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ELECTRICALLY INSULATED CONDUCTOR AND PRODUCTION THEREOF

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Fig. 1

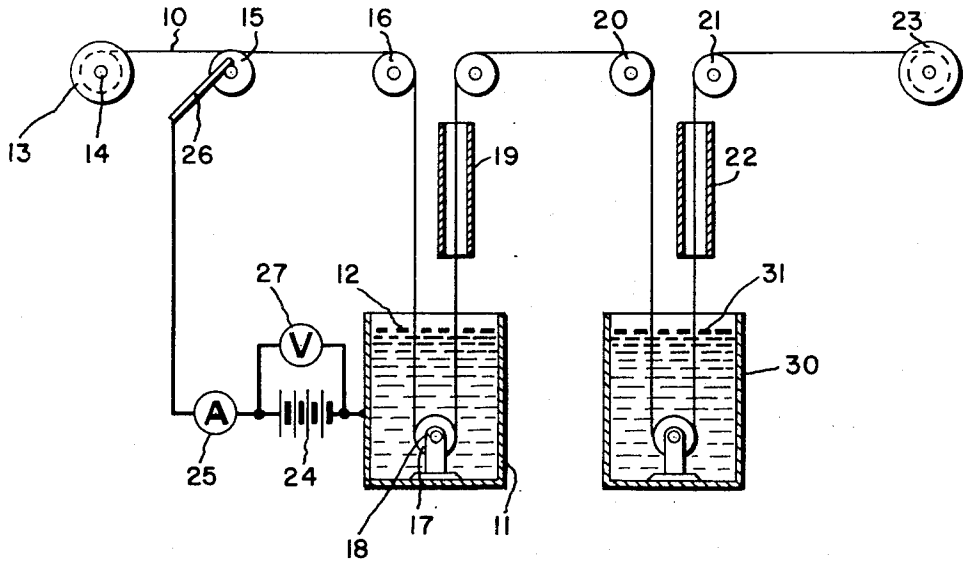
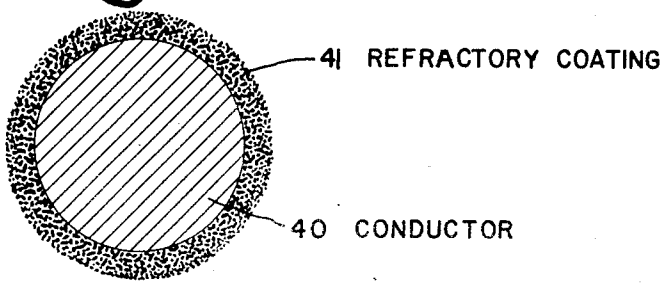


Fig. 2



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ELECTRICALLY INSULATED CONDUCTOR AND PRODUCTION THEREOF

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Continuation of application Serial No. 594,429, May 18, 1945, which is a continuation of application Serial No. 472,465, January 15, 1943. This application March 15, 1950, Serial No. 149,867

19 Claims. (Cl. 201—64)

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The present invention relates to electrical insulating layers and to processes for their production and employment. This application is filed as a continuation of prior application Serial No. 594,429, filed May 18, 1945, which in turn is a continuation of application Serial No. 472,465, filed January 15, 1943, both now abandoned.

The use of refractory inorganic materials for electrically insulating conductors has already been proposed. However, because of the inherent brittleness of materials of this type, they have not been generally suitable for the coating of conductors which are to be subjected to flexing. In attempts to circumvent this difficulty by forming a coating of the refractory material in finely divided form, it is found that because of the poor adhesive and cohesive properties of the material, a loosely adherent, pulverulent and otherwise poorly formed coating results. Such a coating is initially unstable and cannot be further processed without damage.

