution obtained by hydrolyzing and dehydrating/condensing metal alkoxide and thereafter heating the same.

Samples for a heat resistance test of the aforementioned electric wires embodying the present invention were prepared as follows: Each of coating solutions 1 to 6, being prepared by the following methods, was applied onto a copper wire of 2.0 mmϕ in diameter by a dipping method at a lift-up speed of 1.0 m/min., to form a multilayer film on the copper wire.

Coating Solution 1

Tetrabutylorthosilicate [$Si(OC_4H_9)_4$], isopropyl alcohol [C_3H_7OH] and water [H_2O] were mixed in the mole ratio 10:50:40 to obtain a solution, to which nitric acid was added by 1/100 mol of tetrabutylorthosilicate. Then the solution was stirred at a temperature of 80°C for 100 minutes, and thereafter returned to the room temperature.

Coating Solution 2

Tetraethylorthosilicate [$Si(OC_2H_5)_4$], ethyl alcohol [C_2H_5OH] and water [H_2O] were mixed in the mole ratio 3:60:37 to obtain a solution, to which nitric acid was added by 1/100 mol of tetraethylorthosilicate. Then the solution was stirred at a temperature of 70°C for 100 minutes, and thereafter returned to the room temperature.

Coating Solution 3

Tetrabutylorthosilicate [$Si(OC_4H_9)_4$], isopropyl alcohol [C_3H_7OH] and water [H_2O] were mixed in the mole ratio 20:60:20 to obtain a solution, to which nitric acid was added by 1/100 mol of tetrabutylorthosilicate. Then the solution was stirred at a temperature of 80°C for 200 minutes, and thereafter returned to the room temperature.

Coating Solution 4

Tetrabutylorthosilicate [$Si(OC_4H_9)_4$], isopropyl alcohol [C_3H_7OH] and water [H_2O] were mixed in the mole ratio 10:50:40 to obtain a solution of 100 g, to which silicagel by Wako Junyaku (WAKOGEL, C-100) of 30 g was previously added. Then nitric acid was added by 1/100 mol of tetrabutylorthosilicate, and the solution was stirred at a temperature of 80°C for 100 minutes, and thereafter returned to the room temperature.

Coating Solution 5

p-xylene 30% solution of polyimide

Coating Solution 6

Tetrabutylorthosilicate [$Si(OC_4H_9)_4$], isopropyl alcohol [C_3H_7OH] and water [H_2O] were mixed in the mole ratio 10:50:40 to obtain a solution, to which nitric acid was added by 1/100 mol of tetrabutylorthosilicate. Then the solution was stirred at a temperature of 80°C for 100 minutes and thereafter returned to the room temperature. Tetrabutylammonium bromide [$(C_4H_9)_4N^+Br^-$] of 20 g was added to the solution of 100 g and stirred with addition of chloroform [$CHCl_3$], to perform extraction.

This extract was decompressed/dried by an evaporator to remove the solvent, thereby to obtain a pale yellow consistent solution [SiO_2 polymer]. This SiO_2 polymer was mixed into 10 ml of a p-xylene 30%

solution of polyimide, which was then stirred under the room temperature.

Each of the coating solutions 1 to 6 was employed for coating, to form a film by the following treatment. Thus, samples A, B, C, D, E and F were obtained by copper wires having multilayer coating films at least including gel films, as shown in Tables 1 to 6.

Table 1 (Sample A)

	1st Layer	2nd Layer	3rd Layer	4th Layer
Substance	Ni Plating	Gel	Gel	Gel
Coating Solution	--	Solution 1	Solution 2	Solution 2
Treatment	--	Heated at 280°C for 15 min.	Heated at 220°C for 15 min.	Left at 25°C for 6 h.
Film Thickness (μm)	3	2	2.6	20.0

Table 2 (Sample B)

	1st Layer	2nd Layer	3rd Layer	4th Layer
Substance	Gel	Gel	Gel	Resin
Coating Solution	Solution 1	Solution 2	Solution 2	Solution 5
Treatment	Heated at 280°C for 15 min.	Heated at 220°C for 15 min.	Heated at 170°C for 15 min.	Heated at 200°C for 30 min.
Film Thickness (µm)	2	2.6	11.5	7

Table 3 (Sample C)

