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European Patent Office
Office européen des brevets



Publication number:

0 416 131 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art.
158(3) EPC

(21) Application number: **90904938.9**

(22) Date of filing: **26.03.90**

(86) International application number:
PCT/JP90/00401

(87) International publication number:
WO 90/11603 (04.10.90 90/23)

(51) Int. Cl.⁵: **H01B 7/02, H01B 3/12,**
H01B 7/34, H01B 13/16,
C25D 11/38, //C23C28/04

(30) Priority: **28.03.89 JP 77028/89**
20.03.90 JP 70843/90

(43) Date of publication of application:
13.03.91 Bulletin 91/11

(84) Designated Contracting States:
BE CH DE DK FR GB IT LI SE

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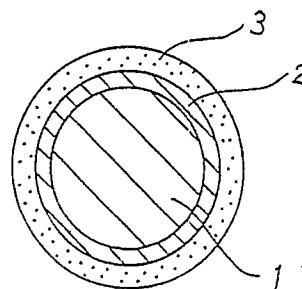
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(54) **INSULATED ELECTRIC WIRE.**

(57) An insulated electric wire of this invention is adapted to be used as a wire for wiring or as a wire for winding in a highly vacuum or high-temperature such as high-vacuum equipment of high-temperature equipment. This wire comprises a base member (1), a chromium oxide layer (2) and an oxide insulating layer (3). The base member (1) includes a conductor. The chromium oxide layer (2) is formed on the outer surface of the base member (1). The oxide insulating layer (3) is formed on the chromium oxide layer (2) by applying a precursor solution of a metal oxide based on the sol-gel method or an organic acid salt pyrolysis method. The insulated electric wire exhibits excellent flexibility as well as heat resistance and does not provide a source of gas adsorption.

FIG. 1



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INSULATED WIRE

Field of the Invention

The present invention relates to an insulated wire, and more particularly, it relates to an insulated wire such as a distribution wire, a wire for winding or the like which is employed under high-vacuum environment or high-temperature environment such as a high-vacuum apparatus or a high-temperature service apparatus. Background of the Invention

An insulated wire may be applied to equipment such as heating equipment or a fire alarm, for which safety under a high temperature is required. Further, the insulated wire is also used under environment in an automobile, which is heated to a high temperature. An insulated wire formed by a conductor which is coated with heat resistant organic resin such as polyimide, fluorocarbon resin or the like has generally been used as such an insulated wire.

As to application for which high heat resistance is required, or employment under environment for which a high degree of vacuum is required, organic coating is insufficient in view of heat resistance, no gas emission property and the like. Thus, an insulated wire of such a form that a conductor is inserted in an insulator tube of ceramics, an MI cable (Mineral Insulated cable) of such a form that a conductor is inserted in a heat resistant alloy tube of a stainless steel alloy etc. which is filled with metal oxide powder of magnesium oxide etc., or the like has been employed for such application.

A fiber-glass braided insulated wire employing textile glass fiber as an insulating member etc. is listed as an insulated wire for which flexibility is required with heat resistance.

In the aforementioned insulated wire coated with organic resin having heat resistance, the highest temperature at which insulability can be maintained is about 200°C at the most. Therefore, it has been impossible to employ such an organic insulated coated wire for application for which guarantee for insulability is required under a high temperature of at least 200°C.

Further, the insulated wire which is improved in heat resistance through an insulator tube of ceramics has disadvantages such as inferior flexibility. The MI cable is formed by a heat resistant alloy tube and a conductor, and hence the outer diameter of the cable is increased with respect to the conductor radius. Thus, the MI cable has a relatively large section with respect to electric energy allowed by the conductor which is passed through the heat resistant alloy tube. In order to use the MI cable as a wire for winding which is wound on a

bobbin etc. in the form of a coil, however, it is necessary to bend the heat resistant alloy tube in prescribed curvature. In this case, bending performed on the heat resistant alloy tube involves difficulty. When the MI cable is wound in the form of a coil, further, it is difficult to improve space factor since the tube of its outer layer is thick as compared with the conductor.

Further, when the fiber-glass braided insulated wire having heat resistance is employed and worked into a prescribed configuration in response to its application, the network of the braid is disturbed to cause a breakdown. In addition, dust of glass is generated from the glass fiber. This glass dust may serve as a gas adsorption source. Therefore, when the fiber-glass braided insulated wire is used under environment for which a high degree of vacuum is required, it has been impossible to maintain a high degree of vacuum due to the gas adsorption source provided by the glass dust.