In certain instances and to decrease the fragility of such coatings it has been proposed to superimpose thereon a second coating of an organic binder such as varnish. However, this does not protect the refractory coating prior to the time that the second coating is applied and does not prevent damage thereof during that interval. Furthermore, at high temperatures, the binder volatilizes and/or decomposes, and the refractory material is again converted into its initial pulverulent form. In certain instances the heating of the organic binder forms decomposition products which remain in the coating and impair its electrical properties.

It is an object of this invention to produce electrically insulated conductors, free from the foregoing and related disadvantages, by novel processes. A further object is to produce electrical insulating layers on conductors, said layers consisting substantially entirely of inorganic refractory constituents and being characterized by great mechanical strength and flexibility and by remarkable adherence to said conductors.

Another object of the invention is to provide electrical conductors having flexible refractory insulating coatings which can be wound into coils without any appreciable damage to the coating.

A further object of the invention is to provide insulating layers which in continuous use at high temperatures exhibit high insulating resistivity and high voltage breakdown strength.

These and further objects of the invention will appear as the specification progresses.

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These objects are attained in accordance with the present invention which comprises a process for the simultaneous deposition at an anode, by means of current, of a refractory material and a colloidal hydrated gel. In a more restricted sense, the invention is concerned with a process for the simultaneous deposition on an electrical conductor of a refractory material, by electrophoretic means, and a colloidal hydrated gel of an oxide, by electrolysis. In a still more restricted sense, the invention is concerned with a process for producing insulated electrical conductors comprising the steps of forming in a suspension medium a suspension of finely divided particles of refractory insulating material, said medium containing in solution an inorganic readily hydrolyzable electrolyte subjecting a conductor and an opposing cathode immersed in the suspension to a current flow whereby said refractory particles are electrophoretically deposited on the conductor and a colloidal hydrated gel, formed at or near the conductor from said electrolyte, is deposited on the conductor by electrolysis.

In a still more restricted sense, the invention is concerned with a process for producing insulated conductors which comprises the steps of preparing a suspension of finely divided particles of refractory insulating material in an aqueous medium, containing in solution a soluble silicate such as sodium or potassium silicate, and simultaneously depositing on a conductor said refractory particles and a gelatinous, colloidal polysilicic acid, formed in the vicinity of said conductor from said soluble silicate.

The invention is also concerned with the process of producing insulated electrical conductors which comprises the steps of preparing a suspension medium containing a suspension of finely divided particles of a metal oxide, preferably zinc oxide or titanium oxide, said suspension also containing a soluble silicate, simultaneously depositing on said conductor said particles by electrophoresis and a gelatinous polysilicic acid formed at or near said conductor from said silicate by electrolysis.

The invention is also specifically concerned with the process of producing insulated electrical conductors which comprises the steps of preparing a suspension medium containing a suspension of finely-divided particles of refractory insulating material and an oxide of zinc, said suspension medium containing a water soluble silicate, simultaneously depositing on the conductor said particles, the oxide of zinc and a

gelatinous, hydrated polysilicic acid formed at or near the conductor from said silicate, by electrophoresis and electrolysis, respectively, heat-treating said coated conductor, and in some cases, immersing it in an aqueous solution of phosphoric acid.

The invention is further concerned with a process for producing insulated conductors which comprises the steps of preparing a suspension of finely divided particles of refractory insulating material in an aqueous medium, containing in solution a soluble silicate such as sodium or potassium silicate and/or some other water soluble silicate and simultaneously depositing on a conductor said refractory particles and a gelatinous, hydrated polysilicic acid, formed at or near the conductor from said soluble silicate, by electrophoresis and electrolysis, respectively, and heat-treating said coated conductor.

The invention is further concerned with electrically insulated conductors produced by the foregoing and related processes.

