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## PROCESS OF INSULATING WIRE AND PRODUCT THEREOF

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This invention relates to the insulation of wires, etc., of alloys containing nickel and chromium, such as nickel-chromium and nickel-chromium-iron alloys, including fine high resistance wires and wires of larger diameter, ribbons, straps and strips. It includes the method of insulating and the insulated wire, etc., and resistances, such as rheostats, made from such wire, etc.

The desirability of insulating wires by coating them with an oxide has long been recognized and for years certain types of wire have been thus coated by treating them with steam, oxygen or other hot oxidizing gas. Alloys of nickel and chromium cannot be insulated with an oxide coating by such treatment. A thin oxide layer may be formed but it is brittle and apt to crack or flake off when the wire is bent or subjected to shock. The oxide produced appears to form a protective coating which prevents the oxygen from penetrating to the unoxidized metal or alloy underneath and so prevents the formation of an oxide layer of substantial thickness.

By the process of this invention durable oxide coatings can readily be formed on wires, etc., of alloys containing chromium and nickel and the process has proved particularly valuable as a method of insulating such wires. The oxide coatings produced are relatively uniform and of substantial thickness. They are not easily removed by bending or shaking the wire or in subjecting it to the usual handling.

According to this invention, the wire, etc., is coated with an alkali metal base such as sodium or potassium hydroxide which fluxes, i. e., dissolves or penetrates the oxides formed by the subsequent oxidation of the alloy in a roasting chamber. The base dissolves chromium oxides as they are formed and fluxes off iron and nickel from the alloy wires, probably in the form of their oxides and it appears that in this way the gaseous oxygen is carried by the solution to the surface of the wire where further oxidation takes place.

Not only does the base aid in carrying the oxygen to the untreated metal by removing or penetrating the oxides but its affinity for water retards the evaporation of water from the surface of the metal while it is being roasted. This makes it possible to continue the roasting for a considerable period in the presence of solutions of the salts and alkali and it appears to be the water which is thus retained which carries the oxygen to the metal. It is known that at 350° C. the rate of evaporation of water from a 98 percent caustic soda solution is only about one-half that of pure water at 20° C. Although the rate of evaporation is greater at higher temperatures the rate of oxidation is so rapid compared to the rate of evaporation of water from such alkaline materials that it is probable that not all of the water is evaporated at the oxidation temperatures employed during any of the time intervals that have been found satisfactory for the oxidation of these wires.

In carrying out my process I therefore first treat the wire with a water solution of an alkali base which has a strong affinity for water at the oxidizing temperature and which fluxes the salts and oxides formed on the alloy. I prefer to use a solution of caustic soda. A hot caustic bath may be used so as to remove oil or soap or other foreign matter from the wire, if necessary. Dilute solutions of caustic soda which do not adhere to the wire have not been found satisfactory, and I use more concentrated solutions containing 25% or preferably solutions containing 40 or 50% by weight of sodium hydroxide which do not readily drain from the wire but are retained in contact with the wire during the roasting operation.

After dipping in the caustic the wire is heated to an oxidizing temperature in an oxidizing atmosphere. It may be heated so high that it is annealed while it is being oxidized, or it may be heated to a lower temperature which causes oxidation without annealing. If oxidized at such lower temperature it may later be annealed, preferably after first washing off the salts, etc., formed on the wire during the oxidizing treatment.

The depth of the oxide layer may be controlled by regulating the oxidizing temperature and time of heating, and thus coatings having a greater or less dielectric strength may be produced. An annealed wire with a coating of predetermined dielectric strength may be produced by first annealing the wire, then dipping in a suitable alkali base and then heating it in an oxidizing atmosphere at the proper temperature for the proper time.

After roasting, the adhering salts are washed off with water, preferably in a bath containing a small amount of acid and then in water to insure freedom from all chemical reagents and salts. The wire so cleaned may be used in electrical appliances without danger of short circuits forming.

The method is particularly applicable to the insulation of very fine wires such as those used in

the formation of rheostats and other radio work. It can likewise be applied to larger wires, ribbons, straps and strips, such as strips one and one-half inches in width and to even larger sizes. Such wires, etc. do not require space winding when used in resistances. When insulated with an adherent coating of oxide, such as is contemplated by this invention, fine wires, etc. can readily be formed into variable resistances. The coated wire may be formed into a coil and the oxide layer in the path of the movable contact may be removed without damaging the balance of the insulation coating, allowing electrical connection at any position of the contact member.

The oxidation may be carried out as a batch operation by forming the wire into coils, treating the coils in caustic and then roasting. Also it may advantageously be carried out as a continuous process by running a single strand of wire through a coating bath and then directly through a roasting chamber. By varying the speed at which the wire travels through the roasting chamber and by varying the temperature of the roasting chamber, the depth of the oxide layer may be controlled.