On the other hand, there has generally been the so-called alumite wire prepared by performing anodic oxidation treatment on a wire of aluminum or an aluminum alloy, as an insulated wire which is excellent in heat resistance, insulability and heat dissipativity. In this alumite wire, its base material is restricted to aluminum. Further, an inorganic insulating layer formed on the base material is also restricted to aluminum oxide. Thus, there has been such a problem that it is impossible to select combinations of the base material and the inorganic insulating layer which are suitable for various uses.

Disclosure of the Invention

Accordingly, the present invention has been proposed in order to solve the aforementioned problems, and its object is to provide an insulated wire comprising the following items:

- (a) It has high insulability under environment of a high temperature.
- (b) It is excellent in flexibility.
- (c) It comprises no gas adsorption source.
- (d) Combinations of a base material and an inorganic insulating layer suitable for various uses can be selected.

An insulated wire according to the present invention comprises a base material, a chromium oxide containing layer, and an oxide insulating layer. The base material has an outer surface, and includes a conductor. The chromium oxide containing layer is formed on the outer surface of the base material. The oxide insulating layer is formed by

applying a precursor solution of a metallic oxide onto the chromium oxide containing layer by a sol-gel method or an organic acid salt pyrolytic method.

The chromium oxide containing layer is preferably formed by an electrochemical technique. The electrochemical technique includes electrolytic plating or electroless plating. The underlayer to be provided with the oxide insulating layer may be a CrO_{3-x} ($1.5 < X < 2.5$) layer, in order to preferably serve as an adhesion layer. Namely, the layer formed by the electrochemical technique has a chromium oxide layer as its outermost layer. The oxide insulating layer preferably contains silicon oxide, aluminum oxide or zirconium oxide. As to the base material, copper or a copper alloy is preferably employed in view of high conductivity and the cost. In consideration of a use at a higher temperature or the like, nickel chromium, silver, iron or a ferroalloy, a stainless steel alloy, or titanium or a titanium alloy is preferably contained in the surface layer of the base material.

It is known that a chrome plated layer is formed on a conductor of copper or a copper alloy etc. as an excellent adhesion layer. However, insulating oxide ceramics such as silicon oxide obtained by heat treatment of a precursor solution of a metallic oxide hardly exhibits adhesion with respect to the chrome plated layer. This is based on recognition of the inventors.

In an insulated wire obtained by directly forming a thin film of ceramics on a surface of a conductor made of copper, further, the ceramics thin film serving as an insulating layer has insufficient adhesion with respect to a base material.

According to the present invention, therefore, a layer having a chromium oxide layer as its outermost layer is formed on an outer surface of a base material. Insulating oxide ceramics adheres onto the chromium oxide layer as a layer having excellent adhesion.

The aforementioned chromium oxide layer is formed by an electrochemical technique. When the chromium oxide layer is formed by electrolytic plating, a substance obtained by adding a small amount of organic acid to an aqueous solution of chromic anhydride is used as an electrolyte. Although a sergeant bath mainly composed of chromic anhydride or sulfuric acid is known as an electrolytic bath employed for chrome plating, it is different from this bath in the following point: Namely, mineral acid mixed into the electrolytic bath has a function of dissolving chromic anhydride which is generated on the surface of a plated layer in electrolytic plating. Therefore, a glossy metallic chrome layer is plated when a sergeant bath is employed. In the present invention, it is necessary to preferentially plate chromium oxide. Therefore, a

small amount of organic acid is added to an electrolytic bath employed in the present invention. In a case of using mineral acid such as sulfuric acid, further, it is necessary to employ a particularly dilute electrolytic bath. Namely, chromic anhydride concentration is not more than 50 g/l and sulfuric acid concentration is not more than 1 g/l. Further, while a thin film of insulating ceramics is formed on the outer surface of a layer mainly composed of chromium oxide by heat treatment of a precursor solution of a metallic oxide, the layer mainly composed of chromium oxide preferably has a roughened surface, in order to further increase adhesion of the thin film.

The chromium oxide containing layer may be formed by electrolytic plating employing an electrolyte which is prepared by adding sodium citrate, sodium carbonate or the like, for example, to an aqueous solution of sodium chromate. In this case, the as-formed layer is mainly composed of chromium oxide, which is generated by trivalent reduction of hexavalent chromium contained in the electrolyte. If copper is used as a base material in this electrolytic plating treatment, the base material surface is oxidized and the chromium oxide containing layer is formed in the exterior thereof. However, adhesion of the chromium oxide containing layer with respect to the base material is not reduced by such oxidation of the base material surface.