In United States patent application Serial No. 472,465, of which the parent application Serial No. 594,429, is a continuation, there are disclosed excellent electrically insulated conductors and methods of producing them, the insulation being composed of refractory ceramic particles and colloidal hydrated gel material. More particularly, in application Serial No. 472,465, it was found that by electrophoretically depositing the refractory material from a suspension thereof containing a soluble metal silicate, such as potassium and/or sodium silicate, refractory insulating coatings are produced having initially high mechanical strength, flexibility and good adherence to the underlying base, even when made in thicknesses of the order of .00025". It was also disclosed that zinc oxide might be incorporated in the refractory coating by electrophoretic means and subsequently converted into a complex zinc orthophosphate cement which is very useful in binding the refractory particles to each other and to the underlying base.

In accordance with the present invention as particularly described in the parent application bearing Serial No. 594,429, I have found that greatly improved insulating layers may be produced on conductors, by the simultaneously deposition at an anode by means of current of a refractory material and a colloidal hydrated gel. More particularly, the desirable insulating layers may be achieved by the simultaneous deposition of a refractory material by electrophoretic means and a colloidal hydrated gel of an oxide, which oxide is both formed and deposited by electrolysis.

In accordance with one of the preferred embodiments of the invention, excellent insulated conductors are produced by forming a suspension of finely divided particles of a refractory insulating material, dissolving in the suspension medium a readily hydrolyzable inorganic electrolyte, and subjecting a conductor and an opposing cathode immersed in said suspension to a current flow whereby said refractory particles are electrophoretically deposited on said conductor and a colloidal hydrated gel is formed from said electrolyte in the vicinity of said conductor and upon formation is deposited on said conductor by electrolysis.

I have found that a certain class of densifying agents are particularly useful in producing the insulating layers. This class includes hydrolyzable inorganic salts, such as sodium and potassium silicates, aluminates, tungstates, zincates, zirconates and titanates. In aqueous solution these densifying agents form at or near the conductor and in the presence of current, hydrated gels which exist in the suspension medium in a colloidal state, and which will remain at or pass to the anode by electrolysis, while, at the same time, the refractory ceramic particles are being deposited on the anode by electrophoretic means. Formation of these gels in the vicinity of the anode is probably due to the difference in the pH of the suspension medium at that location. For that reason it is advisable to employ soluble salts which hydrolyze readily upon a slight change in the pH of their solution. Separation of these two simultaneous processes, namely, electrophoresis and electrolysis, into individual steps, will result in a quite dissimilar coating.

According to one of the specific and preferred embodiments of the invention, improved insulated electrical conductors are produced by preparing a suspension of finely-divided particles of refractory insulating material and/or an oxide of zinc, said suspension medium containing a soluble preferably inorganic silicate, simultaneously depositing on a conductor said refractory particles and a gelatinous, hydrated polysilicic acid, formed at or near the conductor from said silicate, by electrophoresis and electrolysis, respectively, and heat-treating said coated conductor, and immersing it in an aqueous solution of phosphoric acid. The use of zinc oxide as an ingredient of the suspension of refractory material permits the subsequent formation in the insulation of a complex zinc orthophosphate cement which will bond the particles to each other and to the underlying conductor. The treatment with phostional advantage that, in the case of a copper phoric acid to accomplish the above has the addiconductor, any copper oxide on its surface will be converted to a soluble phosphate salt and removed or converted in situ into an insoluble copper oxyphosphate cement, depending upon the kind of copper oxide present.

Another embodiment of the invention concerns the use of zinc oxide and/or other metal oxides such as zirconium oxide, titanium dioxide, etc., as refractory ceramic materials. It has been found that outstanding insulating layers may be produced by using these oxides as ceramic materials, omitting a subsequent chemical treatment with phosphoric acid or other reactant material. The combination of a zinc oxide refractory ceramic material with a hydrated polysilicic acid is particularly suitable.

The suspenson medium employed may contain hydroxyl groups, such as obtained from ethylene glycol, glycerol, ethyl alcohol, propyl alcohol, etc. In most cases, I prefer to use water, sometimes, modifying it with small amounts of the hydroxy compounds mentioned above.