	1st Layer	2nd Layer	3rd Layer
Substance	Ni Plating	Gel	Resin
Coating Solution	--	Solution 1	Solution 5
Treatment	--	Heated at 200°C for 15 min.	Heated at 200°C for 30 min.
Film Thickness (µm)	3	5.2	7

Table 4 (Sample C)

	1st Layer	2nd Layer	3rd Layer
Substance	Ni Plating	Gel	Resin
Coating Solution	--	Solution 4	Solution 5
Treatment	--	Heated at 300°C for 15 min.	Heated at 200°C for 30 min.
Film Thickness (μm)	3	15	7

Table 5 (Sample E)

	1st Layer	2nd Layer	3rd Layer
Substance	Ni Plating	Gel	Resin
Coating Solution	--	Solution 4	Solution 6
Treatment	--	Heated at 300°C for 15 min.	Heated at 200°C for 30 min.
Film Thickness (μm)	3	15	7

Table 6 (Sample F)

	1st Layer	2nd Layer	3rd Layer	4th Layer
Substance	Ni Plating	Ceramics	Gel	Resin
Coating Solution	--	Solution 3	Solution 1	Solution 6
Treatment	--	Heated at 500°C for 15 min.	Heated at 200°C for 15 min.	Heated at 200°C for 30 min.
Film Thickness (µm)		0.3	5.1	7

Each sample thus obtained was subjected to a heat resistance test as follows:

Heat Resistance Test

Insulation Test: As shown in Fig. 2, two samples 7a and 7b were brought into contact with each other to be heated by a heater 12 at a prescribed temperature for 30 minutes with application of voltage of 50 V, thereby to confirm insulating performance.

Vibration Test: In the insulation test, a motor 15 as shown in Fig. 2 was rotated with a dead weight 16 of 5 g, to apply vibration.

Referring to Fig. 2, numerals 7a and 7b indicate the samples, numeral 8 indicates a quartz plate on which the samples 7a and 7b are placed to be in contact with each other, and numeral 9 indicates a quartz pipe for storing the samples 7a and 7b placed on the quartz plate 8, having an end sealed by a closure 10 of silicon rubber and another end blocked by a glass wool member 11. A heater 12 prepared by a tube furnace is provided around the quartz pipe 9, in order to heat the samples 7a and 7b. A thermocouple 13 is inserted into the quartz pipe 9 through the closure 10, in order to measure the temperatures of the samples 7a and 7b. Numerals 14a and 14b indicate lead wires, which are connected to the samples 7a and 7b respectively, to be linked to electrodes for the insulation test. The motor 15 is provided on an end of the quartz plate 8 outwardly extending from the quartz pipe 9 through the glass 9 wool member 11, in order to apply vibration to the samples 7a and 7b. The dead weight 16 of 5 g is mounted on the shaft of the motor 15, which is rotated to vibrate the quartz plate 8, thereby to transfer the vibration to the samples 7a and 7b. A support 17 is provided in order to support the quartz plate 8.

Table 7 shows the results of such a heat resistance test with characteristics of the respective samples under the room temperature. Referring to Table 7, "x mmd" shows the value of a diameter which caused no abnormality in the coated layer when the copper wire of each sample was wound on a rod of x mm in diameter in a bending test. Table 7 also shows voltage resistance (V). Table 7 further shows results of insulation-sustainable temperature (°C) and vibration-proof temperature (°C). The "insulation-sustainable temperature" indicates the maximum temperature capable of sustaining insulating performance and the "vibration-proof temperature" indicates the maximum temperature capable of sustaining insulating performance against the vibration applied in the aforementioned manner.

It is understood from the result of the insulation test that the electric wire in accordance with the present invention is excellent in flexibility and its insulating performance can be maintained under a high temperature.

Table 7

Sample	Characteristics under Room Temperature		Heat Resistance Test	
	Bending Test	Voltage Resistance (V)	Insulation-Sustainable Temperature (°C)	Vibration-Proof Temperature (°C)
A	5 mmd	200	550	380
B	2 mmd	900	700	500
C	2 mmd	600	600	550
D	2 mmd	>1000	>800	720
E	2 mmd	>1000	>800	650
F	2 mmd	700	>800	>800

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

Claims

1. An electric wire comprising a conductor and coating of a gel film formed by applying a solution obtained by hydrolyzing and dehydrating/condensing alkoxide on an outer part of said conductor and thereafter leaving the same.