Conditions for electrolytic plating for forming the inventive chromium oxide containing layer are different from those for general bright plating in treatment current density etc. Although the current density is set at 10 to 60 A/dm² in the bright plating, depending on the treatment temperature, the current density is set at 100 to 200 A/dm² in the present invention. A chromium oxide containing layer having a roughened surface can be formed by this condition of the current density.

On the chromium oxide containing layer, an insulating oxide layer is formed by application of a precursor solution of a metallic oxide. The precursor solution of a metallic oxide mentioned in this specification is a solution prepared from a metal organic compound, which is broadly classified in correspondence to a sol-gel method or an organic acid salt pyrolytic method, and those of the following two types are included:

The first type of precursor solution is a solution which is generated by making hydrolytic reaction and dehydration/condensation reaction of a compound containing hydrolyzable metal-oxygen-organic group bonds such as metal alkoxide or acetate of a metal. This solution may contain an organic solvent such as alcohol, a raw material compound such as metal alkoxide, and water and a catalyst required for hydrolytic reaction. Further, it generally contains an organic residual group such

as alkoxide, dissimilarly to hydroxide sol that is generated from inorganic salt.

The second type of precursor solution is a solution prepared by dissolving a metal organic compound such as organic acid salt of a metal in an appropriate organic solvent. In a method employing this type of precursor solution, a metallic oxide is generated by pyrolyzation through heating after application. Therefore, a decomposition temperature of the employed metal organic compound must be lower than its boiling point or sublimation point.

The metal organic compound mentioned in this specification is a concept similar to "metal-organic compounds" described in Journal of Materials Science 12 (1977) pp. 1203 to 1208, for example.

Further, the applied layer must be left at a temperature higher than the room temperature, for volatilization of the organic solvent and removal of a residual organic substance. However, the temperature of the atmosphere for such leaving must not be higher than the melting point of the metal forming the base material.

It is possible to form almost all metallic oxide-based ceramics covering by application of a precursor solution of a metallic oxide. SiO_2 , Al_2O_3 , ZrO_2 , TiO_2 , MgO or the like can be listed as an example of a metallic oxide formed by this method. Further, ethoxide, propoxide, butoxide or the like can be listed as metal alkoxide employed for the first type of precursor solution. Metallic salt such as naphthanic acid, caprylic acid, stearic acid, octylic acid or the like is preferable as organic salt employed for the second type of precursor solution.

The oxide insulating layer formed from the precursor solution of the metallic oxide by the sol-gel method or the organic acid salt pyrolytic method is an oxide which is completely converted to a metallic oxide. This oxide is preferably formed by heat treatment under an atmosphere in an oxygen current. In general, decomposition of the compound contained in the solution which is applied onto the chromium oxide containing layer is completely terminated at a temperature of about 500°C . If the same is heat treated at a higher temperature, however, reaction between elements forming the chromium oxide containing layer and a metal or semimetal contained in the applied solution is facilitated, whereby adhesion between the chromium oxide containing layer and the oxide layer is improved.

Thus, the oxide insulating layer converted to ceramics exhibits excellent heat resistance/insulability also under a high temperature of at least 500°C . Further, the chromium oxide containing layer is excellent in adhesion to the conductor forming the base material. Therefore, adhesion between the oxide insulating layer and

the outer surface of the base material is improved as compared with the case of directly forming the oxide insulating layer on the outer surface of the conductor by heat treatment of the precursor solution of the metallic oxide. Thus, the insulated wire provided according to the present invention has heat resistance/insulability, as well as excellent flexibility.

Further, the oxide insulating layer formed on the chromium oxide containing layer has a smooth outer surface. Therefore, a high breakdown voltage proportionate to the film thickness can be obtained, while it is possible to reduce a gas adsorption source.

According to the present invention, in addition, the chromium oxide containing layer is formed between the base material and the oxide insulating layer. Therefore, combinations with the inorganic insulating layer suitable for various uses can be selected through the chromium oxide containing layer.

Brief Description of the Drawings

Fig. 1 is a sectional view showing a cross section of an insulated wire according to the present invention in correspondence to Example 1.

Fig. 2 is a sectional view showing a cross section of an insulated wire according to the present invention in correspondence to Example 2.