The invention will be further described with reference to the appended drawing forming part of the specification and in which:

Figure 1 diagrammatically illustrates one form of apparatus suitable for producing refractory insulating coatings in accordance with the invention.

Figure 2 is a cross-sectional view of a wire conductor provided with a heat-resistant flexible refractory insulating coating of the invention.

Referring to Figure 1, a wire 10 is passed through a coating cell comprising a container 11, a coating solution 12 containing particles of a refractory material, and sodium silicate or some

other hydrolyzable inorganic salt, the salt serving as a densifying agent during the deposition of the coating and also providing by electrolysis a bonding medium for the particles, during and following the deposition.

Wire 10 is made of copper or other highly conductive metal or metal alloy in the case of conductors to be used for the winding of coils of electromagnets or the like; or Nichrome or other high resistivity metal in the case of conductors to be used for the winding of resistor elements. The wire, of course, may be coated with a dissimilar metal if desired.

Suitable refractory materials for forming the coating are, for example, bentonite, china clay, talc, aluminum oxide, silicon dioxide, titanium dioxide, zinc oxide, magnesium and aluminum silicates and mixtures of one or more of these materials. To insure uniformity of the coating, the refractory particles generally should be of a small size, for example of the order of one to two microns, which may be obtained by ball-milling the refractory material for about one to two days.

To facilitate the suspending of the refractory particles in the suspension medium, there may be added to the suspension medium a small quantity of a wetting agent such as sodium stearate, a mixture of triethanolamine and stearic acid or the like.

The amount of hydrolyzable inorganic salt employed in accordance with the invention may vary widely depending upon the specific refractory ceramic material and amount thereof in the suspension, the desired suspension resistivity, the type of insulating layer desired, etc. In the case of salts whose electrical conductivity is very high, the salt may be dissolved in a small portion of the suspension medium and dialysed by any standard procedure before being incorporated in the suspension medium. The dialysis process removes ions and lowers the conductivity of the salt solution. In the case of sodium and potassium silicate and other water soluble silicates, it is possible to employ amounts from about 1% to about 45%, based on the total dry weight of refractory material and salt. For other salts, such as sodium and potassium zincate, tungstate, titanate, zirconate, aluminate, etc., a similar range may be used.

The preparation of the suspension medium may take place in any convenient manner. Generally, the finely ground ceramic material is added to about half of the suspension medium with a small quantity (usually less than .01%) of a surface active agent which will aid in the formation and maintenance of the suspension. The mixture is then treated in an attrition mill, preferably being continuously recycled therethrough. The other half of the medium and the hydrolyzable salt is then added. Ball milling also is useful in the preparation of the suspension.

While it is to be understood that the invention is not limited thereto, the following examples of suspensions are given. A suspension useful in the production of insulating layers wherein no chemical treatment thereof is required may be:

19,000 gms. distilled water.
1,750 gms. china clay.
1,750 gms. talc.
3 gms. "Darvan" (a commercially available sodium lauryl sulfate wetting agent).
2,000 cc. of 35% sodium silicate solution (containing 950 gms. of sodium silicate, of sodium to silicon ratio about 1 to 4).

This suspension will have a resistivity of about 125 ohms per cm.^{3}.

A suspension useful in the production of insulating layers, wherein chemical treatment to produce an inorganic binder may be employed if desired, is as follows:

19,000 gms. distilled water.
1,750 gms. china clay.
1,750 gms. talc.
1,750 gms. zinc oxide.
2,000 cc. of a 35% sodium silicate solution (sodium to silicon ratio being 1 to 4).
3 gms. of "Darvan".

The above suspension will possess a resitivity of about 125 ohms per cm.^{3}.

Another suspension which may be employed with excellent results with or without subsequent chemical treatment comprises water, zinc oxide and a water soluble silicate:

19,000 gms. distilled water.
4,000 gms. zinc oxide, finely ground.
2,860 cc. of a 35% sodium silicate solution (sodium to silicon ratio being 1 to 4).