In practice it has not been found practical to control the concentration of caustic as even if a weak solution is used it builds up to a higher concentration in the roasting chamber due to drippings from the wire and spray from it. In practice the roasting chamber is made very small. For wires of larger diameter the batch operation is preferred, and for finer wires the continuous process.

Experiments were conducted on the insulation of wires of various diameters composed of 60 percent of nickel, about 15 percent of chromium and the balance essentially iron to determine the proper temperature of oxidation and the most suitable concentration of caustic. It was found that on continuously passing a wire .002 inch in diameter through a bath containing 29 percent by weight of sodium hydroxide at a speed of 100 feet per minute and then roasting it at 1600° F. for about three seconds, the deposit of caustic on the wire was such that a coating of oxide having a low dielectric strength was obtained. With the same kind of wire using the same speed and temperature treatment, a more satisfactory insulation was produced on using a caustic bath of 42 percent (by weight) concentration. This is explained, at least in part, by the fact that the more concentrated solution of caustic is more viscous and a larger amount adheres to the wire. On further experimentation, it was found that with a wire .0035 inch in diameter, passed continuously through a bath of 29 percent caustic soda at the rate of 70 feet per minute and then through the roasting chamber maintained at 1600° F., and of such length that the wire remained in the chamber for somewhat over four seconds, a coating of low dielectric strength was obtained; using a bath of 42 percent caustic a coating having a higher dielectric strength was produced.

Using 42 percent caustic, wires of this alloy, .002, .0025, .003, .0035, .004 and .0045 inch in diameter were treated at speeds of 100, 85, 75, 70, 60 and 52 feet per minute, respectively, and then heated to 1550° to 1600° F. under oxidizing conditions, for 3, 3.53, 4, 4.28, 5 and 5.77 seconds, respectively. This treatment annealed the wires and oxidized them in one operation. The time of treatment for the wires of larger diameter was greater than that for wires of smaller diameter. The time in the furnace required for the oxidation increases with the size of the wire, whether the wire is annealed as it is oxidized, or not.

Fine wire of similar sizes containing essentially 80 percent nickel and 20 percent chromium can be similarly oxidized and annealed under the same conditions of concentration, temperature, etc. Wires of 18 percent chromium, 8 percent nickel and the balance iron have also been oxidized and annealed simultaneously.

Wire of greater diameter, strips, straps and ribbons of these various alloys can be similarly oxidized and annealed with suitable variations in time, temperature, concentration, etc. depending upon the size of the wire, etc.

With wire made from an alloy containing 60 percent nickel, 15 percent chromium and the balance iron with a roasting temperature of 1600° F., the initial rate of reaction is very fast so that an oxide film of sufficient thickness and impermeability to practically stop further action is formed in a very short space of time. By passing a wire .0035 inch in diameter through a three foot long furnace at a speed of 30 feet per minute, an oxide layer with 50 volt break down was produced. A coating of the same dielectric strength was produced using speeds up to 92.5 feet per minute with 42 percent caustic, a black oxide was produced, and with 25 percent caustic a brownish black coating was obtained. In all cases the dielectric strength of the coating was substantially the same. However, using a roasting temperature of 1350° F. it is possible to control the formation of oxide so as to produce insulations of different dielectric strengths. At this temperature, with 42 percent caustic, using a three foot long furnace and passing the wire through the furnace at speeds of 30, 60, 73 and 92.5 feet per minute insulations having a breakdown of 25, 20, 15 and 5 volts, respectively, were produced.

Instead of oxidizing the wire by continuous passage through a caustic bath and oxidizing furnace, a coil of the wire can be successively subjected to the necessary treating steps. For example, wire containing essentially 80 percent nickel and 20 percent chromium produced by drawing salt-bath-annealed and acid-cleaned wire from a diameter of .040 inch to a diameter of .025 inch was formed into small coils weighing approximately eight to ten pounds each. These coils were tied loosely. It has been found that making the wire into small coils facilitates the penetration of the caustic solution and the subsequent washing and beating operations and allows a more uniform exposure of the wire to the heat during the oxidation. The size of coils may be increased somewhat but in the operation described the difficulty of handling the larger coils makes the treatment of smaller coils preferred. With larger coils, it may be necessary to increase the time in the roasting chamber somewhat.

The coil of wire is boiled in concentrated caustic for an hour and one-half or two hours or for a sufficient time to clean the surface of the wire and to coat it with a film of caustic. A caustic solution containing 40 to 50 percent by weight of caustic, for example, 45 percent of caustic is satisfactory for this purpose. A weaker solution of caustic may be used for cleaning the wire but it is essential to use concentrated caustic for coating the wire as the less viscous weaker solution flows off of the coil too readily. A fairly viscous solution is required to leave on the wire a film of sufficient thickness and stability for uniform oxidation. Weaker solutions have been

found to leave streaks of insufficiently oxidized wire which lack uniformity of color.