Fig. 3 is a sectional view showing a cross section of an insulated wire according to the present invention in correspondence to Example 3.

Fig. 4 is a sectional view showing a cross section of an insulated wire according to the present invention in correspondence to Example 4.

Fig. 5 is a graph showing the result of measurement of surface roughness of a chromium oxide containing layer formed in accordance with Example 3 or Example 4.

Fig. 6 is a graph showing the result of measurement of surface roughness of a chrome plated layer formed in accordance with Reference Example. Best Modes of Carrying Out the Invention

Example 1

(a) Formation of Chromium Oxide Containing Layer

Electrolytic plating treatment was performed on an outer surface of a copper wire of $2\text{ mm}\phi$ in wire diameter. At this time, an electrolyte was prepared from that having concentration of 40 g/l of chromic anhydride and 0.45 g/l of sulfuric acid. As to plating conditions, the bath temperature was 50°C , the current density was 140 A/dm^2 , and the treatment

time was two minutes. Thus, a chromium oxide containing layer was formed on the outer surface of the copper wire with a film thickness of about 1 μm .

(b) Preparation of Coating Solution used for Sol-Gel Method

Nitric acid was added to a solution mixed in mole ratios of tetrabutyl ortho-silicate:water:isopropyl alcohol = 8:32:60 in a ratio of 3/100 mole with respect to tetrabutyl ortho-silicate. Thereafter this solution was heated/stirred at a temperature of 80 °C for two hours. Thus, a coating solution used for a sol-gel method was synthesized.

(c) Coating

The wire obtained by (a) was dipped in the coating solution of (b). A step of heating at a temperature of 400 °C for 10 minutes was performed ten times on the wire whose outer surface was thus coated with the coating solution. Finally, this wire was heated in an oxygen current of 500 °C in temperature for 10 minutes.

An insulated covered wire obtained in the aforementioned manner is shown in Fig. 1. Fig. 1 is a sectional view showing a cross section of the insulated wire obtained according to Example 1. Referring to Fig. 1, a chromium oxide containing layer 2 is formed on an outer surface of a copper wire 1. On this chromium oxide containing layer 2, a silicon oxide layer 3 is formed by the sol-gel method as an oxide insulating layer. The film thickness of an insulating layer formed by the chromium oxide containing layer 2 and the silicon oxide layer 3 was about 4.0 μm .

A breakdown voltage was measured in order to evaluate insulability of the obtained insulated wire. Its breakdown voltage was 800 V under the room temperature, and was 600 V under a temperature of 800 °C. Even if this insulated wire was wound on an outer peripheral surface of a cylinder having a diameter of 10 cm, no cracking was caused in the insulating layer.

Example 2

(a) Formation of Chromium Oxide Containing Layer

A copper wire of 2 mm ϕ in wire diameter was vapor-degreased through use of perchloroethylene. Thereafter the copper wire was dipped in a solution mixed in volume ratios of 85 % phosphoric acid:70 % nitric acid:water = 15:2:3, thereby roughening its surface.

Then, the copper wire was used as a cathode and a stainless steel plate was used as an anode to perform electrolytic plating treatment by feeding a direct current of 0.05 A/dm². At this time, a solution

of about 1 l prepared by dissolving 30 g of sodium chromate, 30 g of sodium citrate and 30 g of sodium carbonate in water respectively was used as an electrolyte.

Thus, a copper oxide layer having a film thickness of about 1 μm was formed on the outer surface of the copper wire, and a chromium oxide containing layer was formed in its exterior with a film thickness of about 0.1 μm .

(b) Preparation of Coating Solution used for Sol-Gel Method

A solution mixed in mole ratios of tetrabutyl orthozirconate [(C₄H₉O)₄Zr]:water:n-butyl alcohol = 5:15:80 was heated/stirred at a temperature of 120 °C for two hours. Thus, a coating solution used for a sol-gel method was synthesized.

(c) Coating

The wire obtained by (a) was dipped in the coating solution of (b). A step of heating at a temperature of 400 °C for 10 minutes was performed ten times on the wire whose outer surface was thus coated with the coating solution.

An insulated covered wire obtained in the aforementioned manner is shown in Fig. 2. Fig. 2 is a sectional view showing a cross section of the insulated wire obtained according to Example 2. Referring to Fig. 2, a copper oxide layer 12 is formed on the outer surface of a copper wire 11. Further, a chromium oxide containing layer 13 is formed in the exterior of this copper oxide layer 12. On this chromium oxide containing layer 13, a zirconium oxide layer 14 is formed by the sol-gel method as an oxide insulating layer. The film thickness of an insulating layer formed by the copper oxide layer 12, the chromium oxide containing layer 13 and the zirconium oxide layer 14 was about 3.0 μm .