The above suspension will possess a resistivity of about 100 ohms per cm.^{3}.

I have found that the resistivity of the suspension should generally be within the range of about 50 ohms per cm.^{3} and about 10,000 ohms per cm.^{3}, for optimum deposition of the insulating layer.

The container 11 may form one electrode of the coating cell, and for this purpose it may be made of a conducting material such as copper. Alternately, a cylindrical copper electrode may be employed. The wire 10 to be coated forms the other electrode of the cell.

The wire 10 is unwound from a spool 13 mounted on a rotatable shaft 14 and passes on its way to the coating cell around a mandrel 15 and over a guide pulley 16. It passes through the coating cell 11 as a loop, reversing at the bottom of the cell, for which purpose there is provided a pulley 17 supported from the bottom of the coating cell by a bracket 18. Thereafter, the wire passes through oven 19 over pulley 20, into cell 30; and then passes through a furnace 22, the purpose of which will be later discussed. Upon emerging from the furnace 22, the wire is wound on a storage spool 23. Suitable driving means (not shown) rotate spool 23 and move the wire through the coating apparatus.

The current for depositing the coating is supplied by a source of direct current indicated as a battery 24, the negative pole of which is connected to container 11. The positive pole of the source 24 is connected through an ammeter 25 to a contact brush 26 which contacts the mandrel 15 and is thus connected to the wire 10. A voltmeter 27 for indicating the coating voltage is connected across the source 24.

The current used for the coating depends somewhat on the suspension employed and its resistivity, on the time of deposition, the length of immersion and speed of the wire in the coating cell, and the desired thickness of the coating. For example, when coating a copper wire .002" in diameter and traveling at the rate of 90 feet per minute in a coating cell in which 3 feet of the wire is immersed and when it is desired to form a coating .0002" thick, a current of 220 milliamperes may be used.

The wire may then be subjected to a heat-

treatment in oven 19, to remove any residual water or other suspension medium, and, in some cases, to render the colloidal, hydrated gel binder more resistant to moisture absorption and transmission. The temperature of furnace 19 depends to some extent upon the treatment employed, the medium employed, etc. In general, the temperature is between about 100° C. and about 1200° C., and preferably between about 250° C. and 1000° C. It is desirable to locate the furnace directly above the coating well, so that the heat-treatment will occur before any elongation of the wire is effected, by passing over a pulley or otherwise. This latter feature is very helpful and profoundly improves the resulting coating.

Heat treatment when applied to copper and copper-alloy wires sometimes oxidizes the wire slightly and consequently reduces the cross-section thereof. Furthermore, copper oxide may contaminate the insulating coating and because of its semi-conductive nature impair the electrical resistivity of the coating. To avoid this when processing copper or copper-alloy wires, the heat-treating may take place in an inert or a reducing atmosphere, for example, in an atmosphere of nitrogen or hydrogen.

According to a further embodiment of the invention, an insulating coating containing zinc oxide may be subjected to a chemical treatment which will convert the zinc oxide into a complex zinc orthophosphate cement. This treatment may take place in cell 30 by employing an aqueous solution 31 of from about 1% to about 5% of phosphoric acid. The insulating coating may first be heat-treated in oven 19 at temperatures from about 400° C. to 600° C. The so-coated wire may be dried finally at 140° C. for about 10 minutes or at 500° C. for about 10 seconds in the furnace 22, further baking the zinc orthophosphate cement.

Treatment with phosphoric acid has a further advantage when applied to copper wires which may have copper oxide on their surface. Depending on the kind of copper oxide present, it may be converted either into a soluble phosphate salt and removed, or is converted in situ into an insoluble copper oxyphosphate cement.