2. An electric wire in accordance with claim 1, wherein said leaving is performed in an atmosphere being at a temperature not less than 25°C, not more than 400°C.

3. An electric wire in accordance with claim 1, wherein said conductor is provided on its surface with a plating layer of either Ni or Cr, said coating of said gel film being provided on its outer part.

4. An electric wire in accordance with claim 1, wherein said gel film is formed as a multilayer film having two or more layers.

5. An electric wire in accordance with claim 1, wherein particulates of at least a metal oxide, a metal nitride or a metal boride are dispersed/mixed in said gel film.

6. An electric wire in accordance with claim 1, wherein an underlayer of said gel film is an adhesion layer of a ceramic film formed by applying a solution obtained by hydrolyzing and dehydrating/condensing metal alkoxide and thereafter heating the same.

7. An electric wire in accordance with claim 1, wherein an underlayer of said gel film is an adhesion layer of a ceramic film formed by CVD.

8. An electric wire in accordance with claim 1, further including a covering layer of organic material formed on an outer part of said gel film.

9. An electric wire in accordance with claim 8, wherein particulates of at least a metal oxide, a metal nitride or a metal boride are dispersed/mixed in said covering layer.

10. An electric wire in accordance with claim 8, wherein said covering layer is formed from a solution of organic material, added to which is a solution obtained by hydrolyzing and dehydrating/condensing alkoxide with addition of tetraalkylammonium halide to be mixable to said solution of organic material.

FIG.1A

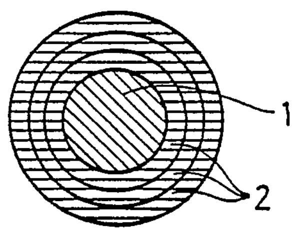


FIG.1B

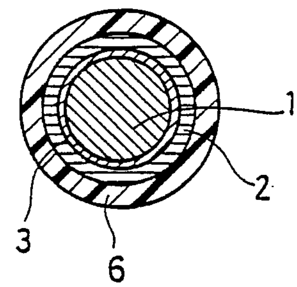


FIG.1C

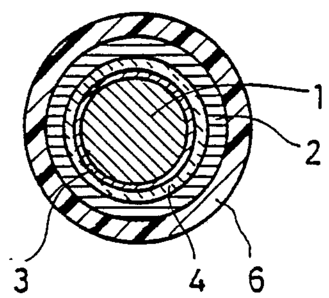


FIG.1D

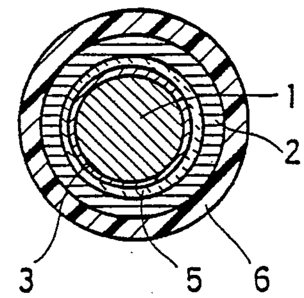
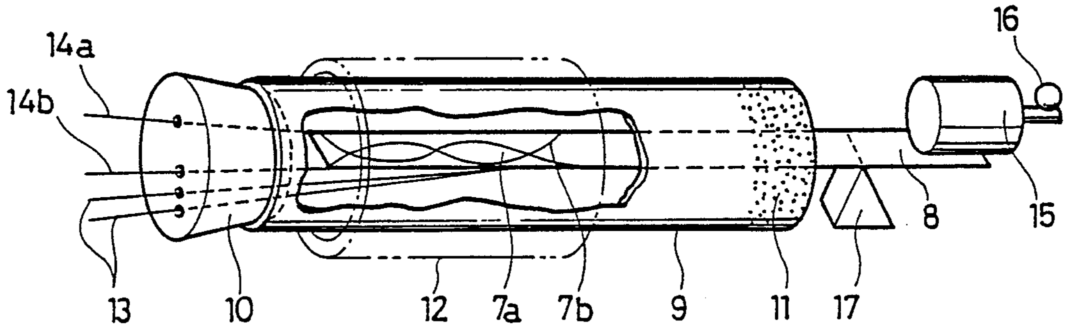


FIG.2



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EUROPEAN SEARCH REPORT

Application Number

EP 88 10 7511

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 170 441 (RAYCHEM) * Whole document * ---	1-10	H 01 B 7/34 H 01 B 7/28 H 01 B 3/10 H 01 B 13/06
X	EP-A-0 188 369 (RAYCHEM) * Whole document * ---	1-10	
X	EP-A-0 188 370 (RAYCHEM) * Whole document * -----	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			H 01 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	13-09-1988	DROUOT M.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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