Large steel tanks resistant to caustic solutions of this concentration and provided with steam coils are advantageously used for carrying out this operation. Metal hooks may be used for handling the wire, that is, putting it into the caustic and withdrawing it from the caustic and placing it in and removing it from the furnaces, etc.

The caustic-coated wire is heated in an oxidizing atmosphere at a temperature, preferably between about 900 and 950° F. for about two hours. The coils are advantageously heated in a partially covered pot in an electrically heated furnace so that moisture is driven off comparatively slowly. They are then allowed to cool in the air and then washed very thoroughly with hot water or with dilute acid first and then hot water. It is advantageous to beat the coils while washing them in order to free the wire absolutely from any black or green sludge that may adhere to the wire. After the wire is thoroughly washed it is allowed to dry. This may be done at room temperature although it is advantageous to first centrifuge the wet coils and then dry them at a fairly high drying temperature in a gas or steam heated drier.

The wire may then be annealed without changing its color and without cracking or otherwise destroying or injuring the oxide coating by heating to a temperature between 1550° and 1600° F. Annealing at higher temperatures, that is, from 1650° to 1850° F. proved increasingly detrimental to the quality and appearance of the oxide as the temperature was increased. Both electric and open oil furnaces have been used successfully in the annealing step. An excess of air is allowed to enter the annealing furnace to insure maintaining an oxidizing atmosphere.

The hot coils after annealing should not be brought into contact with cold objects as this may easily cause cracking of the oxide film. They may be cooled fairly rapidly without injuring the oxide coating by transferring them carefully with a metal hook to a horizontal metallic bar and allowing them to be air cooled. On cooling, the wire will be found to be coated with a thick black oxide layer, free from bare spots. If desirable, it can again be washed with hot water to remove any soluble green oxide which may have been formed during the final heating, and then again dried. It is not necessary to heat the wire during this washing operation.

It has been thought by some that the use of as high a temperature as possible is desirable in the production of oxide coatings on wires of various metals. This may have been based on the assumption that the oxidation rate would increase with increase in temperature since oxidation is an ordinary chemical reaction. However, the results of numerous experiments testing wires of nickel and chromium, and nickel, chromium and iron alloys thoroughly wetted with caustic soda, have shown that for these wires if a long time of heating is necessary (as in the batch oxidation of coils in order to allow the mass of metal to be heated throughout and oxidized as uniformly as possible) a temperature between 750° and 1100° F. is preferred. For oxidizing fine wire or strip on continuous, single strand operation, where the heat is transmitted very quickly and uniformly to the metal being heated, thus making only short time intervals of heating necessary for oxidation, temperatures between 1000° F. and 1800° F. have been found most satisfactory.

Various sizes of wire of nickel-chromium and nickel-chromium-iron may be coated with an insulating layer of oxide in this manner. They may be oxidized and then annealed, or annealed and then oxidized, or by proper regulation of temperature the annealing and oxidizing may be effected simultaneously. Strips, straps and ribbons of various widths and thicknesses may be coated with an insulating layer of oxide by treatment in caustic with subsequent heating, with or without simultaneous annealing, as a batch operation.

The oxidation rates of metals in gases are influenced by the manner in which temperature affects the specific reaction rate of the metal, the rate of transfer of oxygen from the air to the metal surface, the nature of the oxidation products formed, and in case the metal surface is covered by a film of oxidizing liquid, by the oxygen solubility as well as the OH concentration in the film of liquid. The oxidation problem is complicated, in the present instance, by the fact that black insoluble oxide coatings are preferred by the trade, and in the insulation of nickel-chromium and nickel-chromium-iron alloys oxides of different colors and different physical and chemical properties are produced at different roasting temperatures. The oxidation is advantageously made a selective operation in which black or dark oxides are formed.

A study of the oxides and hydroxides of nickel, chromium and iron reveals that the most stable nickel oxides are NiO which is green and $Ni_2O_3$ which is black. At 400° C. (752° F.) NiO takes up oxygen forming the black sesqui oxide, $Ni_2O_3$, and at 600° C. (1112° F.) the $Ni_2O_3$ loses oxygen going back to NiO. If the time allowed for oxidation is long enough to allow equilibrium to be substantially reached the reaction temperature must be controlled between 400° and 600° C. if only the black sesqui oxide is desired.

There are several oxides of chromium. The higher oxides $CrO_2$ and $CrO_3$ are unstable at comparatively low temperatures and decompose into the dark green $Cr_2O_3$ and CrO which is black. The presence of a slight greenish tinge on the wire is a perfectly normal condition due to the formation of $Cr_2O_3$ and should not be regarded as detrimental since $Cr_2O_3$ has good dielectric strength and a high melting point. Of the various oxides of iron, the black magnetic oxide, $Fe_3O_4$, is formed at the oxidation temperature recommended, i. e. 750 to 1100° F.