A breakdown voltage was measured in order to evaluate insulability of the obtained insulated wire. Its breakdown voltage was 700 V under the room temperature, and was 500 V under a temperature of 700 °C. Even if this insulated wire was wound on an outer peripheral surface of a cylinder having a diameter of 10 cm, no cracking was caused in the insulating layer.

Example 3

(a) Formation of Chromium Oxide Containing Layer

Electrolytic plating treatment was performed on an outer surface of a nickel-plated copper wire of 1.8 mm ϕ in wire diameter. At this time, an electrolyte was prepared from that having concentration of 200 g/l of chromic anhydride, 20 g/l of ammonium methavanadate and 6.5 g/l of acetic acid. As to plating conditions, the base material was used

as a cathode, while the bath temperature was 50 °C, the current density was 150 A/dm², and the treatment time was two minutes. Thus, a chromium oxide containing layer was formed on the outer surface of the nickel-plated copper wire with a film thickness of about 1 μm.

As to the surface state of the chromium oxide containing layer, the center line average roughness Ra was 0.15 μm and the maximum height Ry was 0.87 μm in accordance with Surface Roughness of ISO468-1982. The surface roughness was measured by using a surface contour measurer DEKTA3030 made by Sloan Inc., U.S.A., under conditions of a tracer diameter of 0.5 μm, a stylus pressure of 10 mg, a reference length of 50 μm, and no use of a cutoff filter. The result of measurement is shown in Fig. 5.

(b) Preparation of Coating Solution used for Organic Acid Salt Pyrolytic Method

A coating solution was prepared by dissolving 20 g of 2-ethyl-hexanoic silicate in 100 ml of dibutyl ether.

(c) The wire obtained by (a) was dipped in the coating solution of (b). A step of heating at a temperature of 500 °C for 10 minutes was performed ten times on the wire whose outer surface was thus coated with the coating solution.

An insulated covered wire obtained in the aforementioned manner is shown in Fig. 3. Fig. 3 is a sectional view showing a cross section of the insulated wire obtained according to Example 3. Referring to Fig. 3, a nickel-plated copper wire comprising a nickel-plated layer 22 formed on an outer surface of a copper wire 21 is used as a base material. A chromium oxide containing layer 23 is formed on the outer surface of this nickel-plated copper wire. On the chromium oxide containing layer 23, a silicon oxide layer 24 is formed by an organic acid salt pyrolytic method as an oxide insulating layer. The film thickness of an insulating layer formed by the chromium oxide containing layer 23 and the silicon oxide layer 24 was about 5 μm.

A breakdown voltage was measured in order to evaluate insulability of the obtained insulated wire. The breakdown voltage was 500 V under the room temperature, and was 300 V under a temperature of 800 °C. Even if this insulated wire was wound on an outer peripheral surface of a cylinder having a diameter of 5 cm, no cracking was caused in the insulating layer.

Example 4

(a) Formation of Chromium Oxide Containing Layer

The so-called stainless steel clad copper wire

of 1.8 mmφ in wire diameter, in which a stainless steel alloy (SUS304) was engaged on an outer surface of a copper wire, was used as a base material. Electrolytic plating treatment was performed on the outer surface of this stainless steel clad copper wire. At this time, an electrolyte was prepared from that having concentration of 200 g/l of chromic anhydride, 20 g/l of ammonium methavanadate and 6.5 g/l of acetic acid. As to plating conditions, the base material was used as a cathode, while the bath temperature was 50 °C, the current density was 150 A/dm² and the treatment temperature was two minutes. Thus, a chromium oxide containing layer was formed on the outer surface of the stainless steel clad copper wire with a film thickness of about 1 μm.

As to its surface state, the center line average roughness Ra was 0.15 μm, and the maximum height Ry was 0.87 μm in accordance with Surface Roughness of ISO468-1982. The measurement was performed by using a surface contour measurer DEXTAK3030 made by Sloan Inc., U.S.A., under conditions of a tracer diameter of 0.5 μm, a stylus pressure of 10 mg, a reference length of 50 μm, and no use of a cutoff filter. As the result of this measurement, that shown in Fig. 5 was obtained similarly to Example 3.