Outstanding insulated wires and other insulated conductors have been produced by utilizing the simultaneous electrolysis and electrophoresis described herein to deposit refractory ceramic particles on conductors and to bond these particles to each other and to the wire with a colloidal hydrated gel, following this deposition by after-treatments such as electrophoretic impregnation of the pores of the coating with resinous binders, illustrated by the hydrolysis products of aryl, alkyl, and/or arakyl chlor silanes: polyethylene, polytetrafluoroethylene and other vinyl polymers, etc.; impregnation of the pores of the coating with a heat decomposable metal salt, such as aluminum nitrate, followed if desired by treatment of the insulation with a surface active agent, such as stearic or ricinoleic acid; solvent application of top coatings of the aforesaid resinous materials, etc., etc. Pertinent details of the foregoing and related after-treatments which are applicable hereto are disclosed in copending application S. N. 536,448, filed on May 20, 1944, by S. O. Dorst, and U. S. P. 2,421,652, issued on June 3, 1947, to P. Robinson et al.

It should be understood that the refractory coating and hydrated polysilicic acid or other binder may be heat treated and used as such or otherwise processed in accordance with the instructions hereof. Treatment thereof with chemical reactants thereof is optional and may be omitted.

While I am cognizant of the fact that optimum insulating layers may be produced by observing and following the instructions given herein, I am not fully aware of the reason therefor. It appears that from the soluble inorganic salt, there is formed at or near the conductor a colloidal hydrated gel, which is deposited on and held to the conductor. The material thus deposited appears to be a hydrated polysilicic acid (polytungstic acid, etc.) which acts as a binder for the ceramic particles. The colloidal hydrated gel may be composed of trimers and tetramers of silicic acid (or tungstic acid, etc.). Where sodium silicate is employed I have found that the lower ratios of sodium to silicon (e. g. about 1 to 4) give optimum results.

Figure 2 shows an enlarged cross-sectional view of a refractory insulated conductor produced in accordance with the invention, said conductor comprising a metal wire 40 and a coating 41 comprising intermixed particles of a refractory material and of the colloidal gel binder.

As many widely different embodiments of the invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments disclosed therein except as described in the appended claims.

What is claimed is:

1. A method of forming a flexible, adherent insulating coating upon an electrical conductor, which comprises immersing said conductor in an aqueous suspension composed essentially of finely divided particles of refractory insulating material having dissolved in the aqueous suspension medium an inorganic electrolyte selected from the class consisting of silicates, aluminates, tungstates, zincates, zirconates and titanates, said inorganic electrolyte constituting from about 1% to about 45% of the total dry weight of the refractory insulating material and the inorganic electrolyte, connecting said conductor as an anode, passing an electric current through the aqueous suspension whereby the refractory particles and a colloidal hydrated gel formed by hydrolysis of the inorganic electrolyte are simultaneously deposited upon the conductor by electrophoresis and electrolysis respectively, removing the so-coated conductor from the aqueous suspension, and then subjecting it to a heat treatment at a temperature between about 100° C. and about 1200° C. to remove residual water.

2. A method of forming a flexible, adherent insulating coating upon an electrical conductor, which comprises immersing said conductor in an aqueous suspension composed essentially of finely divided particles of refractory insulating material having dissolved in the aqueous suspension medium a water-soluble silicate, said silicate constituting from about 1% to about 45% of the total dry weight of the refractory insulating material and the silicate, connecting said conductor as an anode, passing an electric current through the aqueous suspension whereby the refractory particles and a hydrated polysilicic acid formed by hydrolysis of the silicate are simultaneously deposited upon the conductor by electrophoresis and electrolysis respectively, removing the so-coated conductor from the aqueous suspension, and then subjecting it to a heat treatment at a

temperature between about 100° C. and about 1200° C. to remove residual water.

3. A method as claimed in claim 2, wherein the silicate is sodium silicate possessing a sodium to silicon ratio of about 1 to 4, and wherein the aqueous suspension possesses a resistivity from about 50 ohms to about 10,000 ohms per cm.^{3}.