In a batch operation the reactions will go to equilibrium conditions in the roasting chamber and the color of the oxide coating will depend upon the final roasting temperature. In the continuous operation, however, where the wire is in the roasting chamber for only a few seconds equilibrium is not reached. Higher temperatures are therefore used in the continuous process to form the black or dark oxides.

To test the dielectric strength of these oxide coated wires, etc. I apply what is known as the cup test. The apparatus for this test consists of two mercury cups one and one-half inch in diameter which are set one inch apart. Small slots are cut vertically in the sides of the cups to admit the wire or other material to be tested but the slots are so small that they keep the mercury from leaking out. A voltage difference is applied to the two cups and this voltage can be varied at will by means of a voltage divider in the circuit. A voltmeter is connected in the circuit to

measure the voltage drop. The test is made by drawing the wire through the two cups in series and having a voltage difference impressed on the cups. If there is any deflection in the needle of a voltmeter while the wire is being drawn through the cups, it is an indication of either a bare spot or a low resistance point in some portion of the oxide coating.

This constitutes a severe method of testing the insulation of fine wires and the oxide coatings produced by the method of this invention on wires of alloys containing chromium and nickel are the only oxide insulations on such wires which have stood up under this test. Wire consisting of 60 percent nickel, 15 percent chromium and the balance iron insulated in the manner described above was tested by this cup test and it was found that the .002 inch diameter wire treated with 42 percent caustic had a breakdown voltage of six volts while that treated with 29 percent caustic had a breakdown voltage of only two to three volts. The .0035 inch wire treated with 42 percent and 29 percent caustic had breakdown voltages of ten to twelve and four to five volts respectively. The .0045 inch wire treated as described above had a breakdown voltage of ten to twelve volts. Nickel-chromium wire coated by the batch process as described had a breakdown voltage of from thirty to one hundred and twenty volts.

While the claims refer to the treatment of "wires" and to "wires" as a product, the invention is not limited to this form of the alloy, and the word "wires" in the claims is to be broadly construed to include ribbons, straps and strips.

I claim:

1. The method of coating nickel-chromium wires with an insulating layer of oxide which comprises coating the alloy with an aqueous solution of an alkali metal base and roasting the coated alloy in the presence of air.

2. The method of coating nickel-chromium-iron wires with an insulating layer of oxide which comprises coating the alloy with an aqueous solution of an alkali metal base and roasting the coated alloy in the presence of air.

3. The method of coating wires containing about 80 percent nickel and 20 percent chromium with an insulating layer of oxide which comprises coating the wire with an aqueous solution of an alkali metal base and then heating the coated wire to an oxidizing temperature in an oxidizing atmosphere.

4. The method of coating wires containing about 60 percent nickel, 15 percent chromium and 20 percent iron with an insulating layer of oxide which comprises coating the wire with an aqueous solution of an alkali metal base and then heating the coated wire to an oxidizing temperature in an oxidizing atmosphere.

5. The method of coating and annealing alloys containing chromium and nickel which comprises coating the alloy with a viscous aqueous solution of an alkali metal hydroxide, and then subjecting the coated alloy to an annealing temperature in an oxidizing atmosphere.

6. The method of coating and annealing alloys containing chromium and nickel which comprises passing the alloy through a zone maintained at an annealing temperature, then applying a solution of an alkali metal hydroxide to the alloy and then heating it at an oxidizing temperature in an oxidizing atmosphere.

7. The method of coating alloys containing chromium and nickel which comprises coating the alloy with an adhering solution of caustic soda and then heating the alloy to an oxidizing temperature in an oxidizing atmosphere.

8. The method of coating and annealing alloys containing chromium and nickel which comprises coating the alloy with a solution of caustic soda, and then annealing it in an oxidizing atmosphere.

9. Wires of nickel-chromium alloy insulated by an adherent coating of nickel and chromium oxide and having a breakdown voltage of at least five volts.

10. Wires of nickel-chromium alloy insulated by an adherent coating of nickel and chromium oxide and having a breakdown voltage of greater than twelve volts.

11. Wires of nickel-chromium-iron alloy insulated by an adherent coating of nickel, chromium and iron oxides and having a breakdown voltage of at least five volts.

12. Wires of nickel-chromium-iron alloy insulated by an adherent coating of nickel, chromium and iron oxide and having a breakdown voltage of greater than twelve volts.

13. A resistance of high resistant wire made of about 80 percent nickel and 20 percent chromium insulated by an adherent coating of nickel and chromium oxides and having a breakdown voltage of at least 3 volts.

14. A resistance of high resistant wire made of about 60 percent nickel, 15 percent chromium and 25 percent iron insulated by a coating of nickel, chromium and iron oxides and having a breakdown voltage of at least 3 volts.

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