(b) Preparation of Coating Solution used for Organic Acid Salt Pyrolytic Method

25 g of aluminum tetra-i-butoxide was dissolved in 100 ml of diethylene glycol monomethyl ether, and thereafter heated/stirred at 150 °C for one hour. This solution was stood to be cooled to the room temperature, and thereafter mixed with 3 g of alumina particles of 0.03 μm in nominal particle size, thereby preparing a coating solution.

(c) Coating

The wire obtained by (a) was dipped in the coating solution of (b). A step of heating at a temperature of 500 °C for 10 minutes was performed ten times on the wire whose outer surface was thus coated with the coating solution.

An insulated covered wire obtained in the aforementioned manner is shown in Fig. 4. Fig. 4 is a sectional view showing a cross section of the insulated wire obtained according to Example 4. Referring to Fig. 4, a stainless steel clad copper wire having a stainless steel alloy layer 32 on an outer surface of a copper wire 31 is used as a base material. A chromium oxide containing layer 33 is formed on the outer surface of the stainless steel clad copper wire. On this chromium oxide containing layer 33, an aluminum oxide layer 34 is formed by an organic acid salt pyrolytic method as an oxide insulating layer. This aluminum oxide layer 34 consists of an aluminum oxide mixed layer containing aluminum particulates which have been mixed in the coating solution from the start. The

film thickness of an insulating layer formed by the chromium oxide containing layer 33 and the aluminum oxide layer 34 was about 12 μm .

A breakdown voltage was measured in order to evaluate insulability of the obtained insulated wire. Its breakdown voltage was 900 V under the room temperature, and was 700 V under a temperature of 800 °C. Even if this insulated wire was wound on an outer peripheral surface of a cylinder having a diameter of 15 cm, no cracking was caused in the insulating layer.

Reference Example

(a) Formation of Metallic Chrome Plated Layer

Electrolytic plating treatment was performed on an outer surface of a nickel-plated copper wire of 1.8 mm ϕ in wire diameter. At this time, an electrolyte to be used was prepared from that having concentration of 250 g/l of chromic anhydride and 2.5 g/l of sulfuric acid. As to plating conditions, the base material was used as a cathode, while the bath temperature was 50 °C, the current density was 40 A/dm², and the treatment time was two minutes. Thus, a chrome containing layer was formed on the outer surface of the nickel-plated copper wire with a film thickness of about 1 μm .

As to its surface state, the center line average roughness Ra was 0.06 μm and the maximum height Ry was 0.51 μm in accordance with Surface Roughness of ISO468-1982. The measurement was performed by using a surface contour measurer DEKTAK3030 made by Sloan Inc., U.S.A., under conditions of a tracer diameter of 0.5 μm , a stylus pressure of 10 mg, a reference length of 50 μm , and no use of a cutoff filter. The result of this measurement is shown in Fig. 6. A glossy metallic chrome layer was formed on the outer surface of the nickel-plated copper wire.

(b) Preparation of Coating Solution used for Organic Acid Salt Pyrolytic Method

A coating solution was prepared by dissolving 20 g of 2-ethyl-hexanoic silicate in 100 ml of dibutyl ether.

(c) Coating

The wire obtained by (a) was dipped in the coating solution of (b). A step of heating at a temperature of 500 °C for 10 minutes was performed on the wire whose outer surface was thus coated with the coating solution, whereby the as-formed insulating layer was separated like a film after heating, and exhibited no adhesion.

Industrial Availability

As hereinabove described, the insulated wire

according to the present invention is suitable for a distribution wire, a wire for winding or the like, which is employed under high-vacuum environment or high-temperature environment such as a high vacuum apparatus or a high temperature service apparatus.

Claims

1. An insulated wire comprising:
 - a base material (1) having an outer surface and including a conductor,
 - a chromium oxide containing layer (2) formed on the outer surface of said base material, and
 - an oxide insulating layer (3) formed by applying a precursor solution of a metallic oxide onto said chromium oxide containing layer.
2. An insulated wire in accordance with claim 1, wherein said chromium oxide containing layer (2) is formed by electrolytic plating.
3. An insulated wire in accordance with claim 1, wherein said oxide insulating layer (3) contains any one of silicon oxide, aluminum oxide and zirconium oxide.
4. An insulated wire in accordance with claim 1, wherein said base material (1) contains either copper or a copper alloy.
5. An insulated wire in accordance with claim 4, wherein said base material contains any one of nickel, chromium and a stainless steel alloy in its surface layer (22).
6. An insulated wire in accordance with claim 1, wherein said oxide insulating layer (3) contains ceramics particulates dispersed therein.
7. An insulated wire comprising:
 - A base material (1) having an outer surface and including a conductor,
 - a chromium oxide containing layer (2) formed on the outer surface of said base material, and
 - an oxide insulating layer (3) formed on said chromium oxide containing layer by a sol-gel method.
8. An insulated wire comprising:
 - a base material (21) having an outer surface and including a conductor,
 - a chromium oxide containing layer (23) formed on the outer surface of said base material, and

an oxide insulating layer (24) formed on said chromium oxide containing layer by an organic acid salt pyrolytic method.