4. A method as claimed in claim 2, wherein the electric current that is passed through the aqueous suspension is maintained at a density of from about 1 to about 30 amperes per second exposure per square inch of conductor surface during the deposition.

5. A method as claimed in claim 2, wherein the aqueous suspension contains finely divided particles of zinc oxide and the coated conductor is immersed in an aqueous solution of phosphoric acid prior to the final heat treatment.

6. A method of forming a flexible, insulated electrical conductor which comprises providing a copper wire conductor, immersing said conductor in an aqueous suspension composed essentially of finely particles of refractory insulating material having dissolved in the aqueous suspension medium an inorganic electrolyte selected from the class consisting of silicates, aluminates, tungstates, zincates, zirconates and titanates, said inorganic electrolyte constituting from about 1% to about 45% of the total dry weight of the refractory insulating material and the inorganic electrolyte, connecting said conductor as an anode, passing an electric current through the aqueous suspension whereby the refractory particles and a colloidal hydrated gel formed by hydrolysis of the inorganic electrolyte are simultaneously deposited upon the conductor by electrophoresis and electrolysis respectively, removing the so-coated conductor from the aqueous suspension, and then subjecting it to a heat treatment at a temperature between about 100° C. and about 1200° C. to remove residual water.

7. An electrical conductor wire electrophoretically coated with particles of water-insoluble refractory insulating material uniformly mixed with simultaneously applied anodic electrolytic deposition products of a water-soluble silicate.

8. An electrical conductor electrophoretically coated with particles of china clay and talc uniformly mixed with simultaneously applied anodic electrolytic deposition products of sodium silicate.

9. An electrical conductor wire having a copper surface electrophoretically coated with particles of water-insoluble refractory insulating material uniformly mixed with simultaneously applied anodic electrolytic deposition products of a water-soluble silicate.

10. A copper electrical conductor wire electrophoretically coated with particles of china clay and talc uniformly mixed with simultaneously applied anodic electrodeposition products of sodium silicate.

11. A Nichrome electrical conductor wire electrophoretically coated with particles of china clay and talc uniformly mixed with simultaneously applied anodic electrodeposition products of sodium silicate.

12. An electrical conductor wire having a Nichrome surface electrophoretically coated with particles of water-insoluble refractory insulating material uniformly mixed with simultaneously applied anodic electrolytic deposition products of a water-soluble silicate.

13. A copper alloy electrical conductor wire electrophoretically coated with particles of china clay and talc uniformly mixed with simultaneously applied anodic electrodeposition products of sodium silicate.

14. An electrical conductor wire having a copper alloy surface electrophoretically coated with particles of water-insoluble refractory insulating material uniformly mixed with simultaneously applied anodic electrolytic deposition products of a water-soluble silicate.

15. A wire-wound resistor having a winding consisting of an electrical conductor wire having a Nichrome surface electrophoretically coated with particles of water-insoluble refractory insulating material uniformly mixed with simultaneously applied anodic electrolytic deposition products of a water-soluble silicate.

16. A wire-wound resistor having a winding consisting of a Nichrome electrical conductor wire electrophoretically coated with particles of china clay and talc uniformly mixed with simultaneously applied anodic electrodeposition products of sodium silicate.

17. An electrical coil consisting of a wound electrical conductor wire electrophoretically coated with particles of china clay and talc uniformly mixed with simultaneously applied anodic electrodeposition products of a water-soluble silicate.

18. An electrical coil consisting of a wound electrical conductor wire electrophoretically coated with particles of china clay and talc uniformly mixed with simultaneously applied anodic electrodeposition products of sodium silicate.

19. A flexible metallic electrical conductor having a substantially uniform insulating coating in which said coating comprises a mixture of electrophoretically coated particles of refractory insulating material and a colloidal hydrated gel electrolytically formed from an aqueous solution of an inorganic electrolyte selected from the class consisting of silicates, aluminates, tungstates, zincates, zirconates and titanates.

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