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FIG. 1

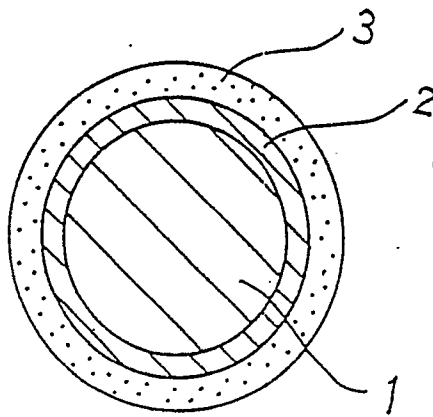


FIG. 2

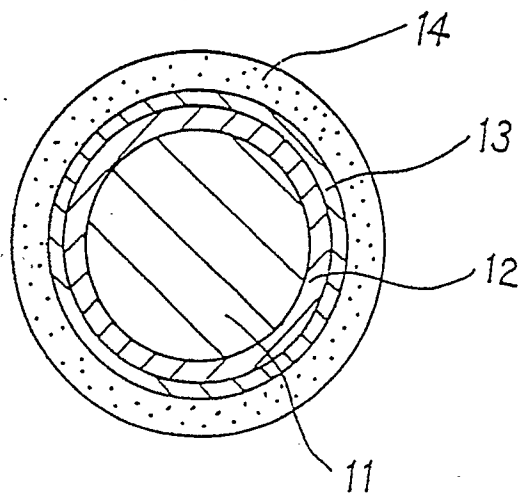


FIG. 3

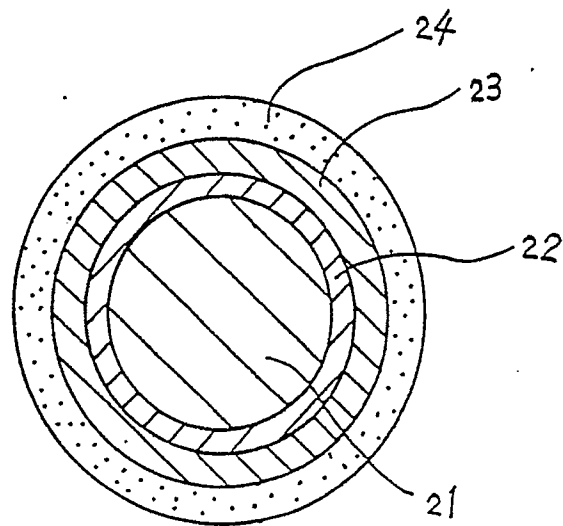


FIG. 4

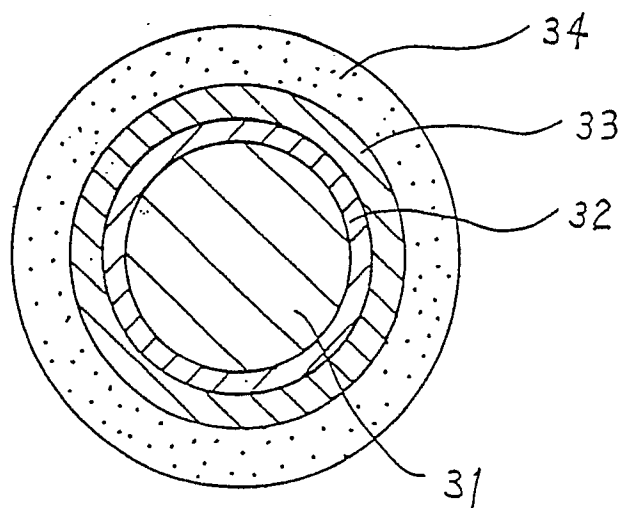


FIG. 5

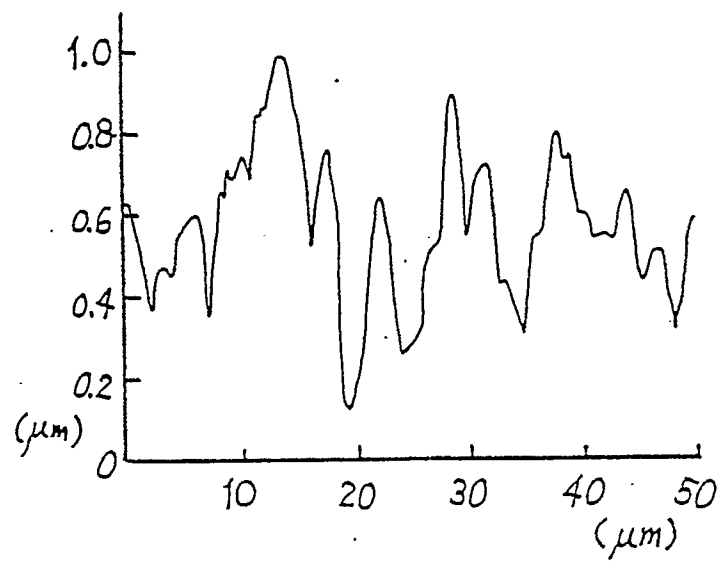
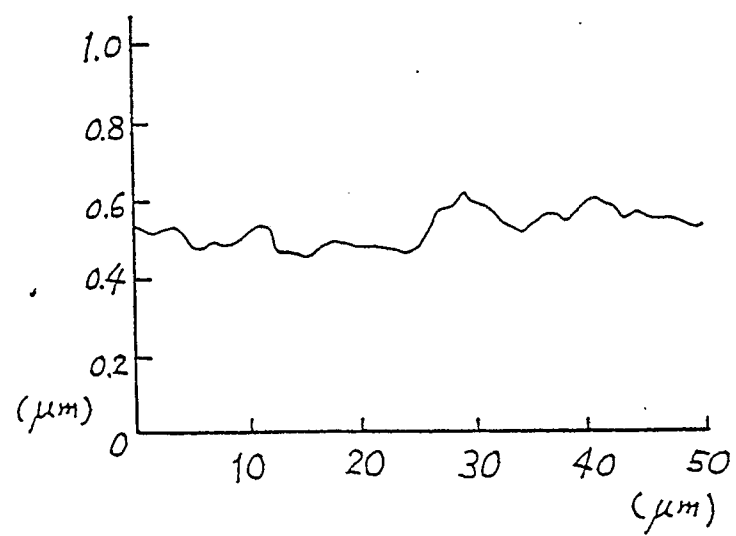


FIG. 6



INTERNATIONAL SEARCH REPORT

International Application No PCT/JP90/00401

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl ⁵	H01B7/02, H01B3/12, H01B7/34, H01B13/16, C25D11/38//C23C28/04	
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC	H01B7/02, H01B3/12, H01B7/34, H01B13/16, C25D11/38, H01B12/06	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched *		
Jitsuyo Shinan Koho	1926 - 1990	
Kokai Jitsuyo Shinan Koho	1971 - 1990	
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	JP, A, 1-81116 (Fujikura Ltd.), 27 March 1989 (27. 03. 89), (Family: none)	1 - 8
Y	EP, A1, 188369 (Raychem Ltd.), 23 July 1986 (23. 07. 86) & EP, B1, 188369 & JP, A, 61-165909	1 - 8
Y	EP, A1, 188370 (Raychem Ltd.), 23 July 1986 (23. 07. 86) & EP, B1, 188370 & JP, A, 61-165910	1 - 8
Y	JP, A, 56-149775 (Kogyo Gijutsuin-cho), 19 November 1981 (19. 11. 81), (Family: none)	3, 5-6, 8
Y	JP, A, 63-239150 (Sumitomo Electric Industries, Ltd.), 5 October 1988 (05. 10. 88), (Family: none)	5-6, 8
* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
April 19, 1990 (19. 04. 90)	May 1, 1990 (01. 05. 90)	
International Searching Authority	Signature of Authorized Officer	
Japanese Patent Office		

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	JP, A, 63-247374 (Perumerc Denkyoku K.K.), 14 October 1988 (14. 10. 88), (Family: none)	8
Y	JP, A, 63-279524 (Sumitomo Electric Industries, Ltd.), 16 November 1988 (16. 11. 88), (Family: none)	8

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers , because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers , because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.